PRINTING INKS

Their Chemistry and Technology

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Preface

The trend in recent years has been toward the production of printing inks composed of or containing substantial proportions of synthetic resins. The work at this laboratory inevitably led up the synthetic-resin trail. It was followed carefully, with the result that numerous compositions possessing novelty of constitution were developed.

In casting about for treatises on the subject of printing inks, it was found that these were notorious because of their limited number. One of these was a book the second edition of which was brought out in 1933. That was some seven years ago, and it seems to us that the advances in the art of producing printing inks certainly demand revision or reissue of a book on the subject at lesser intervals than six years.

The present book attempts to meet these difficulties and to fill the needs of chemists who are groping for information on printing inks and are unable to find the subject discussed in any comprehensive treatise dealing with it in a modern way. A glance at the titles of the chapters of this volume will indicate very promptly that the field covered by this text is a very large one, and a similar brief inspection will show that the text includes the various applications of synthetic resins—such as the glycerol phthalic, urea-formaldehyde and the corresponding aldehyde derivatives of the phenols—in the production of inks adapted for printing purposes. Of these there are so many kinds that it would be undesirable to attempt to list them here.

Among other material which it is hoped will serve to promote a better understanding of the subject, we have found it desirable to add a glossary which defines such terms frequently used throughout the text as may require explanation, not for the printer, but for the chemist or the man who is just beginning a study of printing inks and wishes to learn something about them in the shortest possible time.

Montclair, New Jersey
March, 1940

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Introduction

To the chemist, perhaps more than to the layman, printing inks and coating compositions such as paints, varnishes and lacquers appear to be closely related. In each case the finished product consists basically of a pigment dispersed in a vehicle and there is hardly a compound employed in the manufacture of printing ink which has not, at some time, found favor as an ingredient of a paint or varnish. Moreover, the fundamental processes of the paint-makers' art, grinding, mixing and the blending of colors, are essential steps in the manufacture of printing ink.

In spite of this, it is the rare exception rather than the rule to find both ink and coating compositions being prepared in the same plant. It is true that many of the developments in printing ink can be traced back to prior practices which have been worked out for materials designed for application with a brush. Nevertheless the two fields present their peculiar difficulties and requirements, and the fact that a material has shown promise in one does not mean that it will be equally satisfactory in the other.

The explanation, of course, lies in the different methods by which inks and paints are applied. The question is not one of mere mechanical operation however; there is a great difference between the pigmented mixture which will handle well on a brush and the ink which is coated on type in extremely thin layers and then transferred to paper under heavy pressure. A pound of good quality lacquer which possesses a high degree of covering power will coat approximately one hundred square feet of surface, while the same quantity of cheapest printing ink must be capable of covering at least one thousand square feet. For this reason a pigment which gives excellent results in paint may be worthless in the preparation of colored inks. A well-known example of this is Venetian red which produces blotchy, uneven presswork, but is a common ingredient of fine paints and lacquers. Because of this, the author's previous work on synthetic resins[1] was restricted primarily to applications in the field of molding and coating compositions, although many of the materials described have been adopted by the printing ink industry.

In discussing any printing ink, consideration must be given to two factors, first, the method of application, and secondly, the character of the surface on which the work is to be done. An ink which gives excel-

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[1] Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

Courtesy P. A. Nyholm (photographer)

FIGURE 1. Mural Depicting the Printing Industry (Cincinnati Union Terminal).

lent results in printing from a raised surface will usually be totally unsatisfactory if the transfer is to be made from an engraved plate. Similarly, if the ink is compounded to dry by absorption of the vehicle in a soft paper, it will be worthless for work on a hard-finished surface.

It is not the purpose of the present volume to present an exhaustive study of the mechanical problems of the printing industry, but the fundamental differences between the three branches of the art, typography, intaglio printing, and planography, are so important to one interested in the preparation of inks that the description given in the following paragraphs is necessary.

The process of letter-press printing or typography consists of taking an impression from a raised, pigmented surface. For this reason the term "relief printing" is frequently applied to this branch of the art. This definition is broad enough to include reproduction from type, line-etchings, half-tones, or even the familiar rubber stamp, and of course includes by far the greatest part of all commercial work.

The second general classification, intaglio printing, springs from the use of an engraved or incised plate, on which the ink to be transferred is found in the depressed, instead of the raised, portions of the surface. The processes generally associated with this type of work, copper-plate engravings, etchings and mezzotints, are seldom used where cost is an important factor because of the expense entailed, but rotogravure printing, which employs recessed plates, has found widespread use because of the photographic quality of the prints. Even though rotogravure has found its way into the Sunday supplements of our great newspapers, it is still the most expensive form of reproduction which involves the use of a single color.

Relief and intaglio printing both involve the use of a plate with contoured surface; in the former the ink is carried on the elevations, and in the latter in the depressions. The third group, planographic printing, utilizes, as the name implies, a plane or level plate which in the earlier forms was generally of stone, resulting in the term lithography. All such methods depend upon the fact that water and oil are repellent to each other and if parts of a slightly absorbent surface, such as stone, are moistened with water, it will not be possible to make an oily ink adhere to the dampened areas. Taking advantage of this fact, a design may be drawn on stone or other material of the same characteristics in greasy ink or varnish and the balance of the surface moistened. When this has been done, an inked roller may be passed over the work as frequently as necessary and will transfer only to the undampened portions of the stone. In effect the moistened parts of the lithographic stone correspond to the recesses of the typographic plate. In recent years the development of offset printing, a form of planography, has given new impetus to this branch of the art which was suffering from the rapid advances in intaglio and relief work.

Although the structural details of the equipment used in the execution of these three processes are of only academic interest to the chemist concerned with inks, it will be apparent that the three basic methods of printing differ essentially because of the plates from which the impression is taken. Since the characteristics of an ink will be governed by the plate on which it is to be used and the way it will be applied, the following more detailed description of the three processes, their characteristics and limitations, and the types of work to which each is best suited will be given.

RELIEF PRINTING PROCESSES

Any attempt to trace printing methods leads inevitably to China where wood-block printing had achieved the status of a well-known art in the Tang dynasty about 1000 A.D. It is believed that the Pekin library contained over fifteen thousand volumes at that time which had been reproduced from wood blocks, and some authorities state that printing was originated in China in the first century before Christ. While the art of engraving a single wooden block with characters and printing from this had reached a high state of perfection in the Orient centuries before Gutenberg or Caxton, the enormous number of characters, upwards of ten thousand, which were necessary for reproducing even the most ordinary Chinese writings practically prohibited the use of movable type. While Pi Sheng printed a small number of pamphlets from individual wood blocks carrying only a single character, it does not appear that his process was ever widely adopted.

Apparently printing from wood blocks, xylography, developed in Europe independently of the Chinese and there is no evidence that the Western craftsmen had any knowledge of the earlier practices. It is believed that William the Conqueror had his monogram cut in wood and that the wax seals of the day were impressed with these blocks, and while almost four hundred years were to elapse before the publication of the printed book, it nevertheless was a first step along the road. Printing from carved wood blocks was evidently first used as a means of ornamenting cloth in the twelfth century, but it was not until two hundred years later that it was found that letters, words and illustrations could be duplicated by this process on sheets of paper. Crude as the method was, for no press was employed, it was still a great improvement in that an artisan could make several copies of text while an educated scribe was writing one.

The woodcut of that time was similar to those used today in that the letters or lines to be printed were raised, the balance of the material being cut away to prevent contact with the paper. However, in lieu of a press the printer coated the raised portions of the block with moistened pigment and then, after placing a piece of damp paper on this surface rubbed the back of the sheet until the impression was transferred. It was characteristic of this process that only a single side of the paper could be printed, as the inks of that day would be hopelessly blurred by rubbing, although in some instances the blank faces of two leaves were pasted together, giving the appearance at first glance of a sheet printed on both sides. While the method may have been primitive, it had the advantage of simplicity, and any artisan who had a stock of wood blocks and paper could print books and briefs, as single sheets were called. Consequently the middle of the fourteenth century saw printing from woodcuts a flourishing industry.

It would be inappropriate to burden this book with an elaborate account of the controversy as to who invented the process of printing from movable type. Many scholars who have studied the matter carefully incline to give the credit to Lourens Janszoon Coster of Haarlem as against Johann Gutenberg of Mainz, who is still generally given this distinction. For a long period of time it was thought that the latter was first in the field but considerable doubt has arisen since the discovery that Bodmann, a librarian at Mainz and one of Gutenberg's most ardent supporters, did not hesitate to forge documents to reenforce his case.

Many of the most convincing records were "discovered" at Mainz in 1740, almost three hundred years after Gutenberg's death, but within a short time after his priority was first seriously questioned. Even the famous "Gutenberg" or Mazarin Bible of 1456 may be the work of another printer, Schöffer, who was probably in partnership with Fust, Gutenberg's former financial backer, who took legal proceedings to secure the return of his money in 1455.

Coster is known to have been a printer from wood blocks and tradition says that the idea of printing from movable type occurred to him when he explained the process, as it then existed, to his children by cutting several small blocks, each carrying a single letter and impressing them, one by one, on paper to form words. Documents which are believed reliable indicate that Coster printed by means of movable metal type in 1440 or 1446. However, as recently as 1900, the approximate five-hundredth anniversary of Gutenberg's birth, nation-wide celebrations were held in Germany and the world-famous museum at Mainz containing a most complete collection of historical exhibits was named in his honor as the inventor of printing from movable type. The dispute over priority has continued for hundreds of years and probably will not be settled for some time to come, if ever, but the passage of time and researches by several historians[2] appear to strengthen Coster's case.

Printing from movable type spread rapidly throughout the Continent and the decade after 1460 saw printing offices opened in Strassburg, Cologne, Rome and Venice. Within thirty years there was hardly a town in Europe which did not maintain at least one press.

It is interesting to speculate as to the evolution of type, for it is certain that much effort and experimentation must have been expended to bring the first hand-carved wood blocks to the present metal type. Chief among the problems which were encountered in devising a usable movable type was the difficulty of manufacturing all the type with the same height so that each letter would contact the surface to be impressed. It seems probable that the first solution was found when the wooden blocks were drilled with holes spaced at identical distances from the surface of the letters and were then strung together on cords to form a line. By locking these lines of type in a form with the printing faces resting on a plane surface it was found possible to have all the letters touch the paper to be printed in spite of the variations in height of each piece of type. There is no doubt that some degree of discrepancy in size was unavoidable with the tools and equipment of that day.

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[2] J. H. Hessels, "Gutenberg, Was He the Inventor of Printing?" B. Quaritch, London, 1882.
J. H. Hessels, "Haarlem, the Birthplace of Printing, not Mainz," E. Stock & Co., London, 1887.
O. Hartwig, "Festschrift zum funfhundertjahrigen Geburtstag von Johann Gutenberg, Kommissionsverlag U. O. Harrassowitz," Leipsig, 1900.
A. Borckel, "Gutenberg und seine berühmten Nachfolger im ersten Jahrhundert der Typographie," Frankfort, 1900.
F. Schneider, "Mainz und seine Drucker," 1900.
J. H. Hessels, "The so-called Gutenberg Documents," London, 1910.

Considering the centuries which had been required for the development of movable wood type from a single wood block carrying all the characters necessary to reproduce a complete page, the use of metal type followed wooden type in a surprisingly short time. As a matter of fact Schöffer's "Grammatica vetus Rhythmica" of 1468 carries the notation "I am cast at Mainz," which in all probability refers to the method of manufacture of the type. Probably also the type was cast in sand molds for this art was certainly well known to the metal workers of that day. If sand was the medium employed, this would account for the slight variations in letters which were undoubtedly molded from the same master pattern, as the rough surfaces of the cast type would have been finished by hand to yield smooth surfaces and clear outlines. It was characteristic of the earliest work that each printer was his own type founder, and the styles of type were almost as typical of the individual artisan as was his own handwriting, although in general the characters were patterned as closely as possible after the manuscripts of the locality. Indeed the unavoidable unevenness of line of the manuscript was imitated by the first printers and it was not until the last part of the fifteenth century that type was set in straight lines instead of being deliberately misaligned.

Coming to comparatively recent times we find that type was manufactured from a set of carefully machine-hardened steel punches whose faces were identical with those of the type which was to be made from it. One punch was necessary for each character of every font and by forcing the punch into a block of polished copper, a matrix, or recessed impression of the letter, was obtained. Until the middle of the last century all type was produced in small hand molds using such matrices. These laborious methods have been entirely supplanted by automatic rotary type casting which employs a form of die-casting, and a single machine is now capable of producing upwards of 60,000 pieces of type per hour.

Stereotyping and Electrotyping. It is curious to find that with the perfection of movable type the wheel of development had made a complete revolution. Individual pieces had made it possible for the printer to use the same type for many different jobs, but we find today that most newspapers and magazines are printed from plates in which all characters and illustrations are cast in a single piece. There are several reasons for this. Modern rotary presses run at terrific speeds and it is almost impossible to lock up a page consisting of thousands of pieces of type or even hundreds of linotype slugs so that no unit will be displaced by the centrifugal force of the revolving drum. Secondly, modern newspaper work, particularly in the large metropolitan dailies, requires that the same page be printed on several different presses at the same time if the paper is to be completed on schedule, and obviously a page of type can be in only one machine at a time.[3] Still another reason is found

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[3] "News," The New York Times Company, New York, 1937.

Courtesy P. A. Nyholm (photographer)

FIGURE 2. Mural Depicting the Printing Industry (Cincinnati Union Terminal).

in the case of an advertisement, which is to appear simultaneously throughout the country in many different papers or magazines; it is most desirable that the insertion be identical in every case. If the advertiser should merely send the manuscript to each printer he would probably find that no two copies were the same in all details.[4] It is for this reason that the advertiser will usually make up electrotypes of the copy in the form which he desires and then distribute these identical plates to all papers. Lastly, if the reproduced printing surface is injured in handling, it is not a serious matter, since other electrotypes or stereotypes can be made from the original without great delay.

Of the two processes for the reproduction of a printing surface from the original type, electrotyping, as compared with stereotyping,.is the more costly and more time-consuming, but is capable of producing a larger number of sharp impressions.

Stereotyping consists essentially of casting a metal sheet whose surface is identical with the type from which it was taken. The first processes were carried out by impressing the type in clay which was later

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[4] C. R. Greer, "Advertising and Its Mechanical Production," Thomas Y. Crowell Company, 1931.

baked and used as a mold into which molten metal was poured. Rotary presses, however, require a curved plate and clay does not lend itself to this form; consequently papier-mâché, which may be readily bent to assume any shape, is generally used today. In this process the moistened sheets of thick, soft paper, which are capable of withstanding a high temperature, are placed over the assembled type and pressed under heavy rolls. Immediately thereafter the paper matrix is dried in ovens of progressively higher temperatures and then fitted into casting boxes which are of the same curvature as the rolls on which the plates are to be clamped. The metal, which is somewhat softer than that usually used for type, is sprayed into the box from a number of small jets and the casting is almost immediately removed and, after water cooling, is trimmed to size, when it is ready for use. Some appreciation of the speed at which these steps are carried out in modern practice may be gained from the fact that the finished plate may be produced, ready for service, four minutes after the papier-mâché is first laid on the type.

Electrotyping is used when it is desirable to produce several plates from the original type or linotype slugs. In this process, as in stereotyping, an impression of the surface is made, but here the medium is wax, though resinous compositions and lead also are utilized.[4a] The impressed mold is made conductive by a coating of graphite. The wax and resinous molds then are treated with aqueous copper sulphate and iron to form a thin coating of copper on the mold. Subsequently a layer of copper is deposited upon the surface electrolytically, resulting in a metallic sheet whose surface corresponds to that of the type from which the impression was taken. With lead molds, a thin layer of oxidizing solution is placed upon the lead surface before plating the latter. When a harder shell is desired, the mold is plated with nickel or chromium before the copper plating is applied. The plated shell is stripped from the mold, and reinforced by casting lead as a backing, tinfoil being used as a flux. The electrotype, as the finished plate is called, is mounted on a block of wood so that the whole is type high. If a rotary press is to be used, the metal plate is curved to fit the cylinder exactly.

Typographic Reproduction of Illustrations. By the time Columbus made his first voyage to the New World, printing was a well established art. It is difficult to realize today that up to the date of the American Civil War virtually the only method of reproducing illustrations by typographic means was through the medium of a wood cut, which was the predecessor of printing from movable type. Photoengraving, a term which includes both line etchings and half-tones, is based upon the discovery by Mungo Ponton, about 1840, that exposure to light would convert a mixture of albumin and potassium bichromate from a soluble to

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[4a] One such resinous molding composition, prepared from wax, rubber, paracoumarone and a filler, the whole backed by an aluminum sheet, has been marketed under the name "Tenaplate." See H. Libberton, U. S. P. 2,172,563 and U. S. P. 2,172,564, Sept. 12, 1939, to Tenak Products Company.

an insoluble form. All modern processes for the reproduction of illustrations without the intervention of a human agency stem from this development.

Although the woodcut is seldom seen today in commercial publications, it is still a most effective device in the hands of an engraver who is skilled in balancing the brilliant contrasts which are characteristic of this type of work. A further advantage lies in the fact that the artist may reproduce the illustration in the way he desires, regardless of the actual form of the subject. This advantage becomes a disadvantage, however, when the purpose of the illustration is to serve as an accurate factual record. Furthermore, the time involved in the execution of a fine woodcut is so great that competition with photoengraving is out of the question when speed of manufacture is a factor to be considered. These limitations restrict the woodcut of today to a small field where artistic appearance is a prime requisite, where leisurely production is not impossible, and where a premium will be paid if the finished work is distinctive and appealing.

Even the process of wood-engraving has been changed in comparatively recent years however. Today the design is drawn, not directly on the surface of the wood, but on a separate sheet and then transferred photographically to the sensitized face of the block. The actual cutting of the material, nevertheless, is still a hand operation in which everything depends on the skill of the artisan. Errors or mistakes in the engraving process are serious, since the wood cannot be repaired, and generally it is necessary to discard the piece and make a fresh start.

Practical considerations, therefore, compel the use of photomechanical processes for usual commercial work, and of these the line etching and half-tone are most popular, although mention must be made of the swelled gelatin process and typographic etching.

It is common knowledge that the line etching produces, as the name implies, a print which is made up of lines or pigmented areas with lighter spaces between that are free from any shading. The half-tone, on the other hand, may be broken down into a large number of dots which, in the heavily shaded portions, are of relatively large size and predominate over the intervening white spaces, and are proportionally smaller in the lighter parts of the illustration. A half-tone depends on variations in shading to produce its effect; the darkest areas are never entirely black, and the lightest sections are at best an extremely light gray. This is to be contrasted with the line etching where there is no shading whatsoever, except as it occurs from the arrangement of the lines, and any part of the print is entirely white or completely black. As a consequence of these differences the line etching is ideally suited for the reproduction of pen and ink drawings or similar work which is free from shades. On the other hand, a half-tone is best fitted for work which consists wholly of variations in depth of color, and is at a disadvantage if the subject consists of lines or lettering, because of the loss in clarity. Of the two processes line etching or zinc etching, as it is frequently called, is the less expensive.

In either process the starting point is a negative of the illustration, drawing, or photograph which is to be reproduced. The negative, in the case of a line etching, must have been previously reduced to the exact size of the zinc plate upon which the etching is to be done. The plate is then sensitized in a darkroom with a mixture which generally consists of albumin and ammonium bichromate. The negative is then laid over the metal and exposed to a strong source of light, thus converting the exposed portions of the coating to a film which is insoluble in water. After washing in water, therefore, the zinc is only partially coated, those areas of the plate which are not intended to print being bare metal. The accuracy and clarity of the reproduction may be readily judged if the sensitizing medium is pigmented either before or after application to the plate. When this is done the exact design is clearly indicated, after washing, by the remaining colored coating. While the lines of insoluble film on the zinc provide a certain degree of protection, it is not sufficient to resist the acids which are employed in etching. The usual expedient is to dust the surface of the plate with powdered asphalt or similar bituminous material which will adhere to the somewhat sticky surface of the remaining albumin but may be readily brushed from the bare metal. By heating to a moderate temperature the asphalt is fused into an impervious coating for that portion of the metal which will eventually be in relief. The zinc plate, after the back has been protected, is now placed in a bath of dilute acid for its first etching, generally requiring about half a minute. If the metal is exposed to the acid for too long a period of time there will be a tendency to undercut the lines and greatly weaken the strength of the printing surface. To prevent this, after the process of etching is partially complete, another dusting of asphalt is applied, not only to the previously protected areas, but also extending down the sides of the lines which have been newly exposed. The subsequent etching will not eat away the vertical sides, which would frequently cause the portions in relief to chip and break at the edges. The coating and etching operations are repeated until the depth of cut is sufficient to provide a clearly outlined printing surface. Generally this may be accomplished by four or five repetitions of etching, and any additional metal which must be removed in the valleys between the lines is usually cut out mechanically by a routing machine. After cleaning, the plate is mounted on a wood block to bring it to the correct height and is ready for use. It is apparent from this description of the process that no shading or gradation of color can be obtained by a line etching. If the original negative was sufficiently light at a given point to render the sensitized coating insoluble, that point will not be affected by the acid treatment and will print solid black. If the negative was too dark to prevent the formation of the protective film, the prints taken from the plate will be entirely free from ink in that area.

On the other hand, if a drawing which is made up simply of solid black lines on white paper is reproduced by means of a half-tone, it will be found that the lines as printed are a group of dots and that the "white" portions of the work in reality also contain the same dots although, because of their much smaller size, they are not readily apparent except upon close examination. As a matter of fact, there are just as many dots in a unit area of the lightest portions of a half-tone as in the darkest parts. The seeming difference in depth of shade is due to variations in the proportion between the area of the pigmented dot and that of the surrounding paper.

In the early stages of manufacture, both the line etching and the half-tone engraving are taken from a negative which is reproduced on a sensitized metallic plate. There is one most important difference, however; the negative for the half-tone is made up of a large number of dots of varying size, while that which is used for line engraving is an unbroken blend of lights and shadows, in other words, the usual photographic negative. The dots on the half-tone negative are obtained by placing a screen immediately in front of the film or plate in the camera to break up the image. This screen is made up of two sheets of glass, each carrying a series of equally spaced, parallel, diagonal lines, which are cemented together with the lines of one plate at right angles to those on the other. Because of this intervening screen, the negative is exposed to regularly-spaced points of light which vary in intensity according to the depth of color of the subject. The result is a corresponding group of dots on the sensitized coating of the plate, usually of copper in the case of half-tones, which are rendered insoluble in varying degrees. The number of dots per square inch is dependent on the spacing of lines on the screen and will vary according to the paper on which the printing is to be done. Fifty lines per inch is the minimum number which will give a clear illustration, and this is generally used only in newspaper work because of the roughness of the paper. With such a screen the individual dots are clearly distinguishable. One hundred and twenty lines per inch is the number commonly used for the better grade of commercial work where some degree of detail is necessary. Screens of this fineness require a level or even surfaced paper as the plate is only permitted to touch the paper lightly during the printing. Heavy pressures, although entirely satisfactory with a line cut, cannot be used without blurring the reproductions from a half-tone. Screens with as many as four hundred lines per inch have been made, but these have limited commercial use because of the delicate treatment required in manufacture and printing.

The sensitized copper plate, after exposure, is washed in running water to remove that portion of the coating between the dots which was protected by the screen lines from that rendered insoluble by the effect of light. It is then customary to dip the plate in dye which colors the remaining coating, usually a mixture of ammonium bichromate and glue. The insoluble coating is then heated to make it still more acid-proof and the unprotected copper surface is removed, either by etching in acid or by using the copper as one of the plates of an electrolytic cell. The latter process is more readily controlled and gives more uniform results. Since much less metal is removed from a half-tone than from a line etching, a single bite is all that is usually necessary. However, if a large part of the plate consists of a light background, the contrast can be increased by coating the darker portions of the plate with a protective film, either of enamel or of a bituminous material, and then re-etching. After cleaning, the half-tone plate is cut to size and mounted on a wood block in the same manner as a line cut.

A third method of making typographic plates by photographic means, the swelled-gelatin process, is little used in commercial practice, but will be described since it illustrates a different means of obtaining variations in shading. The principle involved is that a sensitized film of gelatin and potassium bichromate will swell when immersed in water, the increase in volume being proportional to the brilliancy of the light to which it has been previously exposed. This fact has been put to commercial use by employing such a mixture as the coating on a camera plate and then, after the exposure has been made, soaking the plate in water in a dark-room. Those parts of the sensitized coating which have received the greatest amount of light will swell the least and the dark areas will be raised perceptibly, giving a contoured surface. A plaster cast is then made of the gelatin and this in turn is filled with wax to yield a replica of the original plate. By coating the wax lightly with a conducting material such as graphite an electrotype may be made in copper which carries the lines of the original drawing in varying degrees of relief. The highest portions of the electrotype will receive the maximum quantity of ink during printing and will contact the paper with the greatest pressure, thus leaving the darkest impression. The lower printing surfaces will still touch the paper but will yield a somewhat lighter line.

This method is best adapted to stipple work or the typographic reproduction of steel engravings, and its advantage lies in the fact that variations in depth of color of the lines of the original drawing may be reproduced. However, the cost of the process, which is several times that of a half-tone, has prevented its widespread use except in the highest grade of work.

It will be apparent that relief printing may utilize plates of very different physical characteristics and that the nature of the printing surface must be considered in the selection or compounding of ink. Further, the paper which is best adapted to one type of plate may be most unsatisfactory with another, and the ink and paper must be suited to each other if the best results are to be obtained. The characteristics of inks which are suitable for typographic work will be compared with those designed for intaglio and planographic printing in the latter part of this chapter.

INTAGLIO PRINTING PROCESSES

Intaglio printing or engraving is characterized by the use of a plate in which the lines and figures to be reproduced are depressed rather than raised, as is the case in typography. This general classification includes not only copper plate and steel plate engravings, but also mezzotints, etchings, and the commercially important rotogravure. In each case the process depends upon the use of an ink which has greater affinity for paper than for metal so that it may be drawn from the depressions in the surface of the plate. From this it will be seen that wood "engravings" are a misnomer in the sense that the word is used here, as the ink is deposited on that portion of the block which is in relief.

The advantages of the use of engraved plates are well known. No other method can equal intaglio printing in clarity and delicacy, and since the layers of ink which are transferred to the paper are of considerable depth, high degrees of opacity and contrast may be obtained. Artistically, it is important that finer lines may be obtained from an incised plate than in any other way, the reason being that in relief printing the printed image is always slightly larger than the surface from which the impression was taken. This is due to the fact that, no matter how carefully the pressure is controlled, a small amount of ink is squeezed from between the type and paper. In the case of intaglio work, where the width of the line is never any greater than that of the cut in the plate, this cannot occur. When reproducing fine lines and delicate shading this becomes a consideration.

A brief description of the mechanics of copper plate engraving will provide a basis with which other intaglio processes can be compared. Since copper is a relatively soft and ductile metal, the number of copies which may be pulled from a single plate is limited to a few thousand impressions. After this the edges of the engraved characters lose their sharpness, and the clarity of the print is impaired. However, for many forms of letterhead, social stationery, and similar productions, this limitation is not a serious disadvantage.

The first step in the process is to cut upon the plate, in reverse, the figures which are to be reproduced. There are several methods of engraving the metal, but the simplest and the oldest is line engraving in which a burin, a steel tool with much the appearance of a chisel, is used to gouge out the lines. There are many other methods of preparing the plate, which will be described in some detail since they yield entirely different effects.

The incised plate, which is usually less than an eighth of an inch in thickness, is next cemented to the bedplate of the press which slides so that it may be passed under a roller that will bear upon the plate with considerable pressure. The entire surface of the plate is then coated with ink by a suitable applicator, after which it is wiped and polished with cloth or paper so as to remove all pigment from the surface of the metal which will come in contact with the sheet that is to be printed. When the raised areas of the plate are entirely clean, a moistened piece of paper is laid over the engraved copper and is forced against the plate by the pressure roller under which the bed-plate is passed, thus transferring the ink to the paper. When the paper is removed, the cycle of inking, cleaning, and printing is repeated. Much has been done in recent years to expedite the process but, although all these operations may be performed automatically today, the nicety of workmanship which is essential to every step will prevent it from ever competing with typographic methods wherever cost is the chief consideration.

The engraved plate itself, which is the heart of the intaglio process, has changed but little from the earliest days, although various new methods have been developed from time to time for its preparation. It is believed that the germ of the idea came from the craftsmen of Italy, who, in the fifteenth or sixteenth century, were engaged in ornamenting metal surfaces by engraving. Since it was difficult to see the lines which had been recently made and to judge their width and depth in the freshly cut metal, they were filled with an enamel or a pasty pigment which had some resemblance to an ink. This would provide a contrast which enabled the artisan to see the design more readily. It was on such a pigmented plate that some nameless goldsmith pressed a sheet of paper and obtained the first intaglio print. Even the first artist to use the method and obtain general recognition is unknown and, although his work shows evidences of a well developed technique, he is referred to simply as "The Master of 1466."

The history of intaglio printing is a search for artistic, not commercial, advantage. The first mezzotint was made about 1650 and provided a medium for the accurate expression of shades and tones. In the preparation of a mezzotint the polished sheet of copper is worked with a "rocking tool," a curved steel plate which carries raised, parallel, knife-like lines. These cutting edges are spaced closely together, sometimes as many as one hundred and twenty to the inch. By rocking the tool back and forth across the copper a large number of parallel lines are impressed in the surface and when this has been done in several directions, so that the metal is completely roughened, the "ground" has been formed. If the plate is smeared with ink at this point, wiped and pressed on a sheet of paper, the reproduction will be uniform and almost completely black because of the pigment retained in the closely spaced depressions. Variations in tone are obtained by removing more or less of the burred surface from the plate by scraping. If a portion of the plate is carefully scraped away so as to leave a smooth surface, no ink will be retained in that area after wiping and therefore it will print as white. By varying the amount and manner of the scraping infinite variations may be had. As was the case with wood block engraving, mezzotints were almost completely abandoned with the perfection of photoengraving, but the art has been revived in recent years.

In etching, the metal is removed by acid, not with a cutting tool. The usual procedure is to coat the surface of the plate with a layer of wax blended with mastic to impart a degree of adhesion to the metal. The coating may be applied by a roller, in the form of a solution, or by rubbing the surface of the heated plate with a cloth which has been

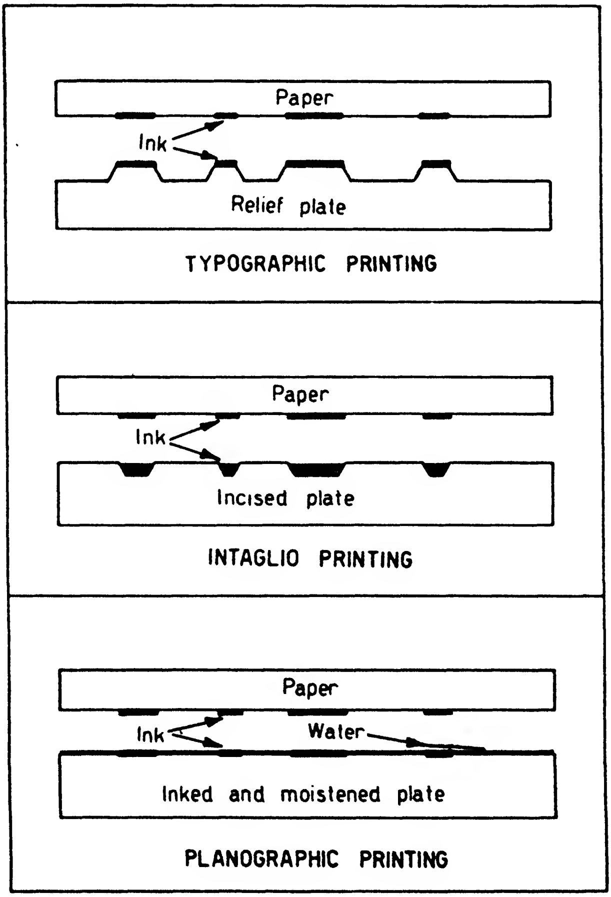

FIGURE 3. Diagrammatic Sketch of the Three Main Divisions of Printing.

wrapped about a ball of the wax. While the protective film should adhere to the copper with sufficient tenacity to prevent the acid from working between the two, it should be possible to remove the wax cleanly by means of the etching needle so that the bare metal will be exposed. After the design has been scratched in the wax, the lines are cut in the plate by exposure to the acid, forming the ink-carrying depressions.

The preparation of a plate by any of these methods calls for a high degree of skill; in fact the plate itself is the medium of expression for the artist. Consequently such processes are little used in commercial work because of the very high costs involved.

In the field of relief printing, the development of photography made possible the half-tone plate. Similarly, in intaglio work, the various photogravure processes, which are of great importance, are based upon the use of a sensitized film which permits an accurate reproduction of the original subject. The term "photogravure" covers all methods of preparing a plate for intaglio printing by photographic means, and the most important branch of the art is rotogravure which employs a curved, etched copper plate adapted to use on a rotary press. Because of the soft, photograph-like quality of rotogravure work, this method of printing is widely used for newspaper supplements, catalogs and similar publications. The process is of especial interest to the manufacturer of printing ink because its peculiarities are reflected in the compounding of the ink.

Although rotogravure is the most popular form of intaglio printing, the photogravure process will be described first since the former process developed naturally from it. In all intaglio processes it is necessary to form a "grain" on the surface of the plate which will serve to hold the ink. In the case of the earliest photogravures this was accomplished by allowing a cloud of extremely finely powdered asphalt to settle in a thin film on the plate. The metal is then gently heated so as to make the particles adhere to the surface, but overheating must be avoided as this would liquefy the bituminous material and cause it to run together, forming an unbroken coating. When properly treated, the plate is partially covered by innumerable, uniformly-spaced, small granules of asphalt. A sensitized film of gelatin and potassium bichromate is then coated on the prepared surface in a darkroom. When this has been done the coated plate is placed behind a transparent positive of the image to be reproduced and exposed to a strong light which converts the sensitized gelatin to an insoluble form in those portions of the plate which are to print most lightly, that is, the highest points of the metal. Even those areas on the surface which correspond to the darkest sections of the print are partially protected by particles of asphalt. Consequently when the plate is etched, after the soluble parts of the film have been washed off, these surfaces are not entirely removed.

The early photogravure process provides an interesting contrast with the modern method of preparing half-tones for relief printing. In the former the darkest areas are the deepest, in the latter the highest. Both are dependent on the use of a coating of bichromated gelatin, but in the former the insoluble portion protects the light areas, in the latter the dark. Similarly the darkest sections are not completely black in either case, but in the former the grain is procured by the dusting of bitumen while a screen is used in the preparation of half-tones.

Photogravure, as previously described, is available only for work where expense is a secondary consideration; rotary photogravure, while more costly than relief printing, has made possible the cheap production of prints of high artistic quality. Although the Sunday newspaper supplement is seldom thought of as an "engraving" it is, nevertheless, the product of an intaglio process.

Rotogravure, as the process is generally known, employs an exquisitely polished copper cylinder as the printing surface and makes use of a screen similar to that developed for the preparation of half-tones to break up the light and dark areas into small, unshaded dots. This ruled screen replaces the asphalt dusting of the earlier photogravures.

In practice, a negative of the image to be reproduced is made up and from this a transparent positive print is obtained on a sensitized glass plate. The positive is in turn printed photographically on a sheet of thin paper coated with sensitized gelatin and, after a suitable exposure has been made, the positive is replaced with a "screen" or sheet which is ruled with crosslines to break up the entire surface into a large number of small squares. The sensitized tissue is subjected to a strong light so that the lines of the screen are superimposed on the image which was previously printed from the positive. The screen used in the rotogravure process is reversed, that is, the lines are transparent and the intervening squares are opaque as compared with the half-tone screen which is ruled with black lines.

The result of these steps is a sheet of tissue carrying an enormous number of dots of sensitized gelatin which, because of the varying degrees of light to which they have been exposed, are soluble in water to a greater or less extent. These dots are separated by lines which have been rendered insoluble by the light admitted through the screen. At this point the entire sheet is dampened and laid over the highly finished surface of the copper cylinder with the sensitized side in contact with the metal. The roll is then drenched in water, loosening the paper so that it may be stripped from the gelatin and washing away the unexposed portions of the coating. If there are any portions of the cylinder which are not intended to print, as for example the margins, they are protected with varnish and the surface is then etched with iron perchloride.

Because the degree of solubility of the protective film varies in different portions of the surface, the thickness of the coating which remains after washing will vary and for this reason the speed with which the metal is etched will be different. Those areas which were exposed to the most intense illumination correspond to the lightest parts of the subject and will be completely protected, while the darker areas will be eaten away to a depth dependent on the shade of the subject at the particular point. The lines of insoluble compound formed by exposure under the reversed screen result in a pattern of closely spaced walls of uncut metal on the surface of the cylinder, breaking up the etched areas into an

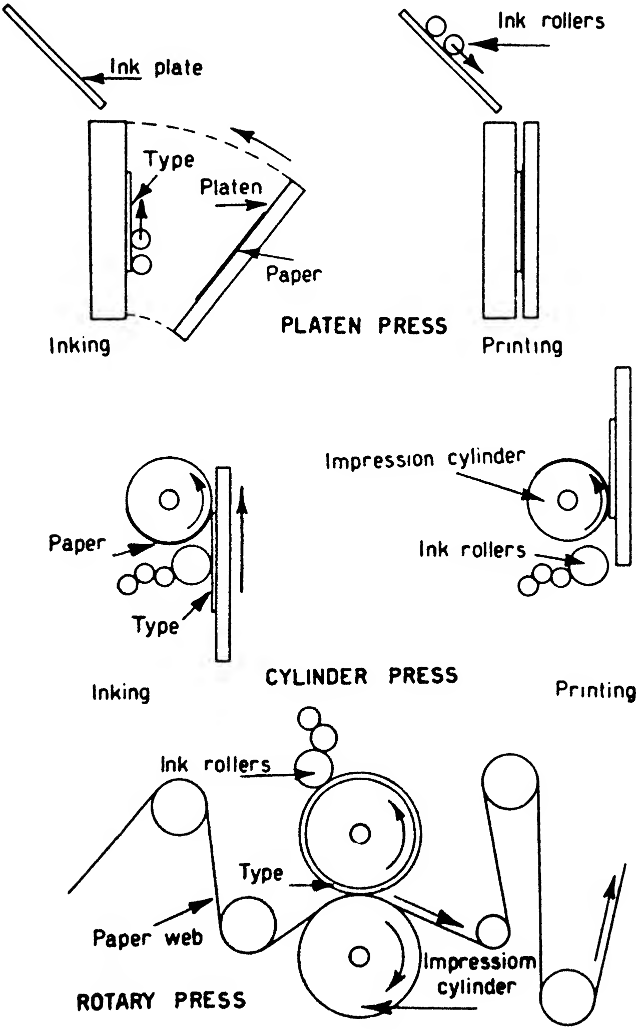

FIGURE 4. Diagrammatic Sketch of Operation of Platen, Cylinder and Rotary Presses.

enormous number of cups of varying depth which serve to hold the ink during printing.

When mounted in the press, the copper cylinder revolves in a bath of ink, only slightly more viscous than water, which fills the cups formed in the etching process. A flexible steel "doctor blade" scrapes the surface of the rolls so that the ink remains only in the cups. When pressed against the paper the ink is transferred and the depth of color at any point will correspond to the amount of ink deposited, which is in turn determined by the depth of the cup. Since the ink is very thin it spreads slightly during printing, mingling with the pigment from adjacent cups and preventing any effect of spottiness. In a finished rotogravure print it is almost impossible to detect the screen which shows up clearly in a half-tone, and it is because of the blending of the pigments that the process is so well adapted to the reproduction of shaded subjects.

Plateless Engraving. Although plateless engraving is a typographic, not an intaglio, printing process it may be considered at this point since it is intended to produce work which is similar in appearance to copper-plate engraving. No plate is used, however, the impression being made from raised type in the usual manner with a densely pigmented ink which retains its tackiness for some period of time. After printing, the inked portions of the sheet are dusted with a powdered resin of low melting point and, after any surplus powder has been blown from the paper, the resin is fused by the application of heat. This method yields characters which are raised above the surface of the paper but the figures are not as clearly defined as in the case of true engraving, and the absence of a plate mark is also apparent on close examination. Since a plate is unnecessary, however, the process is considerably less expensive, and the method is in common use today, especially where relatively few copies are required.

Planographic Printing

Planography, the third grand division of the art, includes those processes which print from a substantially flat surface as contrasted with the elevated areas of typography or the incised lines of intaglio printing. Both lithography, the original form of planography, and offset printing, a comparatively recent development of great commercial importance, fall within this group. Planographic processes, regardless of the plate or stone which may be used, are all dependent upon the fact that a greasy ink will not adhere to a moistened surface, a practical illustration of the homily that oil and water will not mix.

Lithography, literally "stone-writing," is the invention of Alois Senefelder who, by constant experimentation, was able to bring the art to a high state of development before his death in 1834. Senefelder was a printer who, handicapped by the cost of plates, accidentally discovered that a porous stone might be rendered suitable for printing if the design was drawn in wax on the surface and then slightly etched with dilute aqua fortis so that the waxed areas were less than one-hundredth of an inch in relief. Passing an inked roller over the face of the stone he found that the pigment did not adhere to the etched portions which were still moist from the acid and that further treatment was therefore unnecessary. And in addition, he found that the surface could be re-inked an indefinite number of times without blurring so long as the uncoated parts were kept wet.

While stone presses are a rarity today, it is interesting that they have changed but little since Senefelder's time. The limestone which he discovered in Bavaria and with which his experiments were conducted has proved to be the best variety for printing work. Furthermore, the surface is still etched to secure clarity of line just as he did. The image, which must be drawn on the stone in reverse, may be applied either with a "chalk," which is actually a greasy crayon, or with greasy ink.

The first step in the lithographic process is the preparation of the surface which is usually accomplished by grinding with a slowly revolving stone disk and pumice to bring it to a high degree of flatness and uniformity. The stone is then grained by rubbing with powdered glass so that it is covered with a network of extremely fine scratches. The subject matter is then drawn upon the prepared surface with greasy ink or chalk and the stone subjected to etching. Corrections may be made at this time by scratching away any portions of the inked stone which are not to transfer. After being washed to remove the acid, the stone is mounted in a flat bed press which is fitted with moistening and inking rollers that pass alternately over the surface before each impression. The inking rollers are usually faced with leather, and a small percentage of acid may be added to the water supply for the cloth-covered moistening roller so that the edges of the areas in relief are kept sharp and clear.

The earliest lithographic process had two drawbacks. The first was that the weight of the stone, which was generally six inches in thickness, required that the artist work in the printing office, and the second was the confusing necessity of drawing the design in reverse. Both these difficulties were solved about 1870 by the development of a transfer paper on which the drawings could be made. When this was completed the sheet was laid upon the stone and moistened so that the paper backing could be removed, leaving the pigment in reverse on the surface. This invention popularized lithography and was largely responsible for the tremendous vogue of this form of printing in the last quarter of the nineteenth century.

The unwieldy nature of the stone block led to the use of other less cumbersome materials. Of these zinc and aluminum have been the most successful and the most widely adopted, since the surface of the metal may be etched with acid to render it sufficiently moisture absorbent to prevent ink from adhering. The sheets may be made quite thin and pliable and, therefore, it was found possible to bend them into circular form so that a comparatively high-speed rotary press could be used. In this case, the plate is moistened and inked during each revolution of the cylinder.

Photolithography is to planographic printing what the half-tone is to typography. By this means an accurate copy of the subject may be faithfully reproduced and at a lower cost than when the services of an artist are required. The first step in the process is to sensitize a sheet of transfer paper and then expose it to light behind a transparent negative. The bichromated surface is then washed with water to remove those portions of the sensitized film which were not rendered insoluble by exposure. After applying ink to the resulting image, the sheet is laid face down upon the stone or plate and firmly pressed so that the greasy pigment adheres to it. By further wetting, it is possible to remove the paper backing, leaving the design upon the printing surface. From this point on, the usual process is followed, moistening the uncoated areas and inking the remainder during printing.

Essentially, offset printing differs from lithography only in mechanical details. In the latter process the ink is applied directly to the paper from the stone or plate, while in the former the pigment is transferred to a soft rubber pad which in turn contacts the sheet. The modern offset press consists basically of three cylinders. The first, of sheet zinc or aluminum, is similar to that used in lithography and carries the inked design which is usually applied photographically, although a transfer process may be employed. As in the case of lithography, the plate cylinder is alternately moistened and inked once during each revolution. The second roll is covered with a sheet of rubber about an eighth of an inch in thickness which rotates in contact with the plate cylinder and from which the design is transferred. The impression cylinder presses against the rubber covered blanket roll and it is between these that the sheet of paper is passed, receiving the ink which has been offset upon the blanket.

Prints made by the offset process have a softness of outline which is quite different from that obtained from relief plates. If the design has been transferred to the plate cylinder photographically and a screen has been used to obtain variations in shading, the individual dots blend together and lose their identity as compared to a half-tone printed typographically. The chief advantage of the process, however, is due to the resilience of the rubber blanket which is sufficiently soft to absorb any variations in the thickness of the paper. This permits the use of rough papers which would not print evenly from a metallic plate, thus dispensing with the need for a paper with a finely calendered or coated finish.

It is common knowledge that an infinite variety of shades and colors may be obtained typographically by using three or four sets of half-tone

Table 1.—Methods of Printing.

	Method of Printing		Press Used	Type of Work	Nature of Plate	Pressure kg/in^2	Paper Used	Maximum Speed m./sec.	Maximum Speed Sheets/hr	Surface in Contact	Type of Ink Used
Relief	Typographic	Flat	Platen	Characters, Imitation Engraving, Multicolored Small Work	Metallic Plate	From 15 to 70 kg per cm.^{2}	Sheets		2,500	Elements in Relief Only	Oily, firm ink; Drying by oxidation
			Semi-Rotary				Sheets		3.500		
			Cylinder				Sheets and Rolls		3,500		
		Rotary	Rotary Job Press	Same as platen, work medium sized	Metallic Cylinder		Rolls	3			Oily, fluid ink; Drying by absorption
			Rotary Newspaper	Same as platen, large jobs			Rolls	10			
	Elastographic		Rotary	Type and line cuts, multicolored	Rubber Cylinder		Rolls	2			Aniline inks; Water and alcohol
Planographic	Lithographic		Platen	Black and Colors	Stone, Aluminum or Zinc Plate	33	Sheets		2.000	Whole Surface of Plate	Oily, firm ink; Drying by oxidation and absorption
	Offset		Rotary	Black and Colors	Metallic Cylinder	20	Sheets and Rolls	4.5	5.000		
	Phototype		Platen	Black	Gelatin Plate	20	Sheets		1.500		
Intaglio	Rotogravure		Rotary	Black and Colors	Metallic Cylinder	97	Sheets and Rolls	4.5	4,000	Whole Surface	Non-oily, very fluid ink. Drying by evaporation

plates. (The fourth color, black, is often used because of the difficulty in always obtaining a true black from the combination of the other three colors, red, yellow and blue.) However, in planographic work, it is not possible to blend colors on the paper, and consequently a separate plate and impression must be made for each shade. Frequently, six impressions of different shades or colors are used, and as many as forty have been employed on a single sheet to apply the various colors required in a single illustration. Since there is no blending of tones, colored offset work has a characteristic contrast which is most effective in certain designs and has become popular for posters and labels.

Although offset printing as applied to paper was not developed until the first decade of this century, sheets of metal had been ornamented by using a type of offset press for many years because of the difficulty of printing on such material with a metal plate.

Such are the various processes of printing which are in common use today. Little more than the essentials of each method has been given, the purpose being merely to indicate the relationship between the process and the characteristics which are desirable in the appropriate ink. A study of the chart prepared by Jullien,[5] showing the various types of presses, speeds, papers, and inks, will serve as a panoramic view of the printing field. Although some of the units used are in the metric scale, a comparison may be made empirically between the various processes. Reference may be made to any of a number of standard works for a complete discussion of the mechanical phases of the art.[6]

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[5] M. Jullien, *Le Papier*, 1937, 40, 55; *Chem. Abs.*, 1937, 31, 4115.

[6] The following books deal primarily with the development and history of printing processes:

H. R. Plomer and T. P. Cross, "Short History of English Printing," Empire State Book Co., New York, 1927.

John C. Oswald, "A History of Printing," D. Appleton & Co., New York, 1928.

Douglas C. McMurtrie, "A History of Printing in the U. S.," R. R. Bowker Co., New York, 1936.

W. D. Orcutt, "The Kingdom of Books," Little, Brown & Co., Boston, 1926.

George A. Kubler, "Historical Treatises, Abstracts and Papers on Stereotyping," Brooklyn Eagle Press, New York, 1936.

"Printing, A Short History of the Art," Grafton & Co., London, 1927.

The following books contain descriptions of the modern methods of printing:

S. Morison, "The Art of the Printer," 1925.

"American Manual of Presswork," Oswald Publishing Co., New York, 1916.

C. W. Hackleman, "Commercial Engraving and Printing," Commercial Engraving Publishing Co., Indianapolis, Ind., 1924.

L. P. Clerc, "Ilford Manual of Process Work," Ilford, Ltd., London, 1926.

H. A. Groesbeck, "Process and Practice of Photoengraving," Doubleday, Doran & Co., New York, 1924.

E. S. Pilsworth, "Process Engraving," The Macmillan Co., New York, 1922.

N. S. Amstutz, "Handbook of Photo-Engraving," Inland Printer Co., Chicago, 1907.

J. Verfasser, "The Half-Tone Process," Iliffe & Sons, London, 1910.

The following books deal primarily with typographic methods:

Eric Gill, "An Essay on Typography," Sheed and Ward, London, 1936.

C. R. Spicher, "The Practice of Presswork," Chicago, 1929.

Benjamin Sherbow, "Making Type Work," Century Co., New York, 1916.

Arnold Levitas, "Printing and Typography for Beginners," McGraw-Hill Book Co., New York, 1924.

Ralph W. Polk, "The Practice of Printing," Manual Arts Press, Peoria, Ill., 1937.

Douglas C. McMurtrie, "Type Design," Bridgeman Publishers, New York, 1927.

Francis Meynell, "The Typography of Newspaper Advertisements," Frederick A. Stokes Co., New York, 1929.

E. G. Gress, "American Handbook of Printing," Oswald Publishing Co., New York, 1907.

F. Thibaudeau, "Manuel Française de Typographie Moderne," Bureau de l'edition, Paris, 1924.

CHARACTERISTICS OF PRINTING INKS

The purpose of the following description is to outline, in a general way, the qualities which must be found in each type of ink and the reason for these requirements. Subsequent chapters will deal in detail with specific inks and their peculiarities.

Printing inks are divided into three groupings, typographic, intaglio and planographic, corresponding to the main divisions of the art. However, the material on which the impression is to be made must be considered, as a typographic ink which is well adapted to printing on soft paper will be entirely unsuitable for use, for example, on metal.

The trade has given certain names to the various characteristics, and since these are in common use they may be described here. An ink which flows well and which may be drawn out into threads is said to be "long," and if it is sticky and adheres strongly to paper it possesses a high degree of "tack." A "short" ink is one which cannot be pulled into strings. The compound "livers" if it stiffens perceptibly on standing, an indication that the ingredients are not stable. "Offset," as applied to inks, means that the freshly printed sheets smudge and that, when stacked in piles, the pigment on one is partially transferred to those above or below. "Striking through" occurs when the back of the paper is discolored by penetration of the ink. The ink "breaks down" if its viscosity is decreased by stirring or agitation.

In general, printing inks are made up of four different materials, pigments, vehicles, driers and "compounds," each of which has its own function. The pigment, in addition to providing the color and opacity, serves to stiffen the vehicle and give it more body. If a pigment is used principally as a coloring agent it is known as a toner; but if its purpose is to improve the physical characteristics of the batch it is usually white

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The following books are especially concerned with intaglio processes:
"Guide to the Processes and Schools of Engraving," The British Museum, 1930.
Singer and Strang, "Etching and Engraving," 1897.

The following books describe in detail the various planographic processes:
A. Senefelder, "A Complete Course in Lithography," R. Ackermann, London, 1819. (This book, by the inventor of lithography, is only to be found in the more important libraries.)
D. Cummings. "Handbook of Lithography," 1919.
F. T. Corkett, "Photolithographic and Offset Printing," American Photographic Club Publication, 1923.
C. Harrop, "Offset Printing from Stone Plates," 1927.
H. J. Rhodes, "The Art of Lithography," D. Van Nostrand Co., New York, 1924.

As illustrations of the three types of presses, see:
Relief or Typographic presses:
F. Fallert, U. S. P. 1,900,923, March 14, 1933.
H. A. W. Wood, U. S. P. 2,050,031, Aug. 4, 1936, to Wood Newspaper Machinery Corp.
B. C. Stickney, U. S. P. 1,949,223, Feb. 27, 1934.

Lithographic and Offset presses:
W. R. Hotchkiss, U. S. P. 1,988,970, Jan. 22, 1935.
H. M. Barber, U. S. P. 2,003,798, June 4, 1935, to C. B. Cottrell & Sons Co.

Intaglio presses:
A. Weiss, U. S. P. 2,055,272, Sept. 22, 1936, and U. S. P. 1,631,169, June 7, 1927, Reissue 18,856, June 6, 1933.

or colorless and is called an extender. The pigments which are of value for either reason may occur in nature or are the result of a manufacturing process, but the prepared materials dominate the field today.

Of the many substances which are found in nature only a small number are suitable for use in inks, since a pigment must have a high degree of opacity, and at the same time, not be abrasive or gritty, as the plates from which the impression is taken are readily scratched. The pigments of this type which have been most successful are almost exclusively of mineral origin, as the coloring medium should be insoluble in the vehicle if a true suspension is to be formed. On the other hand, natural pigments hold their color well, resist weathering and, for this reason, are especially well adapted to poster and similar work. Indian red, ochre and sienna, which are all mixtures of iron oxides, may be taken as typical. Bituminous materials, including both asphalts and pitches, are frequently made up into varnishes and used for printing, particularly in rotogravure processes. Organic compounds of natural origin such as indigo, alizarin, purpurin, which are extracted from vegetable matter, and carmine, derived from the insect known as cochineal, were known and used as dyes and pigments centuries before any printing process had been developed. These have been almost entirely eliminated from modern inks, however, because of the lower cost, greater uniformity and wider color range of the synthetic preparations.

The manufactured or synthetic pigments also fall into two broad groups, inorganic and organic. Barium sulphate, chrome green, lithopone, titanium oxide, vermilion and white and red lead may be taken as examples of the former type. In general, these compounds are unaffected by ink vehicles or the common solvents and, even when finely ground, have little tendency to fade. The synthetic organic pigments are generally coal-tar derivatives of complex composition and are discussed in a later chapter.[7]

A great step forward was taken during 1937 when an international color code which comprised seven hundred and twenty distinct shades was adopted. This was made possible by the spectrophotometer, a photoelectric recording device which classifies and verifies colors by entirely mechanical processes, thus eliminating the human element. Colors have even been matched by telegraph with the aid of this equipment.

While the pigment determines the color and appearance of the finished ink, the vehicle controls, to a great extent, the way the preparation will dry and also the manner in which it will handle on the press. Therefore, it is the vehicle,[8] not the pigment, which is changed when it is necessary to make an ink tacky for a typographic plate or buttery for intaglio work. The various oils which are in general use as vehicles are classified according to their origin, that is, animal, mineral and vegetable, and the last

[7] See Chapter 6.
[8] See Chapter 3.

and most important group is further subdivided into drying and non-drying materials.

The oils, such as tallow, lard oil and neatsfoot oil, derived from land animals, are in general non-drying and greasy and are little used in inks. However, certain fish oils will form a film by oxidation and these, especially menhaden oil, are sometimes used as substitutes for linseed oil when the characteristic odor is not objectionable.

The mineral oils of petroleum origin will not dry by oxidation but are readily absorbed into soft uncoated paper. Since the oil does not form a film there is a tendency for it to stain and discolor the paper by penetrating through the sheet. If a cheap ink of semi-drying properties is required it is common practice to mix a heavy mineral oil with a drying oil in proportions which are largely determined by the absorption of the paper. There is, of course, a wide variety of modifiers including rosins and resins which may be added to the mineral oil to vary its body, viscosity, penetration and greasiness.[9]

The vegetable drying oils, linseed and tung oil, being the most widely used, are of great importance to the manufacturer of inks because of their ability to form a tough surface film after standing in contact with the atmosphere, the result of oxidation or polymerization. For the purposes of classification an oil may be considered to be drying if it has an iodine value of greater than 120 and non-drying if less than 100, the intervening range including the semi-drying oils.

The methods of preparing and bodying these oils are, essentially, pressing the seed or nuts to express the oil, filtering and settling to remove any portion of the husks and, for certain work, such as lithography, treating with heat to obtain the desired body.

The non-drying oils derived from vegetable matter, for example castor oil and olive oil, will not form a film upon standing regardless of the length of time, and for this reason hold little interest for the ink maker. Even the semi-drying oils, of which cottonseed oil is the most important, are seldom used in printing work except as a blending or thinning medium because of the long period of time required for oxidation.

The vehicle may "dry" either by oxidation, by evaporation, or by penetration into an absorbent paper. When drying oils are used, the length of time required to harden the ink may be greatly decreased by the addition of small amounts of metallic catalysts or driers. The preparations used in the manufacture of inks are the same as those which have proved most valuable in paints or varnishes and are usually derivatives of cobalt, lead or manganese. Cobalt driers are used where speed is of the greatest importance, but where delicate tints are involved the dark color of the organic salts of this metal may be objectionable. In practice it has been found that cobalt driers form a tough gloss film on

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[9] Carleton Ellis, "Chemistry of Petroleum Derivatives," Reinhold Publishing Corp., New York, Volume I, 1934; Volume II, 1937.

the surface of the ink, while the lead salts tend to harden the film uniformly throughout but at a much slower rate. Consequently, the best results are frequently obtained by using a blend of lead, manganese and cobalt.[10]

Driers are added to inks to decrease the time which would otherwise be required for hardening, and similarly there is a large group of materials, known in the pressroom as "compounds," which are added to supply other deficiencies in the vehicle or pigment.[11] One of the oldest of these modifiers is ordinary hard soap which, when added in small amounts, will cause the ink to leave the type or printing surface clean and adhere to the paper. Waxes are frequently incorporated to prevent the printed sheets from sticking together. Tallow, with or without starch, tends to prevent offsetting and blurring of the ink before drying. There are a large number of modifiers on the market at the present time, and it would be difficult to find a printing problem for which some compound has not been suggested. However, all preparations of this type must be used in moderation or the covering power and drying time of the ink will be affected.

TYPOGRAPHIC, INTAGLIO AND PLANOGRAPHIC INKS

Because each of the three printing processes employs an inherently different printing surface it is not surprising to find that there are three corresponding classifications of ink. Their general characteristics will be outlined in the following paragraphs.

Before it is possible to specify with any degree of exactness the qualities which a given typographic ink[12] should possess, consideration must be given to two other factors, the paper on which the impression will be made and the type and speed of the press which will be used. Job presses are commonly used on the better grades of paper, which are comparatively non-absorbent, and the ink must therefore dry primarily by oxidation. Such inks should be quite tacky so that the rollers will not slip on the platen and are generally quite stiff because of the high proportion of pigment to vehicle.

When faster equipment, such as automatic or flatbed cylinder presses is used, the ink must flow more readily so that it will feed properly at higher speeds and must dry more rapidly because of the rate of production of the work. In the case of newspaper presses the ideal ink is extremely thin, the limit of fluidity being reached just before the point at which a mist of ink is formed by the rapidly moving rollers, since everything in the vicinity will be coated when this occurs. Since the paper used on these presses is highly absorbent, the vehicle is generally a non-

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[10] Details of the various types of driers and of the theories advanced to explain their action are given in Chapter 4.

[11] See Chapter 5.

[12] For a more detailed discussion of typographic inks see Chapters 7 and 8.

drying mineral oil that penetrates the newsprint rapidly. The pigment as well as the vehicle must be carefully selected for relief work when a fine line half-tone is used, as a coarse or imperfectly ground filler will clog the plate. Carbon black[13] is used almost exclusively for half-tone printing since it is inexpensive, and, at the same time, has high covering power. However, this pigment slows down the hardening time of the ink and requires the use of a relatively high proportion of drier.

Intaglio inks[14] are of two general kinds, those prepared for copper or steel plate work and rotogravure inks. When printing from an incised plate the ink must be easily wiped from the surface of the metal without drawing it from the depressions. This means that the vehicle must not be tacky or the pigment in the depressions will be removed when the surface is rubbed. On the other hand, if the ink is oily it will be almost impossible to clean the raised portions of the plate so that no mark will be left on the paper when the impression is made. A further limitation is imposed by the fact that the paper is dampened before the impression is made to render it softer and, therefore, the ink must not run on the moistened sheet. The vehicles used for intaglio plate work are almost exclusively of the drying oil type since there is little, if any, penetration of the ink in this process as it is deposited in a thick film on the surface. For this reason also, pigments of lower coloring power may be used, but it is most important that they be finely ground so that the soft copper plate will not be scratched.

While the intaglio inks for plate work are pasty in consistency, rotogravure inks are almost as liquid as water. This extreme degree of fluidity is necessary because of the high speed at which the cylinder revolves and also because the ink dries primarily by evaporation of the volatile vehicle, which may be carbon tetrachloride, toluene, or a similar solvent. The pigment must be one which will not settle out during standing in the reservoir and must be absolutely free of abrasive particles which would accumulate between the doctor blade and the rapidly rotating cylinder and quickly ruin the surface. Mixtures of asphalts or resins dissolved in the vehicle are the most frequently used coloring mediums for this type of ink.

As compared with the other methods of printing, the planographic processes must operate with extremely thin layers of ink and, therefore, the film must have high covering power and concentration of color.[15] Because the transferred films are so light, hardening will usually take place in a short time with a small proportion of drier.

In selecting either pigment or vehicle for lithography, the peculiarities of the process must be considered. Here again the ink will come in contact with moisture and, in this case, a certain amount of acid may be

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[13] H. J. Wolfe, "The Manufacture of Printing and Lithographic Inks," MacNair-Dorland Co., p. 185. New York, 1933.

[14] See Chapter 10.

[15] See Chapter 9.

present in the water resulting from the etching. Since the stone or plate is alternately wetted and inked there is danger of emulsification if the vehicle is too fluid. The ideal ink for this work is one which possesses sufficient body so that it will not run freely, has a considerable amount of tack, and yet is not so adherent that there will be difficulty in pulling the paper from the plate. When a stone is used, the ink should leave a clear image without excessive pressures if the maximum number of copies is to be obtained from the comparatively delicate surface. In general, ink which is to be applied on an offset press will be very similar to one which is suitable for lithography, the use of the rubber transfer cylinder requiring a pigment of strong coloring power.

It is almost impossible to define the characteristics of an ink for a specific purpose with any degree of precision even when the process, paper and type of press are known. Extremes of atmospheric conditions, particularly of temperature and humidity, will require that the material be modified for proper application, and it is known that an ink which handles well in the inland portions of the country may be unsatisfactory along the coast.[16] Consequently, the printing establishment which handles any volume of work frequently finds it necessary to blend its ink to meet variations in weather or paper. In the last analysis much must be left to the judgment of the pressman, but his problems are concerned with the physical characteristics not the chemistry of the material.[17]

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[16] H. G. Kriegel, "Encyclopedia of Printing, Lithographic Inks and Accessories," H. G. Kriegel Co., New York, 1932, 52.

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Chapter 2

History of Printing Inks

The early history of printing ink is found in the development of writing fluids, for the preparations which were used by the early printers were merely adaptations of materials that had been developed through many centuries for work with a pen. In fact, the simple printing inks of the early nineteenth century, consisting of a suspension of finely divided carbon in drying oil, were merely a more viscous form of the writing ink used by the Greeks and Romans.[1]

It is not surprising to find that the inventor of writing ink cannot be named with certainty. Indeed, there is considerable doubt as to the portion of the world in which it originated although the claims of the Egyptians or the Phoenicians are most persuasive.[2] The first writings consisted of characters either incised in stone tablets or marked in damp clay with a stylus and later baked in kilns, as the Assyrians and Babylonians formed their cuneiform blocks.

It is interesting to speculate as to why these laborious methods of writing were used, when dyes which might have been used for ink and cloth which had been known for centuries were available, and would have been much less troublesome. The answer lies in the fact that writing, which was an accomplishment possessed by the very few, was employed only for announcements or memorials of great importance. For such inscriptions the most enduring mediums were chosen and stone and clay were well adapted to the purpose. In short, the forerunners of ink and paper were not developed prior to 2000 to 4000 B.C. simply because there was no need for them. A similar explanation may be given for the lack of interest in printing up to the fifteenth century A.D., although much more intricate devices were invented by the Romans. Here again no one worked on the problem since the number of slaves who could transcribe documents was ample to supply the need, and, in fact, a daily newspaper the "Acta Diurna," which was copied entirely by hand, was mentioned by Cicero as the medium of recording the social and political news of his day. With a sufficient number of manuscript books which could be produced by slave labor at nominal cost the early civilization had no need for printing, and the invention waited until there was a demand, when the problem was quickly solved. So we find that the history of printing and of printing inks is one where development has waited upon the requirements of the times.

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[1] Thaddeus Davids, "The History of Ink," Thaddeus Davids & Co., New York, 1860.

[2] David N. Carvalho, "Forty Centuries of Ink," Banks Law Publishing Co., New York, 1904.

EARLY WRITING MATERIALS

Perhaps the first materials which could be classified as inks were the dyes which were used by the Egyptians to color the engraved markings in stone to render them more conspicuous. The color matter was a suspension of powdered charcoal and gums in water. Probably this preparation was too viscous and pasty to be used with a pen or stylus.

As nations and trade expanded, the need arose for some writing material which was more portable and convenient than stone. Papyrus sheets, made from the reed of the same name, were probably one of the first solutions of the problem. The oldest papyri known today are estimated to have been made about 2500 B.C., although one document of uncertain date records events which are supposed to have occurred before 3500 B.C. Sheets of this material were adopted in all the classical countries at an early date because of their superiority over skins or cloth. The Greeks are known to have used papyrus in the fifth century B.C. and the Romans employed it almost exclusively for correspondence and legal documents. It continued in favor until paper began to take its place after the eighth century A.D. In the fifth century, St. Augustine apologized for writing a letter on parchment instead of the usual papyrus.

Little is known of the very early methods of preparing sheets of papyrus for writing purposes, but the following description taken from a contemporary account[3] relates to the process as it was used about the first century A.D. The stem of the papyrus reed, which was about two inches in diameter, was split lengthwise to form strips of varying width depending on whether they were taken from the middle or near the side of the reed. These strips were laid parallel to one another on a board and then covered with a second layer which ran at right angles to the first. By soaking in water the sheet which had been built up in this manner, the glutinous matter in the pulp was dissolved and cemented the assembly into a coherent mass which was pounded with hammers to form a thin, dense sheet. After drying, the papyrus was ready for use unless rough portions required polishing with ivory to improve the surface. Generally, the single sheets, ranging from six to ten inches in width, were pasted together to form a long sheet which might be rolled and conveniently handled.

The skins of animals were among the first substances to which man turned when he needed a convenient material on which to write. The Egyptians brought the art of manufacturing papyri to a relatively high state of development at an early time, however, and it seems that parchment and vellum did not become a serious competitor of the former material until about the third or fourth century A.D. While this is somewhat surprising inasmuch as the tanning of hides must have been one of mankind's first discoveries, the explanation probably lies in the

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[3] Pliny the Elder, "Naturalis Historia," xiii, 12.

fact that the first parchments were suitable for writing on only one side and also because leather was in demand for many other uses. Pliny relates that parchment of good quality was first made in Pergamun, an ancient town in Asia Minor, about 150 B.C., and that the artisans of that city were compelled to make excellent writing material from skins by their ruler who, by attempting to assemble the largest library of his time, incurred the jealousy of the Ptolemies. The Egyptians, therefore, prohibited the exportation of papyrus which was used almost exclusively at the time and forced Eumenes, the king of Pergamun, to develop a substitute in order to achieve his ambition. Whether or not this is historically accurate, it was not until several hundred years later that parchment came into widespread use in Europe.

Strictly, the terms vellum and parchment are not synonymous, as the former is made from the skin of young or unborn calves while the latter is prepared from the hide of sheep or lambs. The terms are frequently used interchangeably, however, and the methods of manufacture are very similar, the skin first being freed from hair and then soaked in lime water, after which it is stretched and scraped. The unevenness which remains after scraping is removed by rubbing with pumice, and the entire process is repeated until the desired surface is obtained. Refinements in the preparation of parchment were made rapidly, and by the fourth century of our era the sheets had a smooth surface and delicate texture. Shortly after this, cheaper grades came on the market in response to the increasing demand, and it has been suggested that the finer the piece of parchment the greater the probability of its antiquity.

The relative sizes of parchment sheets in use at various times provides an interesting index of its popularity and corresponding scarcity. Up to the year 500 A.D. it was common to write upon only a single side of a sheet although, even at that time, both surfaces could have been used. With the increasing demand and consequent greater cost it became usual to employ both sides, and about the thirteenth century, at the peak of its vogue, parchment was commonly used in the form of extremely small sheets three inches square or even smaller. Shortly thereafter paper came into common use, the demand for parchment decreased and once again large sheets were used. During the Middle Ages, when parchment was almost unobtainable, it was common to scrub out the old ink from a previously written sheet and use it again. Manuscripts of this type are termed palimpsests and have been a source of irritation through the ages to scholars who have been able to recognize fragments of works of great antiquity beneath the relatively recent writings of some scrivener which are of little interest from either a historical or literary point of view.

The manufacture of parchment reached a high state of perfection in the days when the material was most popular. Books, containing upwards of five hundred pages of the better quality of parchment, were not uncommon and, because of the thinness of the sheets, the volumes were not of abnormal bulk. As vellum gained in favor it was sometimes dyed purple and embellished with letters of gold for the more important documents. Occasionally, also, books were made with leaves of parchment interspersed among pages of papyrus, the hope being that the former would reinforce the sheets of vegetable origin which tended to become brittle with the passage of time.

Both papyrus and parchment have been replaced, the first entirely and the second almost entirely, by paper which had become well known in Europe during the twelfth century, if not before.

The Early Writing Fluids

Because the characteristics of the inks of any period are to some extent determined by the nature of the material on which the work was performed, a very brief description of the development of parchment and papyrus has been given. Just what the earliest inks used on papyrus were composed of is uncertain, but probably the pigment was soot, or some other finely divided form of carbon, suspended in a varnish in which a drying oil was the principal ingredient. It is certain, however, that the pigments used have retained their color over a span of almost five thousand years. It has been suggested that the scribe made up his own inks on a small plate as he required them.[4] Two colors, black and red, were in common use; the pigment for the latter was, in all probability, iron oxide. It seems reasonable to assume that the inks of ancient times were all made up of a pigment mixed with water containing dissolved gums or a drying oil. It was typical of these preparations that the pigment was not soluble in the vehicle and, therefore, the coloring matter did not penetrate the body of the sheet but merely lay upon the surface, to which it adhered by virtue of the gum or oil contained in the vehicle. While such inks must have been inconvenient and far from free-flowing, they were generally used, for by the sixth century B.C. the art of handwriting had become widely adopted in place of engraving on stone, scratching on sheets of lead or wax or molding in clay.

Coming to a period shortly before the time of Christ, it seems that ink was made as an article of commerce in the form of blocks of gum and pigment which were ground with water by the purchaser to make writing fluid. One recipe which was used for such an ink was one part of copper sulphate, one part of glue made from ox hooves, and sixteen parts of soot which was prepared by burning resin. This same composition was recommended for the treatment of burns!

The preparation of finely divided carbon for use in inks seems to have been a carefully controlled process since only the cheaper varieties of pigment were made from chimney soot. In the manufacture of the

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[4] J. H. Breasted, "The Physical Processes of Writing in the Early Orient and Their Relation to the Origin of the Alphabet," *Jour. of Semitic Languages*, (1916).

better grades, pitch was burnt in a small room which was completely tiled so that the carbon which was deposited could be readily brushed off and collected.[5]

The inks which have been previously described consisted of an insoluble pigment suspended in a vehicle which merely bound the coloring matter to the surface of the sheet. It is about this time that the first mention of encaustic inks is found, that is, inks which penetrated the body of the sheet rendering erasure much more difficult. One of the first of these preparations is described as being made by boiling apple rind in water to which beer wort had been added. After filtering, a small quantity of alkali was added to aid in the penetration of the writing fluid. Pliny wrote in 76 or 77 A.D. that, "ink whose materials have been liquefied by the agency of an acid is erased with great difficulty." The "vitriolic" ink of that time was, in all probability, a suspension of lampblack and copper sulphate in water and found considerable favor with the priests who used it for their religious manuscripts for two or three hundred years. Indeed, an ink of this sort, containing copperas, was recommended by Celsus as a cure for baldness because of its irritant nature.

In the Orient, meanwhile, the Chinese had by the beginning of the third century developed a satisfactory formula for the product misnamed "India ink" and had abandoned the use of bitumens as coloring matter.[6] While no contemporary account has come down to us of the method of manufacture, the following description, written a few centuries later, is probably representative. The chief ingredient was lampblack which was pounded through fine silk to reduce its size and remove foreign matter. A paste was then made up consisting, in addition to the carbon, of glue, water, the whites of several eggs, cinnabar and musk. After prolonged grinding in a mortar the ink was cast in sticks which is the form in which it was, and still is, sold. The art of ink making made rapid strides in China and by the year 600 A.D. there were at least twenty-five prominent firms engaged exclusively in this line of work; and a government official was appointed whose sole duty was to superintend the preparation of writing materials for use by the government.

Colored inks had, in the interim, become popular in Europe, and red inks, of vermilion and cinnabar, or blue inks, of indigo, cobalt and copper oxide, were commonly used in illuminating manuscripts. India ink was imported from China when the finer qualities of black were required.

With the fall of Rome, development either ceased entirely or proceeded at snail's pace. The last advance of note before the Dark Ages was the invention of the quill pen which permitted the use of a more liquid ink than that which had been employed with reeds. From the standpoint of permanency of the ink this was a change for the worse as

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[5] Pliny the Elder, "Historia Naturalis," xxxv, 25.

[6] Frank B. Wiborg, "Printing Ink," New York, Harper & Brothers, 1926.

the more fluid preparation contained less pigment and hence decreased the coloring power. From this time, for a period of about five hundred years, the progress in Europe, such as it was, was made almost exclusively by the monks who transcribed almost unbelievable quantities of manuscript in the attempt to record and preserve the knowledge of the times in the form of memoranda which they called *secreta*. It was during this same period that papyrus was entirely abandoned in favor of either parchment or the first papers which were made in Spain about 1100 A.D. from rags of cotton or linen.

A typical formula for ink, taken from a *secretum* written about the year 1000 A.D. states that branches of thorn trees (probably Norway spruce) should be cut and dried in the sun, after which the bark should be peeled off and soaked in water for about a week, when the liquor is strained off and boiled down to one-third its original volume. The heat should be continued until the fluid is almost black and shows a tendency to thicken, after which a quantity of wine equal to one-third the volume of the remaining water is to be added. The boiling is then resumed until a skin forms on the surface, and at that point the ink is poured into bags of leather so that the water will drain out and the remaining sludge is dried in the sun to form cakes of ink. When desired for use, the required amount of ink is mixed with wine to which a small quantity of acid is added. Ink of this nature has retained its color well throughout the centuries.

Gall inks were introduced into Europe about the year 1100 A.D. from Arabia, and this type of writing fluid gained great popularity in the succeeding centuries when it was made and used extensively in the monasteries. It is probable that these inks were prepared by crushing the gall nuts and keeping them moist in a warm place for several weeks when a mold forms on the material. The resulting mass was boiled to extract the coloring matter and this liquid, after filtering and the addition of copper sulphate, was the finished ink. Gums were occasionally added to improve the working quality of the fluid and, to some degree, to protect the pigment from oxidation. In more recent times, logwood and similar coloring matter have been used as an adulterant for gall inks. By the fifteenth century inks of this type had almost supplanted the previously popular India inks.

DEVELOPMENT OF PRINTING INK

With the year 1400, the invention of printing was at hand. As mentioned in the preceding chapter, the first European printing consisted of laying a sheet over the carved surface of wood block and then rubbing the back of the paper to transfer the design. The coloring matter used in this simple method was merely a form of distemper, that is, a paste formed of pigment, size and water. In the opening years of the fifteenth century the ***Biblia Pauperum*** or Poor Man's Bible was published. Previous to this time it had been fairly common practice to print the illustration for the text on a page from a carved wood block, leaving the balance of the sheet for the scribe who later filled in the written matter by hand. It occurred to the artisan engaged in the preparation of this book that the text as well as the illustrations might be placed on the same block. The next step was easy, and within thirty years the art of printing from movable type[7] had been developed. Davids[8] describes the ink first used in printing in the following language, "It was writing-ink. It contained sulphate of iron (copperas), in combination with vegetable astringent matter, and with very little carbon. The vegetable substance, imperfectly united to the mineral ingredient, has (in obedience to the laws of organic matter) been decomposed and 'resolved into its original elements.' It has disappeared; but the iron remains with its yellow stain, an imperishable memorial of that humble, nameless workman."

Within the same century, however, printing became increasingly popular, and the inks used were apparently the more suitable mixtures of linseed oil and lampblack which were applied to the surface of the type with inked pads. At that time each printer manufactured his own inks, but the quality must have been good as may be seen by the still brilliant colorings of the Gutenberg Bible. Unfortunately, as competition increased, there was a tendency to adulterate the linseed oil with cheaper mineral oils and rosin or to boil it insufficiently[9] so that the printing ink of the sixteenth century was generally inferior to that of a hundred years earlier. In the case of the better grades of ink, the lampblack was prepared by burning pitch beneath a metal hood on which the soot collected. The drying oil was previously brought to the desired body by boiling, and the pigment and vehicle were then ground together to form the ink. When presses ran slowly and soft handmade papers were used, ink prepared in this manner was entirely satisfactory and few, if any, changes were made during the next three hundred years. In fact, Benjamin Franklin made his own ink in Philadelphia using these same ingredients, and this same mixture of boiled linseed oil and lampblack was described as being the most suitable preparation in the nineteenth century.[10]

In the eighteenth century, it became common practice to burn the linseed oil during bodying which, it was generally believed, prevented the oil from spreading upon the paper.[11] Bread was occasionally thrown into the heated oil in the hope that it would absorb the fatty or greasy portions, according to Fertel.[12]

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[7] See Chapter 1.

[8] Thaddeus Davids, "The History of Ink," New York, Thaddeus Davids & Co., 1860.

[9] J. Moxon, "Mechanick Exercises," London, 1677.

[10] T. C. Hansard, "Typographia," London, 1825.

[11] C. Ainsworth Mitchell, "Inks, Their Composition and Manufacture," Charles Griffin and Co., London, 1937.

[12] J. Fertel, "La Science Pratique de l'Imprimerie," St. Omer, 1723.

While there were various methods of preparing the lampblack and the oil, practically all printing inks consisted solely of vehicle and pigment. In 1823 the first ink recipe which contained a "compound" was published.[13] This formula consisted of linseed oil, rosin and hard soap which was added, as it is today, so that the ink would leave the type easily. Of the same general nature is the following recipe described as a modern ink in the early part of the nineteenth century:[14]

Balsam of capivi	9 oz.
Lampblack	3 oz.
Indigo, or Prussian blue, or equal quantities of both	1¼ oz.
Indian red	¾ oz.
Turpentine soap, dry	3 oz.

Such is the history of typographic inks. Because the quantity of ink found on a printed sheet is so small, it would be impossible to reconstruct the old formulas by analysis even if the material had not been altered by the passage of time. As a result, any attempt to trace the development of ink is dependent on contemporary descriptions, which are not too plentiful as the manufacturer jealously guarded the secrets of his process. Intaglio inks were apparently made from the same ingredients with slight modifications since little reference is found to them in the literature as a distinct type. The reader who is interested in the beginnings of lithographic ink can do no better than to refer to the complete treatise written by Senefelder[15] who describes the composition of the various waxy inks he developed for stone printing. So exhaustive was his work in this respect that there has been no change of consequence in his formulas during the century which has passed since his renowned methodical study.

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[13] "Encyclopaedia Britannica," Sixth Edition, London, 1823.

[14] William Savage, "The Preparation of Printing Ink," London, 1832.

[15] Alois Senefelder, "The Invention of Lithography," London, 1819, or the modern edition published in 1911 by Fuchs and Lang Mfg. Co., New York.

Chapter 3

Printing Ink Vehicles

The vehicle of a printing ink is the liquid material holding and carrying the pigment and providing good workability on the press. Properties of the vehicle must conform to the kind of printing process.[1] One of the most important properties is the viscosity. The varnishes are classified from #00000 to #9 (representing the heaviest), mostly in accordance with the standards as specified by Gardner and Holdt,[2] which are discussed in Chapter 17. Either extremes are very unusual, but the most viscous vehicles are used in special inks which are solid at ordinary temperatures and must be heated before being applied to the paper.

CHEMICAL AND PHYSICAL CONSTANTS OF VEHICLES

Vehicles usually are described by listing certain physical and chemical constants. Iodine number, hexabromide number and thiocyanogen value are indications of the degree and quality of vehicle unsaturation. Acid number, saponification value, and quantities of oxy-acids, unsaponifiable matter, saturated acids and solid fatty acids describe the acidic properties. Specific gravity, index of refraction and viscosity are physical properties.

The iodine number is the number of centigrams of iodine taken up by one gram of oil. The common method of determining this number is to use the procedure of Wijs.[3] The Hanus [4] method also may be employed, but the Wijs procedure apparently is preferred. The iodine value is considered a reliable measure of the total unsaturation of fatty acids and is a measure of the drying potentialities of a vehicle.

The hexabromide number is the weight percentage of hexabromide precipitate obtained by treating fatty acids with bromine. This number is evaluated by multiplying the total weight of hexabromide precipitated by 100 and dividing by the weight of the sample.[5] The hexabromide value is said to be an indication of the amount of acids containing three double bonds, and is reported to be a method of determining adulteration of linseed oil with soybean oil.

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[1] J. D. Cohen, *Paint Manuf.*, 1937, 7, 246; *Brit. Chem. Abs.* B, 1937, 1238; *Chem. Abs.*, 1937, 31, 7673.

[2] H. A. Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," 7th ed., Institute of Paint and Varnish Research, Washington, D. C., 1935, 564.

[3] J. J. A. Wijs, *Analyst*, 1929, 54, 12; *Chem. Abs.*, 1929, 23, 1518; *Chimie & industrie*, 1928, 20, 1043; *Chem. Abs.*, 1929, 23, 2052. *Z. Untersuch. Lebensm.*, 1928, 56, 488. *Ber.*, 1898, 31, 750; *J. S. C. I.*, 1898, 17, 699. H. A. Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," Institute of Paint and Varnish Research, Washington, D. C., 1935.

[4] J. Hanus, *Zeits. Untersuch Nahr. Genussn*, 1901, 4 (20), 913; *J. S. C. I.*, 1901, 20, 1246, H. A. Gardner, *loc. cit.*

[5] H. A. Gardner, *loc. cit.* H. S. Bailey and J. M. Johnson, *Ind. Eng. Chem.*, 1918, 10, 999; *Chem. Abs.*, 1919, 13, 2246.

The thiocyanogen (SCN) value is a measure of the quantity of free thiocyanogen $(SCN)_2$ that reacts with the double bonds of drying oils. A macro[6] or a semimicro[7] method[8] may be employed for the determination of this number. The free $(SCN)_2$ saturates the double bonds of oleic acid, one of the two double bonds in linoleic acid, and two of the three unsaturated double bonds in linolenic acid. The thiocyanogen number provides valuable information when employed in conjunction with the iodine value.

The acid number is calculated by multiplying the number of cubic centimeters of $0.1N$ alcoholic potassium hydroxide required to obtain a phenolphthalein end point with 10 grams of oil (in 50 cubic centimeters of 1:1 mixture of alcohol and benzene) by the factor 0.561.[9] High acid value is said to be a general indication that the oil or varnish will react with certain types of pigment and that the vehicle will wet the pigments easily.

The saponification number is the number of milligrams of potassium hydroxide required to saponify the free fatty acids in 1 gram of oil. The value is regarded as a measure of the free fatty acids present.[10]

The oxy-acids are oxidized substances formed when drying oils harden. Oxylinoleic acid and linoxyn are examples of these oxidation products. Quantitative data in relation to oxy-acids occasionally are given in describing a vehicle.[11]

Unsaponifiable matter and saturated acids usually are found by difference from the various chemical values described above. The term "solid fatty acids" is employed to indicate the percentage of fatty acids which are solid at room temperature.

The refractive index, specific gravity and viscosity are employed for the purpose of distinguishing oils under examination, and in some instances serve as measurements for control of polymerization of varnishes.[12] The refractive index of oils and varnishes is said to increase with increasing molecular weight and increasing unsaturation. Methods of measuring the above properties are described in Chapter 17.

Hydrogenation is recommended as a measure of unsaturation.[13] Meinel's method is suggested for detecting conjugated carbon double bond linkings.[14] Molecular surface properties of the oil medium for

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[6] H. A. Gardner, *loc. cit.*

[7] H. P. Kaufmann and L. Hartweg, *Fette u. Seifen*, 1938, 45, 356; *Chem. Abs.*, 1938, 32, 7756.

[8] R. S. McKinney, *J. Assoc. Official Agr. Chem.*, 1938, 21, 443; *Chem. Abs.*, 1938, 32, 8809.

[9] *Am. Ink Maker*, 1936, 14 (12), 25. H. A. Gardner, *loc. cit. U. S. Bur. Standards Scientific Paper* No. 183.

[10] C. R. A. Wright and C. A. Mitchell, "Animal and Vegetable Fixed Oils, Fats, Butters and Waxes," Charles Griffin and Co., London. 1903.

[11] C. R. A. Wright and C. A. Mitchell, *loc. cit.*

[12] *Am. Ink Maker*, 1936, 14 (12), 26.

[13] W. H. Stitson, *Paint Manuf.*, 1938, 8, 119; *Chem. Abs.*, 1938, 32, 5235.

[14] O. Preise, *Farbe u. Lack.*, 1938, 161, 173; *Chem. Abs.*, 1938, 32, 8804. K. Meinel, *Ber.*, 1937, 70, 429; *Chem. Abs.*, 1937, 31, 3865. The Meinel method consists of treatment of drying oils with a solution of bromine in methyl alcohol. The reaction products are extracted with diethyl ether, and the extract is mixed with a methyl alcohol solution of silver thiocyanate containing ferric ion. The colorations produced at intervals are expressed in terms of Congo red aqueous solutions of varying concentrations.

printing ink may be indicated by the magnitudes of the interfacial tensions and the contact angles with other phases (*e.g.*, pigment, paper, or water).[15]

VEGETABLE OILS

Linseed Oil. In many inks the vehicle consists only of linseed oil which has been "bodied" (polymerized), *i.e.*, heated until the desired viscosity is secured. Oil treated this way is designated also as "stand oil" or "varnish." If the ink is too heavy on the printing press, the printer will thin it by adding some light-bodied oil. This method, however, cannot be used to make stand oil on a large scale, although it would be very convenient to prepare only a #9 varnish and cut it with a very light-bodied oil to the proper viscosity. A varnish so prepared has properties entirely different from one bodied to the same viscosity.[16] Raw and very light-bodied oils represent the unpolymerized phase and are monomolecular. Uniformly cooked heavy varnishes contain only small quantities of monomolecular phase, if any.

According to the older methods of manufacture, the raw linseed oil was heated in a movable pot, ignited, and permitted to burn for five minutes. During and subsequent to this treatment the oil was carefully stirred. After five minutes of combustion the pot was removed from the fire, and the flames were extinguished by means of a closely-fitting lid. Several slices of stale bread were then successively introduced with a pair of tongs and stirred around in the oil until the bread slices were browned, but not burnt. The stale bread was supposed to remove "greasiness" from the oil. Occasionally peeled onions were employed for the same purpose. The action of neither bread nor onions was known.[17]

The preparation of stand oils must be done with utmost care in order to impart the right properties to them and to avoid many hazards which will be discussed later in this chapter. It is assumed and partly proved that deep-seated molecular rearrangements occur during this process, the most important of which are shifting of the double bonds from remote to conjugated positions,[18] also ester interchanges if different oils are cooked together or if rosins, catalysts or synthetic resins are added. Intermolecular diene syntheses perhaps take place.[19] The same oil, bodied by different methods, will yield liquids which behave entirely differently. Of great importance, too, is the pretreatment of the raw

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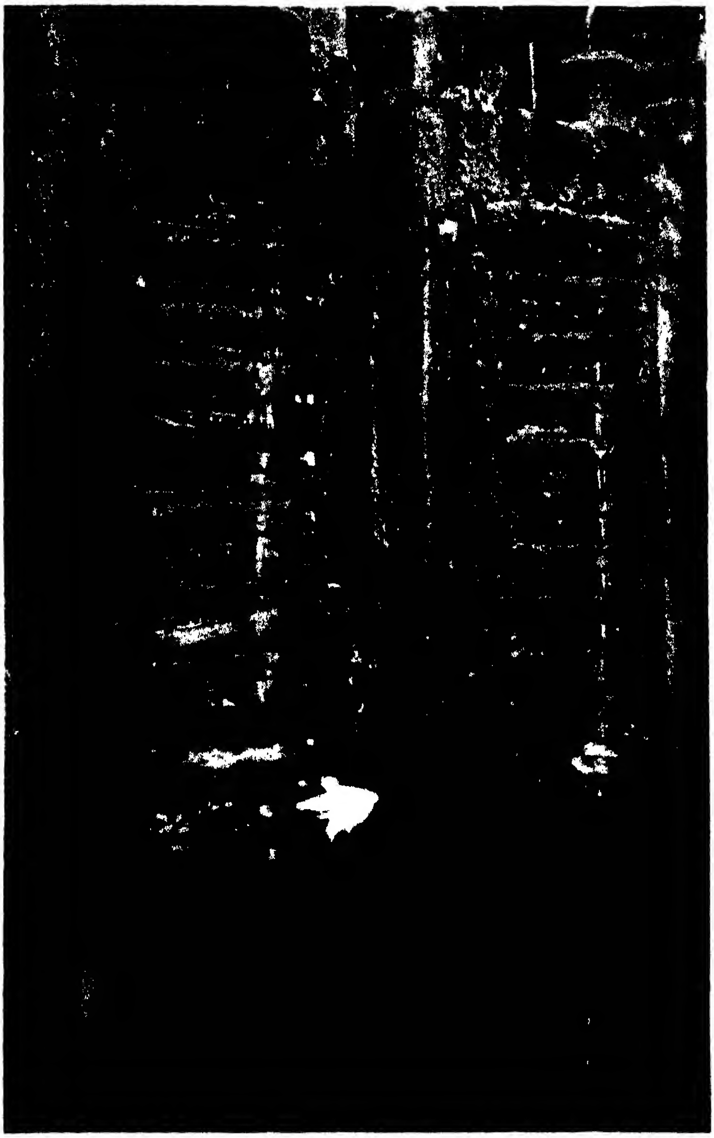
[15] L. A. Kozarovitskii, *Poligraficheskaya proisvodstvo*, 1937, No. 9, 23; *Chem. Zentr.*, 1938, 109 (1), 3116; *Rev. Paint, Colour, Varnish*, 1938, 11, 193. L. A. Kozarovitskii and M. A. Morozova, *J. Applied Chem.* (*U.S.S.R.*), 1938, 11, 442; *Chem. Abs.*, 1938, 32, 6080.

[16] T. H. Barry, *Oil, Col. Chem. Assoc.*, 1930, 13, 220; *Chem. Abs.*, 1930, 24, 5515; *Brit. Chem. Abs.* B, 1930, 1079.

[17] A. M. Villon, *Soc. Chim. Bull.*, 1893, 9, 929; *J. S. C. I.*, 1894, 13, 721.

[18] R. S. Taylor and J. G. Smull, *Ind. Eng. Chem.*, 1936, 28, 193; *Brit. Chem. Abs.* B, 1936, 334; *Chem. Abs.*, 1936, 30, 2409. J. Scheiber, *Angew. Chem.*, 1933, 46 (41), 643; *Chem. Abs.*, 1934, 28, 348; *Brit. Chem. Abs.* B, 1934, 26. B. P. Caldwell and J. Mattiello, *Ind. Eng. Chem.*, 1932, 24, 158; *Chem. Abs.*, 1932, 26, 1463.

[19] C. P. A. Kappelmeier, *Paint, Oil, Chem. Rev.*, 1938, 100 (1), 5; (2), 9; (3), 9; *Chem. Abs.*, 1938, 32, 3641.



Courtesy National Lead Company

FIGURE 5. Hydraulic Presses Removing Linseed Oil from Flaxseed.

oil, since the behavior of the stand oil prepared therefrom depends largely upon whether the raw oil has been hot- or cold-pressed or extracted. Bauer and Freiburg[20] state that oils have better drying power when they have been pressed cold compared with those which have been extracted or hot-pressed. Table 2 shows several properties of linseed oils from the same source subjected to these treatments.

Table 2.—Effect of Processing on Linseed Oil.

	Linseed Oil A Cold-Pressed	Linseed Oil B Warm-Pressed	Linseed Oil C Extracted
Acid number	1.22	2.5	4.81
Iodine number	169.87	169.81	168.58
Sapon. number	194.62	196.32	192.38
Oxy-acids	.52	.41	.55
Unsapon. matter	.66	.74	.64
Solid fatty acids	5.89	8.47	7.62

Heating changes the characteristics of linseed oil as indicated by variations in specific gravity, refractive index, acid number, iodine number, saponification number, thiocyanogen number, hexabromide number, saturated acids (per cent), and per cent of unsaturated acids.[21] Table 3 indicates the changes in these characteristics when linseed oil is heated in an enamel-lined vessel for 4 hours at various temperature ranges.

Table 3.—Effect of Heating on Linseed Oil.

Temperature Range of Heat Treatment	Original Oil	150-175° C.	175-200° C.	200-225° C.	225-250° C.
Specific Gravity (30° C.)	0.9311	0.9275	0.9382	0.9782	0.9843
Index of Refraction (26.5° C.)	1.4785	1.4801	1.4813	1.4833	1.4880
Acid number	3.2	2.3	2.0	1.6	1.3
Iodine number	199.7	195.3	176.2	171.2	149.8
Saponification number	192.0	196.0	199.5	210.8	194.3
SCN number	105.7	103.3	93.3	92.4	91.5
Hexabromide number	48.9	48.2	42.1	37.4	1.2
Saturated acids (%) (Bertram)	11.7	11.7	5.1	9.4	11.0
Unsaturated acids (%)	88.3	88.7	94.9	90.6	89.0

Upon being heated, linseed oil may "break." "Breaking" is a sudden and distinct separation of a gelatinous mass from raw linseed oil.[22] "Break" may be removed from linseed oil by treating the oil with sulphuric acid or superheated steam.[23]

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[20] K. H. Bauer and A. Freiburg, *Chem. Umschau, Fette, Oele, Wachse Harze*, 1931, 38 (6), 78; *Chem. Abs.*, 1931, 25, 2868; *Brit. Chem. Abs.* B, 1931, 551.

[21] P. S. Varma, N. N. Godbole, and G. M. Garde, *Allgem. Oel u. Fett.-Ztg.*, 1936, 33, 249; *Chem. Abs.*, 1936, 30, 6584.

[22] Other vegetable oils may exhibit "break" formation also.

[23] C. W. A. Mundy, *J. Oil Col. Chem. Assoc.*, 1935, 18, 238; *Brit. Chem. Abs.* B, 1935, 813.

Molecular weight determinations, by the freezing point[24] method, are recommended as process control tests for bodying drying oils.[25] According to the older methods of control measurements, the formation of threads, strings or leaves by the oil as it drips from the stirring ladle is employed to determine the heating end point. Some manufacturers decide that bodying is complete when a certain length of thread is obtained by drawing out the oil between the thumb and forefinger. However, the only accurate method, of all those described above, is said to be the one employing molecular weights.[26] Another desirable method of control in stand oil formation is to measure the refractive index, since the latter increases with molecular weight.[27] Specific gravity and viscosity are also possible measurements for control work.

It is to be noted that molecular weights may be found from viscosity measurements as well as the freezing point methods. A special equation known as Staudinger's Law is employed for this purpose.[28]

Much useful research work has been accomplished by determinations of molecular weights. Tabulated results of work done on the bodying of linseed oil indicate that the molecular weight increase is much greater than can be accounted for by the addition of oxygen as calculated by the decrease in iodine number.[29] Figures 6 and 7 show the effect of heat treatment upon the molecular weights of several samples of linseed oil. Two types of reactions are said[30] to take place in the process of body-

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[24] The freezing point lowering of benzene is employed. The calculation of the molecular weight is carried out by the following Raoult equation:

$$\frac{ME}{P} = C$$

M = Molecular weight of the dissolved substance.
E = Depression of the freezing point caused by dissolving the substance whose molecular weight is to be found.
P = The number of grams of substance contained in 100 gm. of solvent.
C = Characteristic constant.

(J. Traube, "Physico-Chemical Methods," Philadelphia, P. Blakiston's Son & Co., 1898.)

Benzene boiling between 80.0 and 80.3° C. and having a specific gravity of 0.87373 is employed. A sample weighing about 0.8 gram is dissolved in 25 c.c. of benzene. By use of carbon tetrachloride, carbon bisulfide, and nitrobenzene, the freezing point constant was found to be 5.065 to 5.067 for the benzene used.

[25] J. S. Long and J. G. Smull, *Ind. Eng. Chem.*, 1925, 17, 138; *Chem. Abs.* 1925, 19, 901.

[26] J. S. Long and J. G. Smull, *loc. cit.*

[27] *Am. Ink Maker*, 1936, 14 (12), 26.

[28] H. Wolff, *Fettchem. Umschau*, 1935, 42, 169; *Brit. Chem. Abs.* **B**, 1935, 1101; *Chem. Abs.* 1936, 30, 2026. H. Staudinger, *Ber.*, 1932, 65, 267; *Chem. Abs.*, 1932, 26, 2633. *Helv. Chim. Acta*, 1932, 15, 213; *Chem. Abs.*, 1932, 26, 2632. *Ber.*, 1934, 67, 92; *Chem. Abs.*, 1934, 28, 1589. H. Staudinger, "Die Hochmolekularen Organischen Verbindungen," Berlin, Julius Springer, 1932. The Staudinger equation is given as follows:

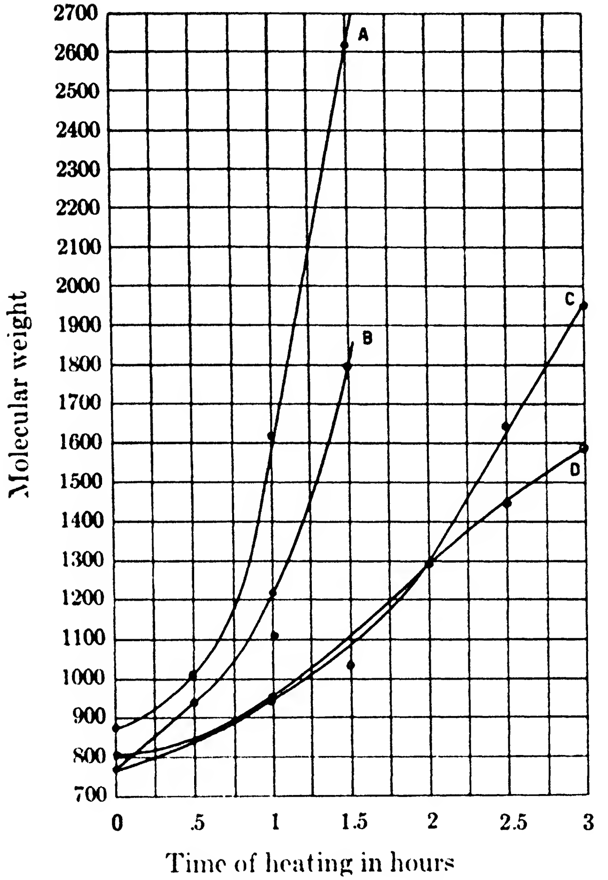
$$\frac{K_m}{M} = \frac{\eta_{sp}}{C}$$

Where: η_{sp} is the specific viscosity,
M is the molecular weight,
C is the concentration,
K_m is a constant.

The equation is applicable to dilute solutions of stand oil only, and hence the oil is dissolved in chloroform or toluene before determinations of viscosity are made. The formula is derived for use with compounds of long-chain molecular structure. The derivation is given in: H. Staudinger and W. Heuer, *Ber.*, 1930, 63, 222; *Chem. Abs.*, 1930. 24, 2993.

[29] J. S. Long and J. G. Smull, *Ind. Eng. Chem.*, 1925, 17, 138; *Chem. Abs.*, 1925, 19, 901.

[30] J. S. Long, C. A. Knauss, and J. G. Smull, *Ind. Eng. Chem.*, 1927, 19, 62; *Chem. Abs.*, 1927, 21, 657. J. S. Long and G. Wentz, *Ind. Eng. Chem.*, 1925, 17, 905; *Chem. Abs.*, 1925, 19, 3026. C. P. A. Kappelmeier, *Paint, Oil, Chem. Rev.*, 1938, 100 (1), 5; (2), 9; (3), 9, 19; *Chem. Abs.*, 1938, 32, 3641. H. Kurz, *Angew. Chem.*, 1936, 49, 235; *Brit. Chem. Abs.* **B**, 1936, 749.



Courtesy Industrial and Engineering Chemistry

FIGURE 6. Effect of Heating on Molecular Weight of Linseed Oil (J. S. Long and G. Wentz).

Curve A. 400 grams linseed oil and 40 grams fatty acids from linseed oil in open 13-cm. casserole
Curve B. 300 grams linseed oil and 0.6 gram $Mn_2B_4O_7$ in open 13-cm. casserole
Curve C. 200 grams linseed oil in open 13-cm. casserole
Curve D. 200 grams linseed oil in 13-cm. casserole covered with glass plate

ing. These reactions are:

(1) Reactions leading to a decrease in the number of ethenoid linkages, with little corresponding change in molecular weight.

(2) Condensations, involving elimination of water and other products and great changes in molecular weight.

The molecular changes may be represented as follows:[31]

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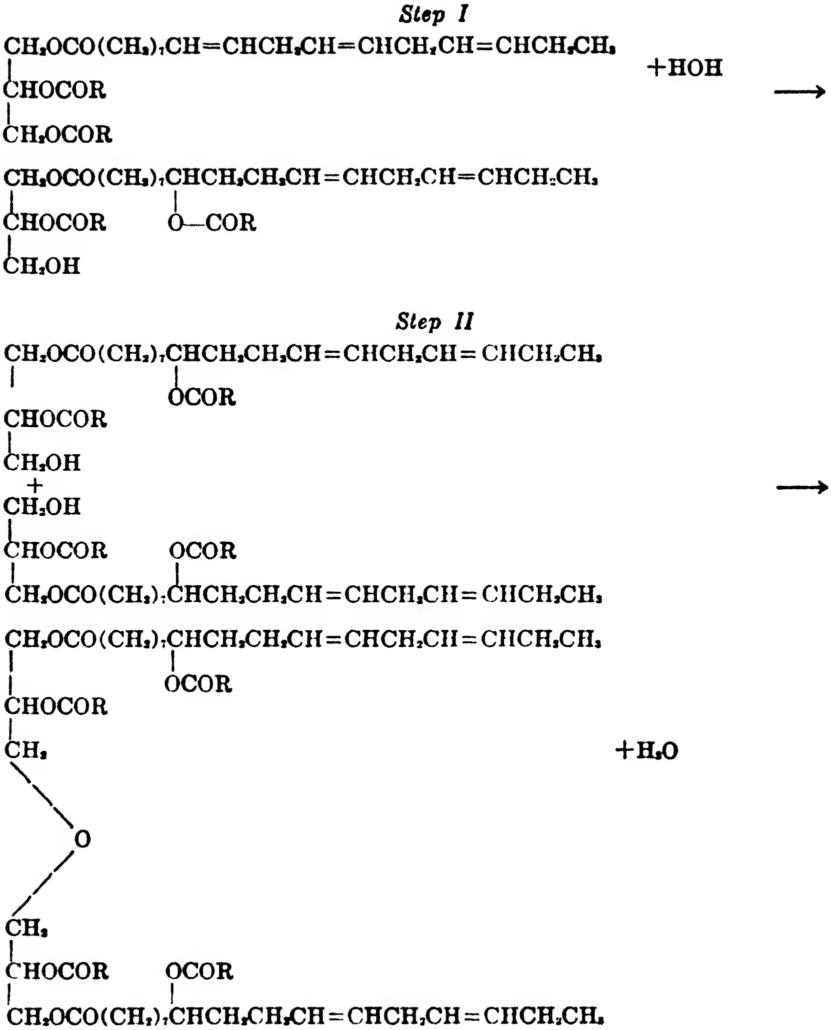
[31] A. H. Salway, *J. S. C. I.*, 1920, 39, 324T; *Chem. Abs.*, 1921, 15, 770. J. S. Long and G. Wentz, *loc. cit.*



Step I

$$\begin{array}{l} CH_2OCO(CH_2)_7CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH_3 \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array} + HOH \longrightarrow$$

$$\begin{array}{ll} CH_2OCO(CH_2)_7CHCH_2CH_2CH{=}CHCH_2CH{=}CHCH_2CH_3 & \\ | \qquad\qquad\quad | & \\ CHOCOR \quad O{-}COR & \\ | & \\ CH_2OH & \end{array}$$

Step II

$$\begin{array}{l} CH_2OCO(CH_2)_7CHCH_2CH_2CH{=}CHCH_2CH{=}CHCH_2CH_3 \\ | \qquad\qquad\quad | \\ \qquad\qquad\quad OCOR \\ CHOCOR \\ | \\ CH_2OH \\ + \\ CH_2OH \\ | \\ CHOCOR \qquad OCOR \\ | \qquad\qquad\quad | \\ CH_2OCO(CH_2)_7CHCH_2CH_2CH{=}CHCH_2CH{=}CHCH_2CH_3 \end{array} \longrightarrow$$

$$\begin{array}{l} CH_2OCO(CH_2)_7CHCH_2CH_2CH{=}CHCH_2CH{=}CHCH_2CH_3 \\ | \qquad\qquad\quad | \\ | \qquad\qquad\quad OCOR \\ CHOCOR \\ | \\ CH_2 \\ \quad \diagdown \\ \qquad O \\ \quad \diagup \\ CH_2 \\ | \\ CHOCOR \qquad OCOR \\ | \qquad\qquad\quad | \\ CH_2OCO(CH_2)_7CHCH_2CH_2CH{=}CHCH_2CH{=}CHCH_2CH_3 \end{array} + H_2O$$

From the values of the hexabromide and iodine numbers and the molecular weights, it is indicated [32] that in the first stages of heating of linseed oil intramolecular change is the main reaction.

When direct-fired kettles are used certain precautions are necessary.[33] Drying oils in contact with the sides of direct-fired metal kettles undergo destructive distillation, which causes cracking at the double bonds rather than hydrolytic splitting of the esters. The fumes given off when linseed oil is heated consist largely of fine droplets of decomposition products

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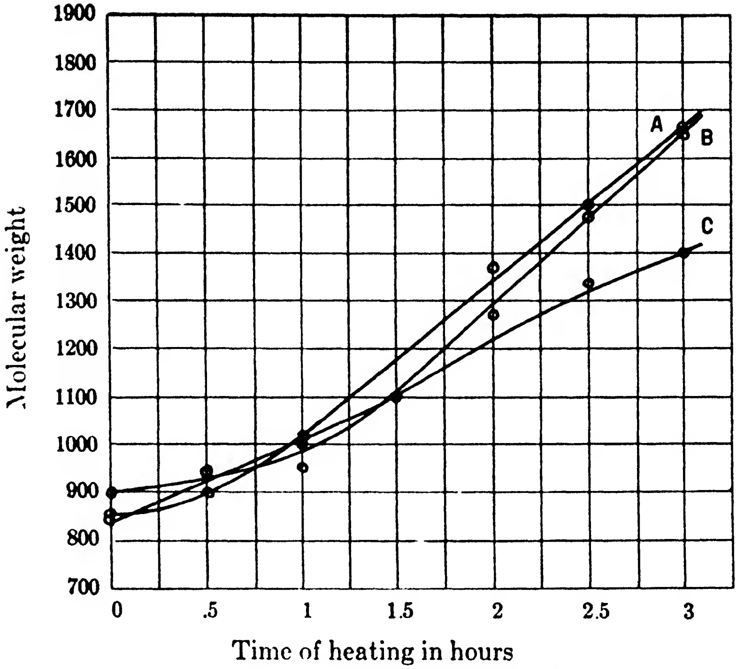
[32] J. S. Long, C. A. Knauss, and J. G. Smull, *loc. cit.*

[33] D. S. Chamberlin, E. R. Theis, P. F. Schlingman, and J. S. Long, *Ind. Eng. Chem.*, 1929, 21, 333; *Chem. Abs.*, 1929, 23, 5335.



Courtesy Industrial and Engineering Chemistry

FIGURE 7. Effect of Heating on Molecular Weight of Linseed Oil (J. S. Long and G. Wentz).

Curve A. 250 grams linseed oil and 25 grams fatty acids from linseed oil heated in stream of N_2 in 500-cc. "Pyrex" flask
Curve B. 200 grams linseed oil heated in stream of N_2
Curve C. 200 grams linseed oil heated in stream of N_2 carrying acrolein (15 cc. in 2.5 hours)

of the oil. Addition of small percentages of metallic driers to linseed oil during heat-bodying is said to decrease the gross kettle loss by changing the course of the chemical reactions. Increasing the proportion of lead monoxide (litharge) leads to a higher rate of molecular weight increase during heating.[34]

A slight decomposition of the oil into free fatty acids and glycerol occurs in the varnish kettle and is inevitable, and for drier action and wettability is even desirable. The glycerol decomposes further to acrolein and carbon dioxide. Excessive decomposition of the oil is prevented and undesirable volatile substances are removed by heat treatment *in vacuo*[35] and in the presence of inert gases.[36] Vacuum bodying of oils mostly leads

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[34] J. S. Long and W. J. Arner, *Ind. Eng. Chem.*, 1926, **18**, 1252; *Chem. Abs.*, 1927, **21**, 658.

[35] J. S. Remington, *Ind. Chemist*, 1929, **5**, 403; *Chem. Abs.*, 1930, **24**, 514. H. V. A. Briscoe, British P. 476,563, 1937; French P. 821,514, 1937; *Chem. Abs.*, 1938, **32**, 3992; *Brit. Chem. Abs.* **B**, 1938, 694.

[36] M. Ogura, *J. Soc. Chem. Ind., Japan*, 1935, **38**, suppl. binding, 129; *Chem. Abs.*, 1935, **29**, 4608; *Brit. Chem. Abs.* **B**, 1935, 598.

to slightly darker varnishes, but local decomposition and spontaneous ignition are avoided.[37] Subjecting the oil during heating to tangential currents of superheated steam is considered advantageous.[38] These methods yield the finest varnishes, and it is the endeavor of every varnish maker to keep the acid number as low as possible and the color very light. Improper heating of the varnish leads to such defects as skinning,[39] discoloration and greater livering tendency.[40] The latter effect is not yet fully understood, but it has been found that a reaction of the free fatty acids with certain basic pigments occurs in connection with the presence of large quantities of polymerized molecules. The soap formation alone is not wholly responsible for this effect, since varnishes of high viscosity will liver just as badly after the removal of free fatty acids. In some other cases livering tendency could even be reduced by adding small quantities of acidic bodies. Bogin[41] recommends malic acid for this purpose; oxalic acid also is said to be useful,[42] and even fatty acids have been mentioned as inhibitors and also as agents which restore livered inks.[43]

It is reported that the most economical bodying temperature for linseed oil is 575° F.[44] Above 575° F. both large and small batches require about the same length of time for bodying. Table 4 indicates heating rates employed with Monel kettles and Gilbert oil-fired radiant heaters. Rapid heating tends to prevent livering (gel formation).

Table 4.—Time Required to Raise the Temperature of Linseed Oil[45] to 575° F.

Kettle Type	Gallons		Time to Raise from Cold to 575° F.	
	Kettle Capacity	Actual Batch	Min. per Batch	Min. per Gallon
Portable	150	100	40	0.40
Portable	200	135	60	0.44
Portable	250	167	75	0.45
Portable	300	200	90	0.45
Set	750	500	90	0.18
Set	1000	667	105	0.16
Set	1250	825	120	0.145
Set	1500	1000	135	0.135

Linseed oil may be polymerized[46] by heating under pressure. Alkali-

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[37] N. A. Kozulin and A. S. Konoplev, *Org. Chem. Ind.* (*U.S.S.R.*), 1937, 3, 708; *Chem. Abs.*, 1937, 31, 7674; *Am. Ink Maker*, 1938, 16 (2), 39.

[38] J. Sommer, German P. 517,506, 1929; *Chem. Abs.*, 1931, 25, 2866.

[39] R. Dieterle, *Seifen-Ztg.*, 1932, 59, 401.

[40] J. Mattiello and L. T. Work, *Natl. Paint, Varnish, Lacquer Assoc. Circ.*, 1936, 502, 31; Chem. *Abs.*, 1936, 30, 3665.

[41] C. Bogin, U. S. P. 2,092,300, Sept. 7, 1937, to Commercial Solvents Corp.; *Natl. Paint, Varnish, Lacquer Assoc. Abs.*, 1937, 51, 167; *Chem. Abs.*, 1937, 31, 8232.

[42] A. Chwala, French P. 788,001, 1935; *Chem. Abs.*, 1936, 30, 1594.

[43] T. F. Bradley, U. S. P. 1,478,017, Dec. 18, 1923; *Chem. Abs.*, 1924, 18, 759; *Brit. Chem. Abs.* B, 1924, 8224.

[44] International Nickel Company Bulletin C-7.

[45] Monel kettles and oil-fueled Gilbert Radiant Fire Heaters were used.

[46] E. W. Fawcett, R. O. Gibson, and M. W. Perrin, U. S. P. 2,155,009, April 18, 1939, to Imperial Chemical Industries, Ltd.

refined linseed oil (iodine number 183.6 and acid number .09) is heated for 1.5 hours at a temperature of 325° C. and a pressure of 3000 atmospheres. The product has an acid value of 9.4, a viscosity of 103 poises and an iodine number of 123. Comparison of the product with commercial stand oil and heated linseed oil indicates that drying time is shortened by the above treatment (Table 5).

Table 5.—Effect of Heating on Drying Time of Linseed Oil.

	Drying Time in Hours		
	Surface Set	Hard Set	Tack-free
Varnish from Linseed oil heated at 325° C. for 1.5 hours at atmospheric pressure	5.5	Over 10	Not after 24 hours
Commercial stand oil	5.75	Over 10	Not after 24 hours
Linseed oil heated at 325° C. for 1.5 hours under 3000 atmospheres	3.5	7	After 24 hours

It has been suggested that slightly polymerized phases be removed by means of solvent extraction.[47] Distillation of the varnish *in vacuo* is said to remove the free fatty acids.[48]

Even after the preparation of stand oil has been finished, changes will occur. Storage in a cool and dark place is to be preferred to exposure to heat and sunlight, in order to prevent the varnish from becoming yellowish and cloudy.[49] In this case the cloudy particles may be removed by filtering. It is maintained, however, that raw oils after exposure to sunlight dry faster than those kept in the dark.[50]

Storage in a cool, dark place prevents or decreases changes in the oil which will occur if it is exposed to sunlight. Table 6 shows the same oils as investigated above (Table 2) after storage for one year in closed white bottles exposed to daylight. Cathode rays are said to thicken and to bleach linseed oil.[51] Experimental data are reported to indicate that an isomeric change takes place upon treatment of the oil with cathode rays. No skin formation results[52] from ultraviolet ray treatment. Linseed oil may be oxidized[53] by being sprayed vertically downward through a chamber illuminated by ultraviolet rays. Purified and dried air is supplied to the chamber, under pressure and at a temperature of 250° C.

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[47] *Oil Col. Trades J.*, 1932, **81**, 1665.

[48] W. Schmidding and A. Schaefer, British P. 363,190, 1932, to firm of William Schmidding; *Chem. Abs.*, 1933, **27**, 1529.

[49] F. Köhler, *Farbe u. Lack*, 1932, 488.

[50] K. H. Bauer and A. Freiburg, *Chem. Umschau Fette, Oele, Wachse Harze*, 1931, **38** (6), 78; *Chem. Abs.*, 1931, **25**, 2868; *Brit. Chem. Abs.* **B**, 1931, 551.

[51] J. S. Long and C. N. Moore, *Ind. Eng. Chem.*, 1927, **19**, 901; *Chem. Abs.*, 1927, **21**, 3136.

[52] Carleton Ellis and A. A. Wells, "Chemical Action of Ultraviolet Rays," Chemical Catalog Company, Inc. (Reinhold Publishing Corp.), New York, 1925.

[53] H. Schofield, British P. 227,212, 1923, *J. S. C. I.*, 1925, **44**, B180.

Table 6.—Effect of Light on Linseed Oil.

	Linseed Oil A Cold-Pressed	Linseed Oil B Warm-Pressed	Linseed Oil C Extracted
Acid number	2.02	2.91	6.05
Iodine number	178.5	174.7	170.7
Sapon. number	188.4	191.7	187.7
Oxy-acids	.74	.57	.80
Unsapon. matter	.46	.74	.64
Solid fatty acids	7.31	6.44	7.75

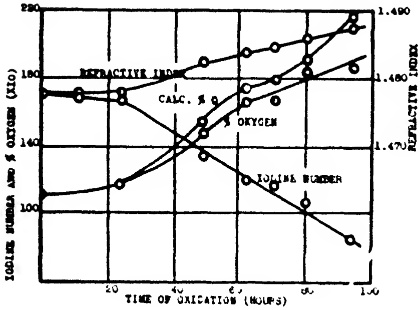

FIGURE 8.

Change in Refractive Index, Oxygen Absorbed, and Iodine Number of Linseed Oil with Time (R. S. Taylor and J. G. Smull).

Courtesy Industrial and Engineering Chemistry

Storage also allows mucilaginous matter to settle. These substances may then be withdrawn by filtration or decantation. Refining of the oil with alkali to remove free fatty acids has proved advantageous.

Another kind of varnish is represented by the "blown" oils. Air is conducted through the oil while the latter is heated. These varnishes do not frequently serve as printing vehicles[54] but are sometimes used in special inks. Gelation is very likely to occur during the blowing process, due to application of too much heat. The transformation is analogous to overheating stand oils, especially tung oil. In Figure 8 are shown the changes in refractive index, oxygen absorbed, and iodine value of a sample of linseed oil upon being blown for various periods of time.

The mechanism of bodying oils is not yet entirely known; stand oil is regarded by some persons as a colloidal complex of slower and faster drying phases.[55] This would mean, however, that besides highly polymerized particles, unpolymerized particles are present to a considerable extent.

There is disagreement as to the reactions involved in the drying of linseed oil and its stand oil. Drying is not due only to oxidation;[56] polymerization has an important role in thickening and is regarded today by some as the sole cause. Drying can be influenced greatly by cata-

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[54] G. Ruth and E. Asser, German P. 545,595, 1929; *Paint Var. Prod. Mgr.*, 1932, 8, Sect. I, No. 6, 22; *Korr. Metall.*, 1933, 9 (1), 24. British P. 353,949, 1929; *Chem. Abs.*, 1932, 26, 3943; *Brit. Chem. Abs.* B, 1931, 895. German P. 518,322, 1939, to Firma Hermann Frenkel; *Chem. Abs.*, 1931, 25, 2580. British P. 351,824, 1929; *Chem. Abs.*, 1933, 27, 1529. R. S. Taylor and J. G. Smull, *Ind. Eng. Chem.*, 1936, 28, 193; *Brit. Chem. Abs.* B, 1936, 334; *Chem. Abs.*, 1936, 30, 2409.

[55] *Farben-Ztg.*, 1929, 34, 2573.

[56] J. S. Long and H. D. Chataway, *Ind. Eng. Chem.*, 1931, 23, 53; *Chem. Abs.*, 1931, 25, 1105; *Brit. Chem. Abs.* B, 1931, 401.

lysts[57] (see Chapter 4), humidity,[58] gases, action of light and presence of naturally occurring or added[59] inhibitors. Pigments[60] also have an influence. It is said that, in some instances, prolonged drying time is indicated by a low iodine value.[61] The absorption of O_2 is accelerated by turpentine, depending on its content of peroxide.[62] That a certain time is required before the oil will start drying, the so-called "induction period,"[63] is attributed to the presence of natural inhibitors. Oils containing conjugated double bonds dry faster than those in which the double bonds are separated further.[64] Autoxidation and auto-polymerization work hand in hand to promote drying, though opinions vary as to which causes the other or takes place first. The whole drying effect should be regarded as due to chemical as well as colloidal factors, and it has been found that drying is accomplished in several successive stages: induction period, formation of micelles, coagulation and solvation of these, and changes in the solid gel film.[65] In the first stage oxidation and formation of peroxides occurs; the second stage is a change of peroxides to ketols or dienols; the third involves polymerization by a diene mechanism, it is stated.[66] The physico-colloidal properties of printing inks, their behavior during manufacture, storage and application have been called a "dynamic system."[67]

Other investigators state that the drying of linseed oil films takes place in two stages. The first stage is oxidation or, more generally, formation of polar molecules (temperature and humidity will modify the reactions occurring). The second stage involves the association of the polar molecules produced in the first stage to form the solid, gel-like coherent structure of the film. Some further oxidation occurs after the oil has "set," but this film is soon oxidized to a stage corresponding to the addition of two oxygen atoms at each double bond. The percentage of oxygen remains practically constant thereafter.[68] A study of the variations of index of refraction, heat of combustion and iodine number as linseed oil absorbs oxygen is said to indicate that one step in the oxidation of the oil is the formation of conjugated systems of double bonds.[69]

It is impossible to understand fully drying of linseed oil as long as its exact composition has not been ascertained. Its drying principle is

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[57] P. Slansky, *Kolloid. Beihefte*, 1932, 35, 49; *Chem. Abs.*, 1932, 26, 2877; *Brit. Chem. Abs.*, B, 1932, 391.

[58] C. R. Conquergood, *Printing*, July, 1934.

[59] B. F. Chow, *J. A. C. S.*, 1934, 56, 894; *Chem. Abs.*, 1934, 28, 3054; *Brit. Chem. Abs.* A, 1934, 607.

[60] R. Benerle, *Farben-Chem.*, 1936, 7, 246; *Chem. Abs.*, 1936, 30, 8653; *Brit. Chem. Abs.* B, 1936, 894.

[61] F. Scofield, *Natl. Paint, Varnish, Lacquer Assoc., Sci. Sect. Circ.* 1937, No. 530, 119; *Chem. Abs.*, 1938, 32, 8804.

[62] H. C. Cohen, *Verfkroniek*, 1938, 11 (2), 27.

[63] J. S. Long, *Paint, Oil. Chem. Rev.*, 1930, 89 (1), 8; *Am. Paint J.*, 1929, 14 (10), 60; *Chem. Abs.*, 1930, 24, 978.

[64] W. Kronsbein, *Farben-Chem.*, 1932, 3, 373; *Chem. Abs.*, 1933, 27, 198.

[65] J. Scheiber, *Farbe u. Lack*, 1928, 33, 518; *Chem. Abs.*, 1929, 23, 1764.

[66] A. E. Rheineck, *Paint, Oil, Chem. Rev.*, 1937, 99 (5), 9; *Chem. Abs.*, 1937, 31, 3716.

[67] R. F. Bowles, *Paper Maker & Brit. Paper Trade J.*, 1937, 93, TS70; *Chem. Abs.*, 1937, 31, 7268; *Brit. Chem. Abs.* B, 1937, 810.

[68] J. S. Long, A. E. Rheineck and G. L. Ball, *Ind. Eng. Chem.*, 1933, 25, 1086; *Chem. Abs.*, 1933, 27, 5557.

[69] R. S. Taylor and J. G. Smull, *Ind. Eng. Chem.*, 1936, 28, 193; *Chem. Abs.*, 1936, 30, 2409.

linolenic acid, octadeca-9,12,15-trien-1-oic acid, the amount of which in the oil is calculated to be 35 to 45 per cent.[70] One investigator reports that it was found to the extent of only 18 per cent,[71] together with an unusually high quantity of linoleic acid and correspondingly little oleic acid. It is recommended that more data be obtained on the part played by the unsaponifiable components of these oils.[72]

A mathematical formula derived from diffusion theory is said to indicate the rate of absorption of oxygen by a linseed oil film, after the induction period.[73] Experimental data are reported to indicate that, if no drier is present, the data curve shows an induction period followed by a logarithmic diffusion curve. The latter has the formula:

$$\frac{Q}{Q_0} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n-1)^2} e^{\frac{-D(2n-1)^2\pi^2 t}{4a^2}}$$

where $\frac{Q}{Q_0}$ is the ratio of oxygen absorbed at time, t, to the total absorption of O_2; a is the film thickness, D is the diffusion coefficient; n is the number of oxygen molecules per unit volume. Values of D are: oil alone, 1.98×10^{-11}; with 0.20 per cent cobalt, manganese, and lead, 2.76, 2.67, and 2.55×10^{-11} respectively.

Several studies[74] indicate the change in the properties of linseed oil when it is oxidized at 160° C. The rate of oxidation of drying oils decreases almost as a straight-line function of the degree of oxidation, until gelation occurs. Gelation is said to be a colloidal association process depending upon the size, complexity, polarity and free energy of the molecules. The degree of oxidation is regarded as only a contributory cause of the phenomenon. Fatty acids are reported to form compounds with the glyceride molecule, and this union is said to be a primary factor leading to gelation. Lead, cobalt, and iron greatly shorten the time of gelation, but selenium powder and sodium oleate delay gel formation. Lead decreases the amount of oxygen required for gelation and is therefore considered a polymerization as well as an oxidation catalyst. Figures 9, 10, 11, and 12 indicate the effect of temperature, acid value, molecular complexity and driers and inhibitors on the total oxygen absorption of linseed oils oxidized at 160° C.

Examination of oxidized and boiled oils by means of a Langmuir surface-tension balance[75] shows that oxidized oils occupy a greater area

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[70] H. E. Mestern, Inaugural-Diss., Münster, Germany, 1936.

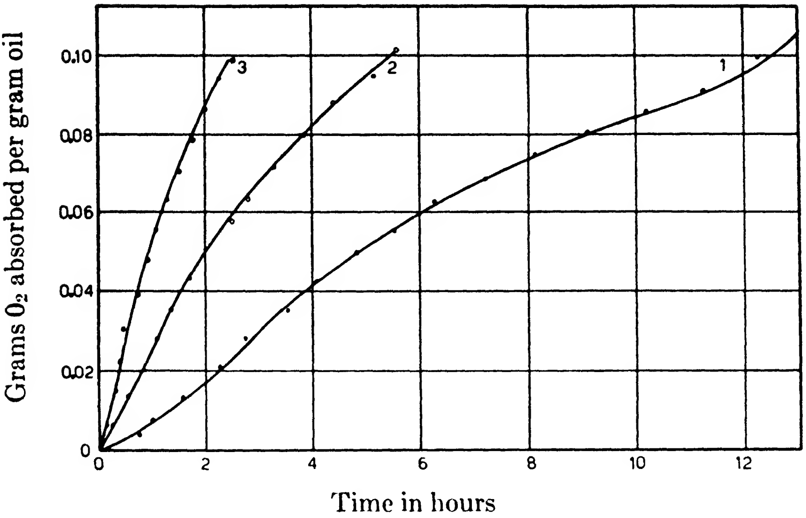
[71] N. E. Cocchinaras, *Analyst*, 1932, 57 (673), 233; *Chem. Abs.*, 1932, 26, 3127; *Brit. Chem. Abs.* B, 1932, 560.

[72] J. Van Loon, *Verfkroniek*, 1938, 11, 69; *Chem. Abs.*, 1938, 32, 5645.

[73] S. Iwai, *Phys.-Math. Soc. Japan, Proc.*, 1938, 20, 223; *Chem. Abs.*, 1938, 32, 5235.

[74] J. S. Long and H. D. Chataway, *Ind. Eng. Chem.*, 1931, 23, 53; *Chem. Abs.*, 1931, 25, 1105. J. S. Long and W. S. W. McCarter, *Ind. Eng Chem*, 1931, 23, 786; *Chem. Abs.*, 1931, 25, 4417.

[75] This balance was improved by using strips of gold leaf to prevent leakage of the oil film around the ends of the float. J. S. Long, W. W. Kittleberger, L. K. Scott and W. S. Egge, *Ind. Eng. Chem.*, 1929, 21, 950; *Chem. Abs.*, 1930, 24, 251.



Courtesy Industrial and Engineering Chemistry

FIGURE 9. Effect of Temperature on Total Oxygen Absorption of Linseed Oil (J. S. Long and W. S. W. McCarter).

Curve 1. Linseed oil at 110° C.
Curve 2. Linseed oil at 160° C.
Curve 3. Linseed oil at 200° C.

per molecule and require a greater compressive force to crumple the monomolecular film than do heat-bodied oils of the same molecular weight. This is a means of measuring the variations in oils bodied by blowing or heating or by processes involving oxidation, polymerization or condensation reactions. Figures 13 and 14 indicate the relation of the force at the crumbling point to the area per molecule of linseed oil with and without driers present.

"Tekaols" ("stand oil extract," "purified stand oil," "bodied linseed oil extract") are linseed stand oils from which the low polymerized (saturated) highly dispersed phase has been removed.[76] Stand oils are said to be heterogeneous colloids, consisting of a highly dispersed, saturated, non-drying phase of low molecular weight constituents and a slightly dispersed, unsaturated, drying phase of high molecular weight substances. Of these two phases, the slightly dispersed unsaturated phase contains almost all the constituents which promote drying.[77]

In the manufacture of "Tekaols," the linseed oil is heated at 300° C. until it attains an iodine number of 95 to 110. The stand oil, produced

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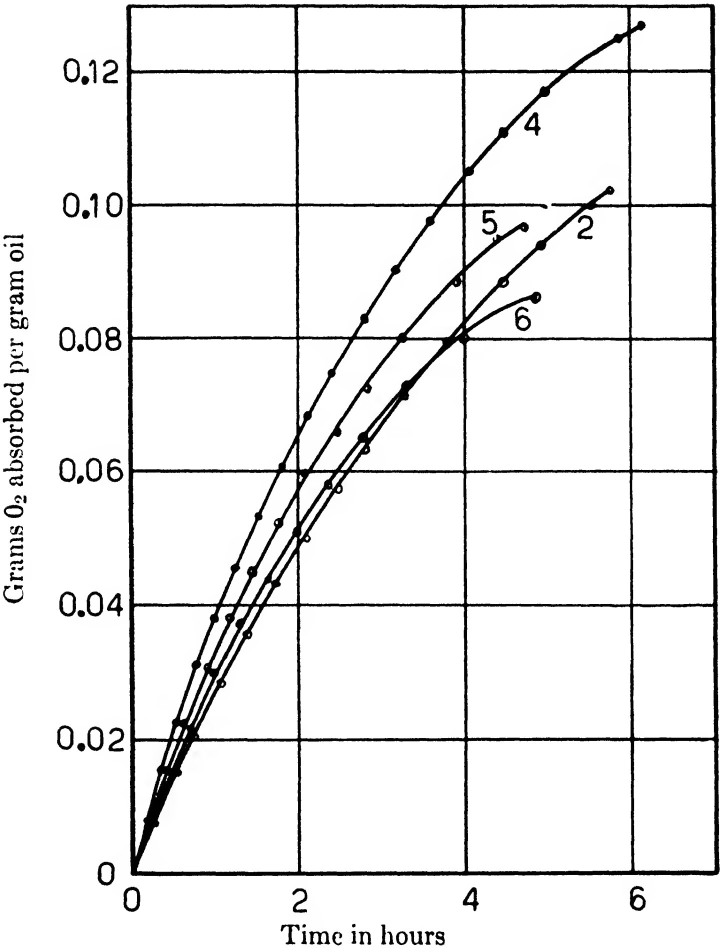
[76] A. Eibner, French P. 708,465, 1930; *Chem. Abs.*, 1932, 26, 1142. A. Eibner and M. Miller, German P. 546,679, 1929, to Firma T. Kotthoff; *Chem. Abs.*, 1932, 26, 3685. A. Eibner, German P. 548,152, 1930, to Firma T. Kotthoff; *Chem. Abs.*, 1932, 26, 4190. A. Eibner, *Farben-Ztg.*, 1931, 37, 13, 54, 88; *Chem. Abs.*, 1932, 26, 606.

[77] E. Rossman, *Angew. Chem.*, 1937, 50, 246; *Chem. Abs.*, 1937, 31, 4142. A. Eibner, *loc. cit.*



Courtesy Industrial and Engineering Chemistry

FIGURE 10. Effect of Acid Value on Total Oxygen Absorption of Linseed Oil at 160° C. (J. S. Long and W. S. W. McCarter).

Curve 2. Linseed oil, acid number 0.6
Curve 4. Linseed oil fatty acids, acid number 200
Curve 5. Linseed oil plus acids, acid number 100
Curve 6. Linseed oil plus acids, acid number 50

by the above process, is extracted, at 300° C., with 6-8 volumes of acetone. When the mixture is cool, the drying, unsaturated, slightly dispersed phase settles out. The saturated, non-drying highly dispersed phase remains in solution with acetone and forms the upper layer.[78] Other selective solvents may be employed for Tekaolization, such as amyl acetate, amyl alcohol, butyl alcohol or malonic ester.[79]

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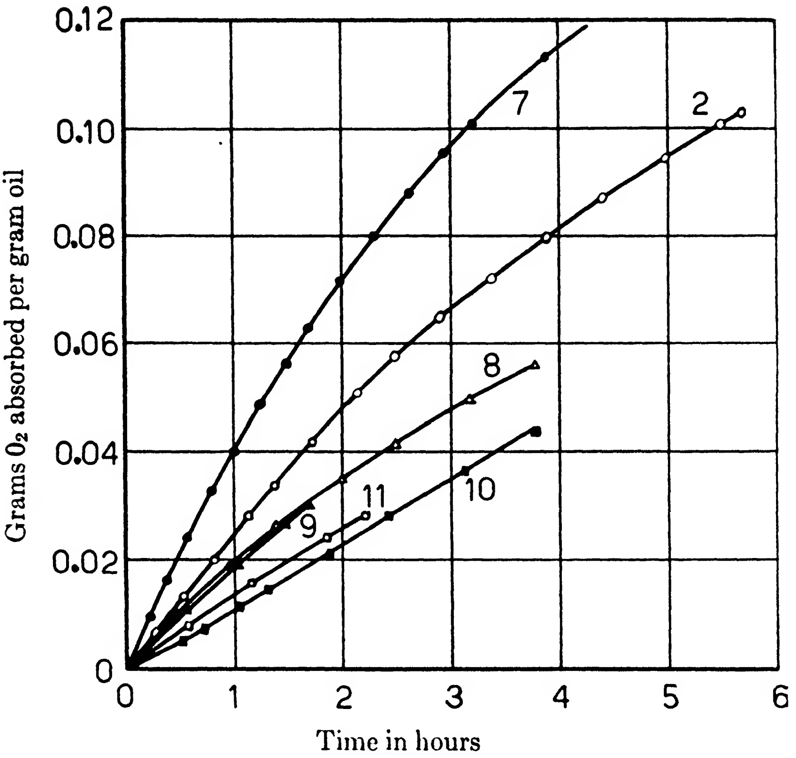
[78] German P. 656,182, 1938, to Firma T. Kotthoff; *Chem. Abs.*, 1938, 32, 8177.

[79] A. Eibner, *loc. cit.*



Courtesy Industrial and Engineering Chemistry

FIGURE 11. Effect of Molecular Complexity on Total Oxygen Absorption at 160° C. (J. S. Long and W. S. W. McCarter).

Curve 2.	Linseed oil
Curve 7.	Methyl ester of linseed oil acids
Curve 8.	Glycol ester of linseed oil acids
Curve 9.	Pentaerythritol ester of linseed oil acids
Curve 10.	Linseed oil, 3 hour heat-body
Curve 11.	Linseed oil, 6 hour heat-body

Several advantages are reported for these purified stand oils. On exposure they do not oxidize but dry by polymerization. Drying is said to be more rapid and to produce more durable films than when employing ordinary stand oils (with or without driers).[80] Iodine values and molecular weights of "Tekaols" are interpreted as indicating that only a fraction of saturated acid triglycerides are present and that the stand oil extract is composed almost entirely of triglycerides of unsaturated acids.[81] This condition is said to be the result of the heating process employed in the preparation of the stand oil.

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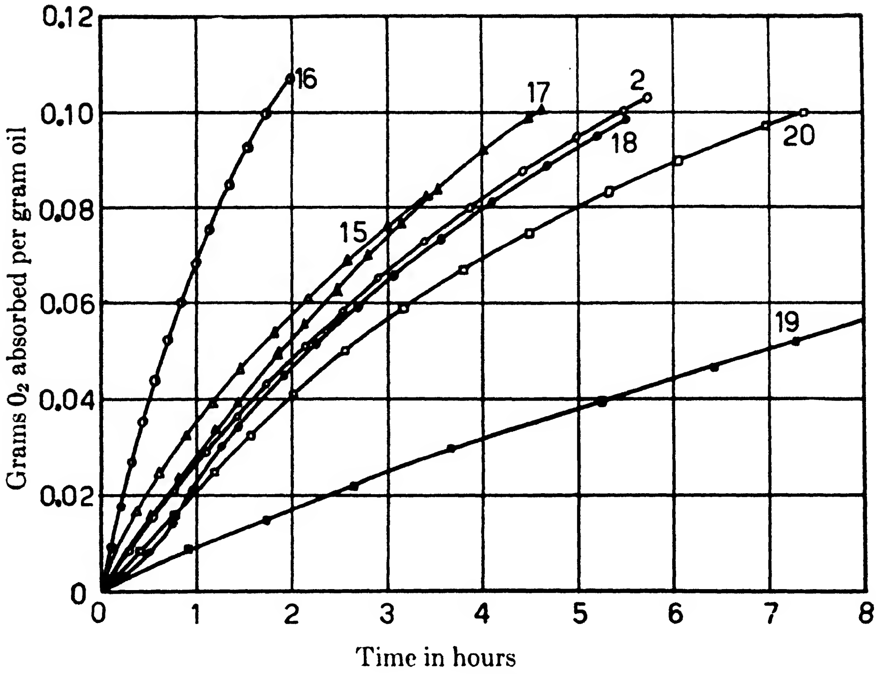
[80] T. H. Barry and L. Light, *Brit. Plastics*, 1932, 3, 3, 28; *Chem. Abs.*, 1933, 27, 2048.

[81] *Am. Ink Maker*, 1939, 17 (3), 41. E. Elöd and U. Mach, *Kolloid Z.*, 1936, 75, 338; *Chem. Abs.*, 1936, 30, 6218; *Brit. Chem. Abs.* B, 1936, 700.



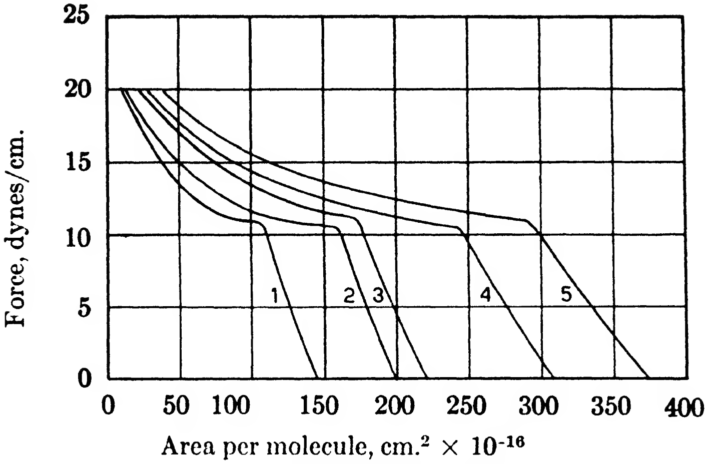
Courtesy Industrial and Engineering Chemistry

FIGURE 12. Effect of Driers and Inhibitors on Total Oxygen Absorption of Linseed Oil at 160° C. (J. S. Long and W. S. W. McCarter).

Curve 2. Linseed oil
Curve 15. Linseed oil + 1.00 per cent lead (as resinate)
Curve 16. Linseed oil + 0.29 per cent cobalt (as resinate)
Curve 17. Linseed oil + 0.27 per cent iron (as ferric oxide)
Curve 18. Linseed oil
Curve 19. Linseed oil + 0.39 per cent selenium (as powdered selenium)
Curve 20. Linseed oil + 0.11 per cent sodium (as sodium oleate)

Table 7.—Properties of Fractions Extracted from Linseed Oil.

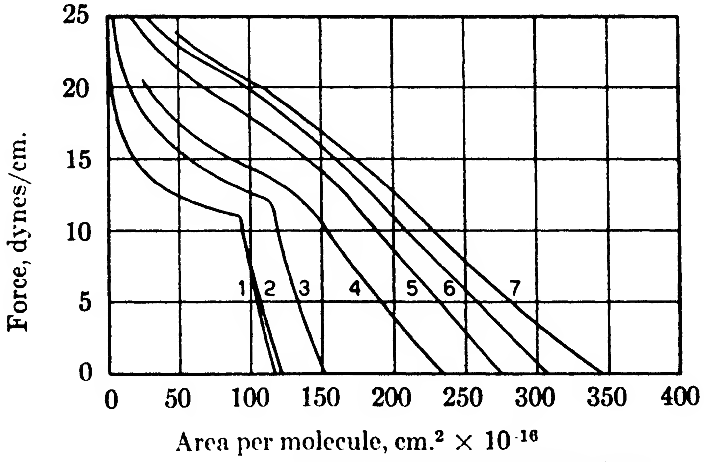
	% of Varnish Extracted by Solvent	Acid Number	Iodine Number	$\frac{\eta_{sp}}{C}$	Molecular Weight $M = \frac{K^1 \eta_{sp}}{C}$	% of Oxygen Contained in Oxidized Product
First acetone—soluble fraction	54	38.67	131.0	3.51	1398	5.25
Second acetone—soluble fraction	10.5	39.62	123.0	4.46	1776	14.88
Fraction not soluble in acetone	35.5	53.55	105.0	9.01	3588	12.32
Soluble in methyl alcohol	13.5	97.83	140.8	2.12	844	1.54
Soluble in ethyl alcohol	5.5	45.18	133.2	2.90	1155	1.08
Insoluble in ethyl alcohol	35.0	9.27	127.7	3.92	1561	7.77
Linseed oil before extraction	100.0	45.7	123.8	4.89	1947	17.58



Courtesy Industrial and Engineering Chemistry

FIGURE 13. Effect of Compressive Force on Monomolecular Films of Heat-bodied Linseed Oil (J. S. Long, W. W. Kittelberger, L. K. Scott, and W. S. Egge).

Refrigerated linseed oil with 0.028 per cent cobalt as linoleate, heat-bodied at 293° C.
Curve 1. Oil bodied for 0.75 hour, molecular weight 960
Curve 2. Oil bodied for 2.25 hours, molecular weight 1332
Curve 3. Oil bodied for 3.00 hours, molecular weight 1510
Curve 4. Oil bodied for 4.50 hours, molecular weight 2223
Curve 5. Oil bodied for 5.50 hours, molecular weight 2500



Courtesy Industrial and Engineering Chemistry

FIGURE 14. Effect of Compressive Force on Monomolecular Films of Blown Linseed Oil (J. S. Long, W. W. Kittelberger, L. K. Scott, and W. S. Egge).

Refrigerated linseed oil blown at 138° C.

Curves 1, 2.	Unblown oil, molecular weight 795
Curve 3.	Oil blown 2.5 hours, molecular weight 931
Curve 4.	Oil blown 8.0 hours, molecular weight 1314
Curve 5.	Oil blown 10.5 hours, molecular weight 1409
Curve 6.	Oil blown 13.0 hours, molecular weight 1567
Curve 7.	Oil blown 18.0 hours, molecular weight 1717

Mixed glycerides, on being heated, are said to rearrange so that like fatty acids are found on the same glyceride. Saturated and unsaturated glycerides are separated by the rearrangement, and it is then possible to employ preferential extraction.[82]

Table 7 lists the products of linseed oil extraction. It is to be noted individual fractions absorb less oxygen, on a percentage basis, than does the unextracted oil. Staudinger's Law, previously described, is employed in finding the molecular weights listed in this table.[83]

Tung Oil (China Wood Oil). Whenever rapid drying is required, tung oil is recommended as a vehicle because of its high content of eleostearic acid,[84] (octadeca-9,11,13-trien-1-oic acid) which is isomeric with linolenic acid but has the double bonds in conjugated positions. Moreover, the percentage of this acid in tung oil is about twice as high as that of linolenic acid in linseed oil.

Resins are reported to have a marked influence on the drying rates of tung oil. This effect depends upon the individual resin employed. Drying of China Wood oil is accelerated, in the presence of light, by addition of β-naphthol.[85]

Tung oil may be bodied if heated gradually to 300° C., but at higher temperatures it may degel (depolymerize). Polymerization is said to be the cause of this thickening of China Wood oil, since hydrolytic, intramolecular or other extraneous reactions are reported to occur to a negligible extent. It is stated that the observed molecular weight-iodine values of heat-thickened tung and linseed oils correspond closely to those which are typical of a hexafunctional system (*i.e.*, having six reacting groups on the molecule take part in the polymerization).[86] Changes in tung oil, upon heating, are shown in Table 8.

Table 8.—Changes in Tung Oil Upon Heating.

Property	Before Heating	After Heating
Specific gravity[87]	0.9418	0.9631
Iodine number	166.8	140.5
Relative viscosity	3.36	13.4
Refractive index	1.5191	1.5106
Acid number[88]	4.7	12.5 to 16.1
Saponification value	180.9	187 to 194

China Wood oil, because of its peculiar behavior under certain conditions, has offered some problems to the manufacturer. Among these difficulties are: solidification through the action of sunlight, tendency

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[82] A. Eibner, *Farben-Ztg.*, 1931, 37, 13, 54, 88; *Chem. Abs.*, 1932, 26, 606.

[83] E. Elöd and U. Mach, *Kolloid Z.*, 1936, 75, 338; *Chem. Abs.*, 1936, 30, 6218; *Brit. Chem. Abs.* **B**, 1936, 700.

[84] J. Van Loon, *Farben-Ztg.*, 1930, 35, 1767; *Chem. Abs.*, 1930, 24, 4178; *Brit. Chem. Abs.* **B**, 1930, 724.

[85] C. A. Thomas and P. E. Marling, *Ind. Eng. Chem.*, 1932, 24, 871; *Rev. Paint, Colour, Varnish*, 1932, 5, 224; *Chem. Abs.*, 1932, 26, 4967.

[86] T. F. Bradley, *Ind. Eng. Chem.*, 1938, 30, 680; *Rev. Paint, Colour, Varnish*, 1938, 11, 265; *Chem. Abs.*, 1938, 32, 6080.

[87] M. Tachimori, *J. Chem. Soc. Japan*, 1938, 59, 125; *Chem. Abs.*, 1938, 32, 5235.

[88] C. L. Schumann, *Ind. Eng. Chem.*, 1916, 8, 5; *Chem. Abs.*, 1916, 10, 534.

toward gel formation when heated, and the frosting, flatting or crystallizing tendency ("gas crazing") on drying.[89]

The most striking characteristic of China Wood oil is its transformation by heat into a transparent, solid mass possessing considerable elasticity which becomes more brittle as further heat is applied. This process, known as gelatinization (livering), is still a subject of much controversy. One view is that thickening or gelatinization of tung oil is a colloidal reaction.[90] The change in physical properties upon heating is reported to be brought about by polymerization,[91] and partially by an interchange of radicals. Dimolecular triglycerides which are soluble in the monomolecular form are said to be formed to some extent and α-eleostearic acid is reported to be converted into the β-acid with some molecular decomposition. A process of aggregation is said to cause the oil to thicken further and finally to gelatinize.[92]

Another view is that fatty oils are isocolloids and that thickening and gelation of drying oils may be explained by the "gas coagulation theory."[93] Isocolloids are systems in which the dispersed phase and the dispersion medium are chemically similar, and the dispersed phase is an aggregate form of the dispersion medium. These isocolloids are said to form solid films in layers as a result of absorption of coagulating gases (*e.g.*, oxygen). Ostwald is reported to have described isocolloids as systems in which the dispersed phase is a polymerized form of the dispersion medium.[94]

Gelatinization (livering) of tung oil may be prevented by heating the latter rapidly to 330-340° F. Rapid heating is said to produce a viscous non-gelatinizing oil, because long-chain polymers are broken up by the rapid motion of the molecules.[95] Also, it has been reported that addition of small quantities of oxidized turpentine oil, phenol, resins or acid resinates, linseed oil acids, perilla oil acids, naphthalene, sulphur or sulphides, selenium or selenides, sulphur chloride or aniline to tung oil will inhibit gelatinization of the latter.[96] Tung oil gels may be liquefied by heating at 100° C. in the presence of an acetone-insoluble reaction product of litharge and linseed oil.[97]

A method of bodying tung oil by aeration below 250° F. is designed to prevent gelation.[98] Previous to being heated or blown, the oil is dis-

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[89] J. Hyman and T. Greenfield, *Ind. Eng. Chem.*, 1936, 28, 238; *Chem. Abs.*, 1936, 30, 2410; *Brit. Chem. Abs.* B, 1936, 335. W. W. Bauer, *Ind. Eng. Chem.*, 1926, 18, 1249; *Chem. Abs.*, 1927, 21, 659.

[90] H. Wolff, *Z. Angew. Chem.*, 1926, 39, 10; *Chem. Abs.*, 1926, 20, 3092. *Chem. Umschau Fette, Oele, Wachse u. Harze*, 1926, 33, 70; *Chem. Abs.*, 1926, 20, 2910.

[91] T. F. Bradley, *Ind. Eng. Chem.*, 1938, 30, 1087; *Chem. Abs.*, 1938, 32, 8803. W. F. Stark, *Natl. Paint Bull.*, 1938, 2, 12 (Oct.); *Chem. Abs.*, 1939, 33, 411.

[92] W. W. Bauer, *Ind. Eng. Chem.*, 1926, 18, 1249; *Chem. Abs.*, 1927, 21, 659.

[93] L. Auer, *Ind. Eng. Chem.*, 1938, 30, 466; *Chem. Abs.*, 1938, 32, 4361. *Ind. Eng. Chem.*, 1938, 30, 1087; *Chem. Abs.*, 1938, 32, 8803.

[94] L. Auer, *loc. cit.*

[95] E. Fonrobert and F. Pallauf, *Chem. Umschau, Fette, Oele, Wachse u. Harze*, 1927, 34, 1; *Chem. Abs.*, 1927, 21, 1193.

[96] E. Fonrobert and F. Pallauf, *Chem. Umschau, Fette, Oele, Wasche u. Harze*, 1926, 33, 41; *Chem. Abs.*, 1926, 20, 2418.

[97] A. Ruff, *Farben-Chem.*, 1935, 6, 415; *Chem. Abs.*, 1936, 30, 3259.

[98] R. D. Bonney and W. S. Egge, U. S. P. 2,133,889, Oct. 18, 1938, to Congoleum-Nairn, Inc.; *Chem. Abs.*, 1939, 33, 886.

persed in castor oil which is non-volatile. After being blown, the oil is separated from the castor oil by extraction with alcohol. In the procedure 4 parts of raw tung oil are mixed with 1 part of castor oil. The mixture is heated to 160° F., and 0.5 per cent of lead naphthenate incorporated in the mixture. The whole then is aerated for 20 hours at 160° F. The batch is cooled to 70° F. and is extracted with twice its volume of denatured alcohol. The upper layer consists of alcohol and castor oil and the lower layer of bodied tung oil.

Employment of hydroxy- or polyhydroxyalkyl esters of fatty acids containing at least 12 carbon atoms per molecule is also recommended as a means of reducing the gelatinization tendency of China Wood oil.[99] The tung oil is admixed with hydroxyethyl esters of China Wood oil acids in the proportion of 10 parts of oil to 3 parts of esters.

Crystallization (gas crazing, gas-checking, frosting, flatting, wrinkling, throwing out, mat drying and crazed drying) is the wrinkling of the tung oil film under certain drying conditions. Wrinkling, which occurs during drying at elevated temperatures, is said to be caused by rapid absorption of oxygen on the surface, forming a thin film (above the rest of the oil) which increases in volume on further oxygen absorption and forms folds and wrinkles.[100] Oxygen and nitrogen oxides (or nitric acids) appear to be essential for crystallization to take place.[101] Experiments with carbon dioxide and nitrogen are said to demonstrate that crystallization does not occur in the absence of oxygen.

The rate and extent of crystallization are increased by factors which permit an acceleration of the rate of oxygen absorption. It was indicated that, when pure oxygen is used in place of compressed air (in the presence of nitrogen oxide), the rate of formation of wrinkles is increased. In the absence of nitrogen oxides neither compressed air nor oxygen is reported to cause frosting in one hour. Hence the presence of nitrogen oxides appears to be essential for mat drying to occur. The critical nitrogen dioxide concentration, necessary to produce crystallization in a given standard varnish, is 4 parts in 10 million parts of air.[102] In general, crystallization tends to take place whenever the oxygen absorption rate is suddenly changed from a lower to a higher value.[103] Films which are subject to crystallization form gels on their surfaces. This phenomenon is employed as a test for crystallization-tendency of tung oil.

Various means have been devised for preventing wrinkling. If the oil is extensively polymerized, it will not crystallize.[104] Rapid heating up to 270 to 280° C. is said to prevent frosting by causing the rate of

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[99] German P. 529,077, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 5048.

[100] E. Fonrobert and F. Pallauf, *Chem. Umschau Fette, Oele, Wachse u. Harze*, 1927, 34, 1; *Chem. Abs.*, 1927, 21, 1193.

[101] W. W. Bauer, *Ind. Eng. Chem.*, 1926, 18, 1249; *Chem. Abs.*, 1927, 21, 659.

[102] J. Hyman and T. Greenfield, *Ind. Eng. Chem.*, 1936, 28, 238; *Chem. Abs.*, 1936, 30, 2410; *Brit. Chem. Abs. B*, 1936, 335.

[103] W. W. Bauer, *loc. cit.*

[104] W. W. Bauer, *loc. cit.*

polymerization to exceed the rate of conversion of alpha glycerides to beta glycerides. Since alpha glycerides do not crystallize easily, wrinkling is prevented by the above treatment.[105] Addition of 1 to 2 per cent of solidified tung oil, dissolved in a solvent, is said to be beneficial, if admixed with the raw China Wood oil. Another heating procedure, which is reported to produce non-frosting oil, comprises heating tung oil at 120 to 260° C. until a viscosity of 3 to 150 poises is obtained. A solvent is added to the bodied oil and the vehicle is aged in air.[106] Rapid polymerization of tung oil is stated to be obtained by adding 0.5 pound of ferric linoleate to 50 gallons of oil, at a temperature of 400° C. Heating is continued at temperatures above 400° C. until sufficient body is secured.[107] Thinners usually are added to the cooled polymerized oil. The vehicle thus produced is said to be non-wrinkling.

Resin acids may be employed to convert eleostearin to monoeleostearin. Since the presence of eleostearin is said to be the cause of mat drying, prevention of the latter phenomenon is said to be accomplished by this procedure.[108]

Compositions having highly satisfactory properties are secured by bodying mixtures of linseed and tung oil.[109] Through ester interchange either oil influences the other, giving a pale varnish that dries to a glossy film and does not smell as strongly as tung oil itself. Waterproofness and weather resistance, which are other advantages of tung oil, are of minor importance for printing ink vehicles in contrast to the paint industry. In paint compositions, in some cases, the rapid-drying tung oil (due to its eleostearic acid content) has been lessened by incorporation of oleic acid, olein or other less active substances.[110] Alkali-proofness, however, is desirable for certain purposes, *e.g.*, printing on soap wrappers, where alkali-proof inks are required. Vehicles for these inks may contain tung oil and alkali-fast resins.

Tung oil has been recommended as vehicle for high-gloss inks.[111] These inks dry to a very high gloss on a number of printing surfaces and eliminate the necessity for subsequent overprinting. The chief vehicle requirements for such inks are high surface tension and high index of refraction. Tung oil possesses these characteristics, and in addition is quite fluid.

Oiticica Oil. A natural oil, closely related to tung oil in composition and properties, is oiticica oil. This is indicated in Figure 15, showing temperature *versus* gelation time for tung oil and oiticica oil and in

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[105] E. Fonrobert, *Paint Manuf.*, 1935, 5, 364; *Chem. Abs.*, 1936, 30, 1593.

[106] A. M. Alvarado, U. S. P. 2,112,354, Mar. 29, 1938, to E. I. du Pont de Nemours & Co., *Chem. Abs.*, 1938, 32, 3992.

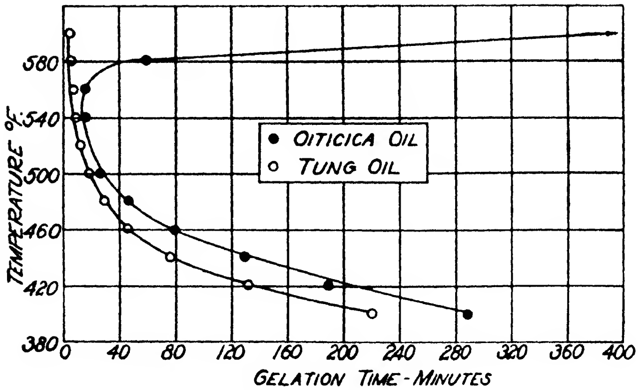
[107] R. F. Schneider, R. H. Coe and E. E. Ware, Canadian P. 373,394, 1938, to Sherwin-Williams Co.; *Chem. Abs.*, 1938, 32, 4808; *Am. Ink Maker*, 1938, 16 (8), 37.

[108] H. Ulrich, *Farben-Ztg.*, 1934, 30, 704; *Chem. Abs.*, 1934, 28, 5688.

[109] C. Eckmann, *Farben-Chem.*, 1935, 6, 295; *Chem. Abs.*, 1936, 30, 2409.

[110] J. Scheiber, *Farbe u. Lack*, 1935, 411; *Chem. Abs.*, 1935, 29, 8365.

[111] R. C. Chandler, *Am. Ink Maker*, 1937, 15 (9), 39; *Rev. Paint, Colour, Varnish*, 1938, 11, 24.



Courtesy Industrial and Engineering Chemistry

FIGURE 15. Effect of Temperature on Gelation Time of Tung and Oiticica Oils (S. O. Sorenson, C. J. Schumann, J. H. Schumann, and J. Mattiello).

Figure 16, showing gelation time *versus* viscosity for these substances.[112] The crude (unbodied) oil is said to be the form usually imported in the United States.[113] The crude product is reported to be solid. However, Brazilian liquid oil (bodied, "Polimerisado Oil") is available. A liquid form, known as "Cicoil" is reported to retain its smooth, liquid consistency indefinitely, if stored at ordinary temperatures.[114]

In the crude state, oiticica oil is said to produce wrinkled films (gas checking, frosting, crystallization). If white pigments are used, wrinkling may be prevented by introducing 3 per cent of lead and 5 per cent of glycerol into the heated oil.[115]

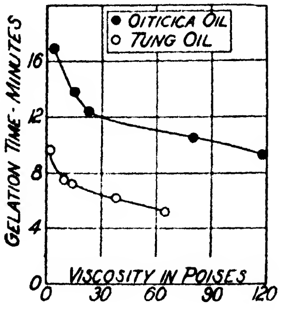


FIGURE 16.

Effect of Viscosity on Gelation Time of Tung and Oiticica Oils at 540° F. (S. O. Sorenson, C. J. Schumann, J. H. Schumann, and J. Mattiello).

Courtesy Industrial and Engineering Chemistry

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[112] S. O. Sorenson, C. J. Schumann, J. H. Schumann, and J. Mattiello, *Ind. Eng. Chem.*, 1938, 30, 211; *Chem. Abs.*, 1938, 32, 2766.

[113] M. J. Hausman, *Am. Ink Maker*, 1937, 15 (1), 16; *Chem. Abs.*, 1937, 31, 2840.

[114] *Am. Ink Maker*, 1938, 16 (7), 37.

[115] H. A. Gardner, *Natl. Paint, Varnish & Lacquer Assoc. Circ.*, 1934, No. 470, 218; *Chem. Abs.*, 1935, 29, 362.

Frosting or wrinkling of oiticica oil may be avoided by heating the oil in contact with air to about 120-260° C. until a viscosity of 3 to 150 poises is obtained.[116] A solvent such as "mineral spirits" is admixed with the oil, after heating to the viscosity described above, and the oiticica oil is then aged in contact with air.

Oiticica oil is used as a substitute for tung oil. The advantages of oiticica oil over tung oil are said to be: formation of more durable, glossier surfaces, freedom from skinning, and decreased wrinkling. Oiticica oil films have less resistance to boiling water than those made with tung oil.[117] The drying time of oiticica is reported to be longer than for tung oil. This disadvantage may be overcome by using larger quantities of driers such as lead and cobalt driers (see Chapter 4.)[118] Though tung and oiticica oils have defects, it has been stated that use of the two oils together will in many cases eliminate the faults of both.[119] If one-third of the required amount of tung oil is replaced with oiticica oil, films are obtained which have a satisfactory luster. If one-half or all the tung oil is replaced with oiticica oil, a relatively larger amount of drier is necessary.[120] Nonwrinkling rapid-drying films are stated to be secured by mixing oiticica with other drying oils.[121]

Bodied oiticica oil may be prepared by heating the oil at 270° C. (518° F.) for 30 minutes.[122] Other bodying temperatures recommended lie in the range 435-490° F.[123] Also, it has been recommended that oiticica oil be heated to 250° C., with constant stirring, over a period of 20 minutes. The oil is held at this temperature for one-half hour.[124] A stand oil is reported to be produced by this process.

Both tung and oiticica oils have a tendency to gelatinize.[125] The gelatinization of oiticica oil is said to result from the decomposition, at 250° C., of keto acids with the expulsion of carbon dioxide and the formation of ketones.[126] On further heating, water is given off and highly unsaturated hydrocarbons are formed. The latter polymerize to form a rubber-like substance, which is insoluble in most solvents but which may be decomposed by alkalies into hydroxyacids. Heating at 316° C. produces no gelation, even when heat is applied for a long time.[127]

[116] A. M. Alvarado, U. S. P. 2,112,354, Mar. 29, 1938, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1938, 32, 3992.

[117] M. J. Hausman, *loc. cit.*

[118] *Am. Ink Maker*, 1936, 14 (9), 35.

[119] C. P. Holdt, *Nat. Paint Bull.*, 1937, 1, 10; *Chem. Abs.*, 1937, 31, 3716. *Drugs, Oils, Paints*, 1936, 51, 191, 194, 196; *Chem. Abs.*, 1936, 30, 5060.

[120] *Oil, Paint and Drug Reporter*, 1935, 128 (22), 53; *Chem. Abs.*, 1936, 30, 4699.

[121] H. A. Gardner, *Paint, Varnish Production Mgr.*, 1936, 14 (6), 16, 18, and 30; *Chem. Abs.*, 1936, 30, 5432.

[122] M. J. Hausman, *Am. Ink Maker*, 1937, 15 (1), 16; *Chem. Abs.*, 1937, 31, 2840.

[123] S. O. Sorenson, C. J. Schumann, J. H. Schumann and J. Mattiello. *Ind. Eng. Chem.*, 1938, 30, 211; *Chem. Abs.*, 1938, 32, 2766. *Oil, Paint and Drug Reporter*, 1935, 128 (22), 53; *Chem. Abs.*, 1936, 30, 4699.

[124] E. Stock, *Farben-Chem.*, 1936, 7, 45; *Chem. Abs.*, 1936, 30, 5059.

[125] *Am. Ink Maker*, 1936, 14 (9), 35. W. W. Bauer, *Ind. Eng. Chem.*, 1926, 18, 1249; *Chem. Abs.*, 1927, 21, 659.

[126] A. Machado and A. S. Peixoto, *Rev. Chim. Ind. (Rio de Janeiro)*, 1937, 6, 464; *Chem. Abs.*, 1938, 32, 8647.

[127] S. O. Sorenson, C. J. Schumann, J. H. Schumann and J. Mattiello, *loc. cit.*

The characteristic unsaturated acid of oiticica oil is reported to be licanic acid.[128] This acid is said to exist in a *cis* and *trans* form.[129] The average composition of oiticica oil with respect to the glyceride structure is stated to be as follows:

Per cent of unsaturated acids, conjugated diene system....	73
Per cent of other unsaturated acids........................	16
Per cent of saturated acids................................	11
Mean molecular weight of saturated acid..................	274

Table 9.—Composition of Oiticica Oil.[130]

	Per cent
Saturated acids (Bertram method)	10.7
Oleic acid	5.9
Licanic acid	78.9
Glycerides of saturated acids	11.2
Glycerides of oleic acid	6.2
Glycerides of licanic acid	81.7

The physical properties of the crude oil are indicated in Table 10.

Table 10.—Physical Properties of Oiticica Oil.

Property	Value	
Specific gravity	0.9700	
Refractive index (15.5° C.)	1.5181	
Refractive index (25° C.)	1.5146	
Free fatty acids as oleic (%)	2.11	
Equivalent acid number	4.19	
Saponification number	186.8	
Iodine number (Wijs)	160.6	
Unsaponifiable matter (%)	0.64	
Moisture, volatile matter (%)	0.15	
Insoluble impurities (%)	0.02	
Heat test, quality:		
Initial coagulation	9.5	minutes
Complete coagulation	12.5	minutes
Consistency: light, soft and sticky.		
Color: clear golden yellow.		

Castor Oil. Castor oil, in admixture with turpentine, linseed stand oil and similar varnishes, has been employed in making offset printing inks.[131] However, as this vegetable oil is practically non-drying, it is of little value in most inks, except as a plasticizing agent, or as a solvent [132] for coal-tar dyes. Distillation of castor oil does furnish an oily product possessing drying properties. This transformation, as is well known, is due to the loss of water from the ricinoleic acid radical (which contains a hydroxyl group close to a double bond) with the result that it is

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[128] W. B. Brown and E. A. Farmer, *Biochem. J.*, 1935, **29**, 631; *Chem. Abs.*, 1935, **29**, 5294.

[129] R. S. Morrell and W. R. Davis, *J. C. S.*, 1936, 1481; *Chem. Abs.*, 1937, **31**, 368. *J. Oil Colour Chem. Assoc.*, 1936, **19**, 359; *Chem. Abs.*, 1937, **31**, 5607. *Paint Varnish Production Mgr.*, 1937, **16**.

[130] M J. Hausman, *Am. Ink Maker*, 1937, **15** (1), 16; *Chem. Abs.*, 1937, **31**, 2840.

[131] C. P. Shaw, U. S. P. 2,043,397, June 9, 1936, to Detroit Moulding Corp.; *Chem. Abs.*, 1936, **30**, 5436; *Brit. Chem. Abs.* **B**, 1937, 1242.

[132] W. Obst, *Allgem. Oel u. Fett-Ztg.*, 1934, 31 (2), 58; *Rev. Paint, Colour, Varnish*, 1934, **1**, 87.

changed into an isolinoleic acid radical. Or, stated in other words, distillation of the glycerides of ricinoleic acid (characteristic of castor oil) furnishes the glycerides of isolinoleic acid (a drying oil).[133]

The residues from distillation also serve as printing ink vehicles.[134] In this connection it is noted that distillation residues from cottonseed oil[135] or stearin (*i.e.*, cottonseed foots or stearin pitch, respectively) may be employed as printing inks. When cottonseed foots are used, because of its bluish black color, addition of carbon black to the ink composition is not always necessary.

Dehydrated, or distilled, castor oil has better drying power than linseed oil, resembling tung oil rather closely in its properties[136] and is almost odorless.[137] It is now manufactured commercially in the United States and elsewhere. It is reported[138] that dehydrated castor oil, when substituted for tung oil in varnishes normally containing tung-perilla oils and resins, gave inferior drying power and body to the product. Other treatments of castor oil yield similar products;[139] catalysts such as aluminum oxide and metallic zinc may accelerate the process.[140] Reaction of the hydroxyl group (in castor oil) with unsaturated fatty or resin acids gives rise to esters which are said to be drying oils.[141]

Synourin oil (Scheiber Oil, Synouryn Oil, or dehydrated castor oil) is said to be a synthetic triglyceride of octadeca-9,11-dien-1-oic acid.[142] It is prepared by the Scheiber method from castor oil.[143] In the process of manufacture, castor oil is heated at 200 to 250° C. in the presence of a substance which retards thickening or gelatinization, until a product having an acid number of about 30 or less is obtained. The added substance may be a fatty oil (such as linseed oil), naphthenic acid, polyhydric alcohols, sulphur, natural or synthetic resin, selenium, a halogen or a primary amine. A similar method of preparation comprises heating castor oil for one hour at 250 to 300° C. in the presence of 0.5 mol of phthalic anhydride for each mol of hydroxylated fatty acid in the castor oil.[144] A catalyst, which is employed at temperatures of 220 to 230° C. for a time interval of one hour, is ascanite (askanite, bentonite).[145] Six

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[133] J. Böeseken, W. C. Smit and Gaster, *Proc. Acad. Sci. Amsterdam*, 1929, 32, 377; *Chem. Abs.*, 1929, 23, 4192; *Brit. Chem. Abs.* A, 1929, 910. F. Fritz, *Chem. Umschau*, 1920, 27, 62; *Chem. Abs.*, 1920, 14, 2093.

[134] J. Scheiber, German P. 522,277, 1928; *Chem. Abs.*, 1931, 25, 3184.

[135] J. J. Bibby, British P. 12,863, 1893; *J. S. C. I.*, 1894, 13, 145.

[136] *Peintures, pigments, vernis*, 1934, 11 (8), 173.

[137] J. Scheiber, German P. 522,486, 1928; *Chem. Abs.*, 1931, 25, 3184.

[138] *Nat. Paint, Varnish Assoc., Sci. Sect.*, 1938, Circular 568, 359, (Northwestern Club); *Brit. Chem. Abs.* B, 1939, 77. A. Adams, *et al.*, (Northwestern Club), *Am. Paint J.*, 1938, 23, Convention Daily 22; *Chem. Abs.*, 1939, 33, 415.

[139] See Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[140] B. N. Tyutyunnikow and Y. G. Borisyuk, Russian P. 37,211; *Chem. Zentr.*, 1935, 106 (2), 3016.

[141] K. Ott and B. Breyer, German P. 572,359, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3627.

[142] J. Scheiber, *Farbe u. Lack*, 1936, 361; *Chem. Abs.*, 1936, 30, 8657.

[143] J. Scheiber, German P. 555,496, 1929; *Chem. Abs.*, 1932, 26, 5223. J. Rinse and W. H. Wiebols, *Ind. Eng. Chem.*, 1937, 29, 1149; *Chem. Abs.*, 1937, 31, 8956; *Rev. Paint, Colour, Varnish*, 1937, 10, 401.

[144] S. L. M. Saunders, British P. 487,681, 1938; *Brit. Chem. Abs.* B, 1939, 72; *J. Inst. Pet. Tech.*, 1938, 24, 506A.

[145] A. Zinoviev, *Masloboino Zhirovoe Delo*, 1938, No. 4, 32; *Brit. Chem. Abs.* B, 1938, 1445. Ascanite or askanite is a form of bentonite mined at Askana, Caucasus, U.S.S.R. (A. L. Lyubimov, *Inst. Econ. Mineral, Trans.*, 1933, 10-year Volume, 73 (U.S.S.R.); *Chem. Abs.*, 1935, 29, 2314.)

to 8 per cent of kaolin may also be used for the same purpose at 275 to 280° C.[146] Other catalysts suggested are tungstic oxide, uranium oxide or molybdenum oxide. With these oxides zinc oxide or ferric chloride may be admixed.[147] Sodium bisulphate, inert earthy materials and sufficient acid to dehydroxylate the castor oil are heated, at temperatures of 350 to 500° F., with the castor oil, in another method.[148]

Synourin oil is recommended for use in printing inks,[149] and is said to be satisfactory (drying more rapidly than linseed oil), except for a slight stickiness of the film (from traces of ricinoleic acid).[150] The physical properties of this product are said to be as follows: iodine number (Wijs), 120.5; viscosity (G-H scale), G; color (Hellige), IL-I; does not gel in 2 hours under Brown heat test; specific gravity, 0.937; index of refraction, 1.487 (25° C.)[151]; and acid value, 35.[152]

Synourin oil is said to dry with a minimum of decomposition and to form a stable film. These properties are reported to make the Scheiber oil superior to unsaturated fatty oils with non-conjugated double bonds, to fatty oils containing acetylene linkages, and to tung oil.[153] This oil is said to improve the ageing qualities of films.[154]

Drying oils secured by eliminating water from fatty glycerides containing hydroxyl groups may be esterified with glycerol.[155] The esterification step was reported to increase the drying properties of the dehydrated glyceride.

Cashew Nut Shell Oil. Cashew nut shell oil is not a drying oil, but consists of phenolic compounds with long side-chains. After special treatment, *e.g.*, with maleic acid, it does possess drying properties and may be used as a varnish base.[156] The oil frequently causes skin eruptions [157] on persons susceptible to poison ivy (see Chapter 14). Gelation of the quick-drying oil may occur during storage of the ink composition of which it forms a part.[158]

ROSIN AND ROSIN OILS

Addition of rosins to natural oils formerly was regarded as an adulteration [159] because of their low price. However, some workers called

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[146] P. V. Seib-Seibin and A. V. Sakharnov, *Org. Chem. Ind.* (*U.S.S.R.*), 1938, 5, 203; *Chem. Abs.*, 1938, 32, 8168.

[147] F. Münzel, Swiss P. 193,931, 1938; *Chem. Abs.*, 1938, 32, 7294.

[148] A. Schwarzman, U. S. P. 2,140,271, Dec. 13, 1938, to Spencer Kellogg and Sons, Inc.; *Chem. Abs.*, 1939, 33, 2744.

[149] J. Scheiber, German P. 522,277, 1928; German P. 522,486, 1928; *Chem. Abs.*, 1931, 25, 3184.

[150] A. Zinoviev, *Masloboino Zhirovoe Delo*, 1938, No. 4, 32; *Brit. Chem. Abs.* B, 1938, 1445.

[151] G. G. Sward, *Am. Paint and Varnish Mfrs. Assoc. Circ.*, 1931, No. 377, 126; *Chem. Abs.*, 1931, 25, 1689.

[152] J. Rinse and W. H. G. Wiebols, *Ind. Eng. Chem.*, 1937, 29, 1149; *Chem. Abs.*, 1937, 31, 8956; *Rev. Paint, Colour, Varnish*, 1937, 10, 401.

[153] J. Scheiber, *Farbe u. Lack*, 1935, 411, 422; *Chem. Abs.*, 1935, 29, 2365.

[154] A. Nauroy, *Peintures, pigments, vernis*, 1937, 14, 210; *Chem. Abs.*, 1938, 32, 6081.

[155] French P. 828,203, 1938, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1939, 33, 417.

[156] Carleton Ellis, U. S. P. 2,033,133, March 10, 1936, to Ellis-Foster Co.; *Chem. Abs.*, 1936, 30, 3282. German P. 562,646, 1928, to Harvel Corp.; *Farben-Ztg.*, 1933, 38, 434; *Chem. Abs.*, 1933, 27, 1217.

[157] L. Tulipan, *Ind. Med.*, 1936, 5, 626; *Chem. Abs.*, 1937, 31, 2455.

[158] For a review of patents relating to synthetic drying oils, see A. W. Van Heuckeroth, *Natl. Paint, Varnish, Lacquer Assoc., Sci. Sec. Circ.*, 1937, 531, 123; *Chem. Abs.*, 1937, 31, 4835.

[159] F. H. Leeds, *J. S. C. I.*, 1894, 13, 203.

the blending of oils with rosins uneconomic, since large quantities of the vehicle are required, but nevertheless these varnishes were recommended because of their improved properties, such as luster and hardness.[160] It is now known that greater drying and bodying power will be imparted to the varnish through blending with rosins.[161] Wood rosins are considered superior to gums, since the former give tack and flow without imparting deleterious effects to the ink, such as slow drying, livering or excessive tack.[162] Satisfactory varnishes are derived from rosin oils after partly or completely esterifying,[163] dehydrating[164] or reacting with a sulphonic aromatic acid.[165] It is recommended that rosin be admixed with 15 per cent or less of a rosin-distillation residue before incorporation into printing ink.[166] Resinic acids and resinates dissolved in a petroleum fraction also serve as drying oil substitutes.[167] Saponified rosin is suggested as a substitute for linseed oil[168] (100 parts of rosin are saponified with 18 parts of caustic soda).

A study of the effect of rosin and rosin oils on news inks indicates[169] that:

(1) Viscosity of ink is slightly increased by rosin (Figure 17).
(2) The rate of penetration of the paper by the ink is slightly increased when rosin is employed (Figure 18).
(3) "Draw outs"[170] indicate no change in color strength of inks by the inclusion of rosin.

The above statements are limited to compositions containing 5 per cent or less of rosin. If more than 5 per cent of rosin or if a low grade of rosin is employed, the phenomenon known as "strike through" will result.[171] In order to decrease "strike through," it is preferable to employ a non-staining oil rather than to use rosin which at best can produce only a slight decrease in this effect.

It is considered too expensive to use rosin to increase the viscosity of ink. Increased viscosity can be obtained more cheaply by the employment of an oil of higher viscosity. In general it may be said that wood

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[160] H. Pfanner, *Farben-Chem.*, 1936, 7 (6), 209; *Chem. Abs.*, 1936. 30, 8657; *Brit. Chem. Abs.* **B**, 1936, 700.

[161] L. M. Larsen, *Proc. Am. Soc. Test. Mat.*, 1926 (65), 17; *Chem. Abs.*, 1926, 20, 3090.

[162] J. M. Schantz, *Am. Ink Maker*, 1930, 8 (6), 55; *P. I. A. Abs.*, 1930 4, 262.

[163] R. C. Palmer and P. O. Powers, U. S. P. 2,022,973, Dec. 3, 1935, to Newport Industries, Inc.; *Chem. Abs.*, 1936, 30, 886; *Brit. Chem. Abs.* **B**, 1936, 1167.

[164] B. Föhre, German P. 576.262, 1933; *Farben-Ztg.*, 1933, 38 (40), 1114; *Chem. Abs.*, 1933, 27, 3835.

[165] A. C. Johnston, U. S. P. 1,975,211, Oct. 2, 1934, to Hercules Powder Co.; *N. P. V. L. Abs.*, 1934, No. 83, 376; *Chem. Abs.*, 1934, 28, 7561; *Brit. Chem. Abs.* **B**, 1935, 814.

[166] I. W. Humphrey, U. S. P. 1,931.226, Oct. 17, 1933, to Hercules Powder Co.; *Chem. Abs.*, 1934, 28, 352.

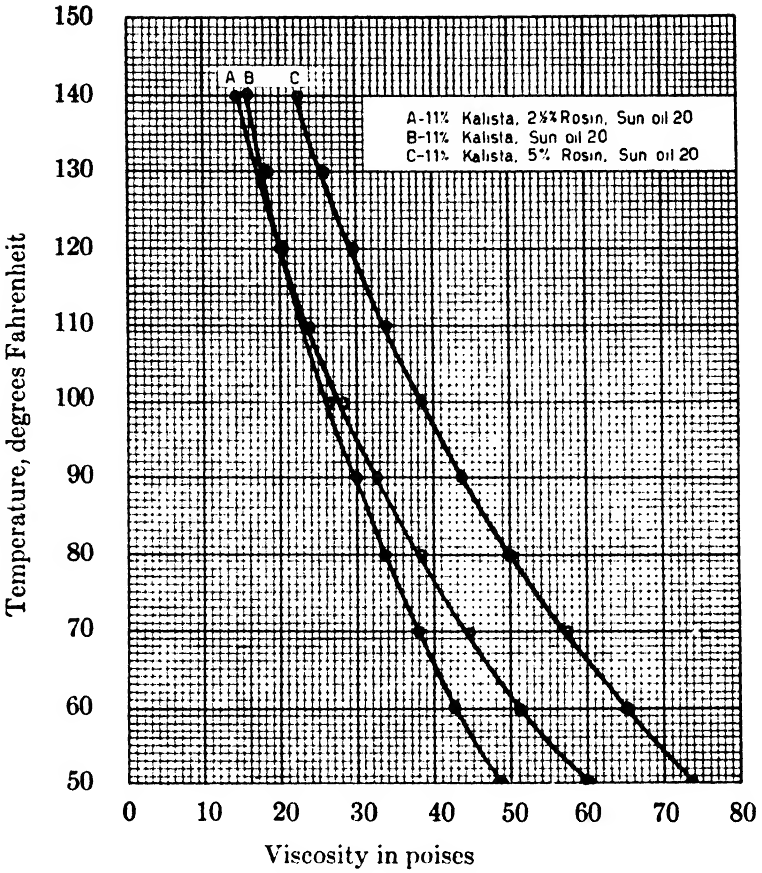
[167] L. Adamyan, *Neft*, 1935, 6 (11), 19; *Chem. Abs.*, 1936, 30, 3666.

[168] S. Banner, British P. 29,728, 1897; *J. S. C. I.*, 1898, 17, 1158.

[169] B. L. Wehmhoff, D. P. Clark and D. H. Boyce, "Newsprint and News Ink," *U. S. Gov. Printing Office, Tech. Bull.* No. 18.

[170] A draw out is a small portion of a colored paste spread out in a thin layer on a sheet of white paper to indicate its color properties.

[171] "Strike through" is a term employed to designate the yellow stain which is caused by the penetration of the sheet by the ink.



Courtesy United States Government Printing Office

FIGURE 17. Effect of Addition of Rosin on Viscosity of News Ink (B. L. Wehmhoff, D. P. Clark, and D. H. Boyce).

rosins have a lesser tendency to crystallize from varnish than gum rosins.[172]

Rosin oil is reported[173] to contain at least 61 organic compounds. Abietic acid, colophene and three oils of the composition $C_{20}H_{32}$ are said[174] to be the main substances present in this oil.

Products similar to rosins are prepared from pine tar, which attains drying properties after being heated with lead, manganese or copper salts.[175] Dipentene[176] and turpentine also can be converted into drying

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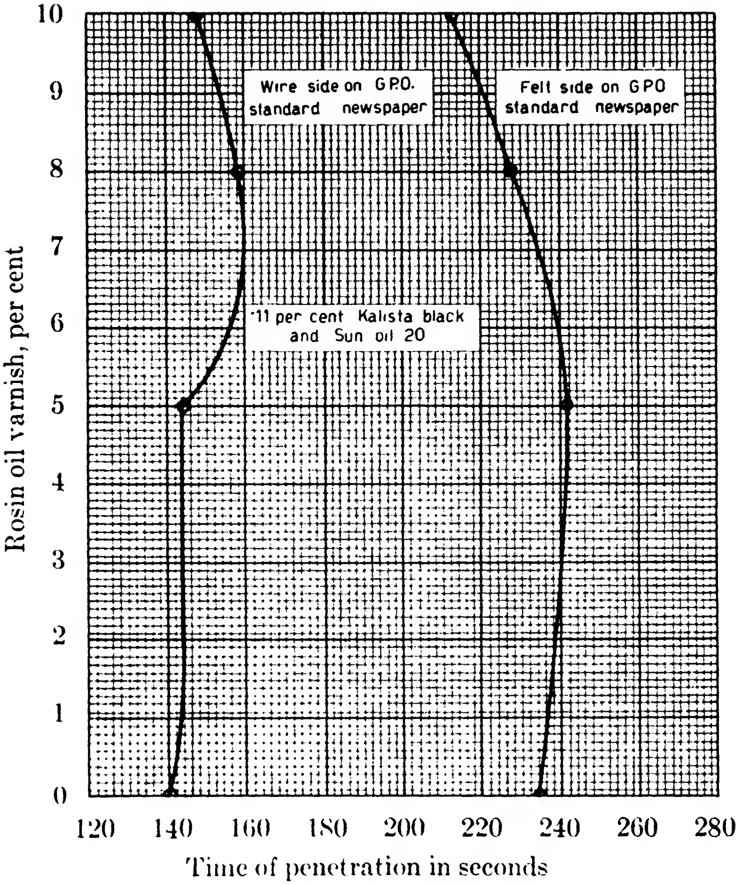
[172] B. L. Wehmhoff, D. P. Clark and D. H. Boyce, *loc. cit.*

[173] J. Lagerquist, *Svensk Kem. Tids.*, 1925, 37, 89; *Chem. Abs.*, 1925, 19, 2881.

[174] E. Knecht and N. B. Maurice, *J. Soc. Dyers and Col.*, 1925, 41, 356; *Brit. Chem. Abs. B*, 1926, 21.

[175] M. M. Chilikin, Russian P. 164, 1922; *Chem. Abs.*, 1933, 27, 4428.

[176] L. P. Rankin, U. S. P. 1,910,564, May 23, 1933; *Chem. Abs.*, 1933, 27, 4108; *Brit. Chem. Abs. B*, 1934, 108.



Courtesy United States Government Printing Office

FIGURE 18. Effect of Per Cent Rosin Oil Varnish on Time for Penetration of News Ink (B. L. Wehmhoff, D. P. Clark, and D. H. Boyce).

oils[177] after treatment with ozone and sulphuric acid[178] or with aluminum chloride.[179]

Tall oil (rosin oil, tallöl, pinolein, liquid rosin, pine oil, "fluid resin," or Swedish olein) is a dark brown, viscous liquid, obtained as an alkaline waste liquor in the sulphate pulp process.[180] Three products from tall oil are sold commercially, namely, tall oil, tall oil distillate and tall oil pitch.

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[177] See Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[178] *Syn. App. Fin.*, 1933, 3 (36), 149. L. P. Rankin, U. S. P. 1,886,586, Nov. 8, 1933, to Hercules Powder Co.; *Brit. Chem. Abs.* **B**, 1933, 718; *Chem. Abs.*, 1933, **27**, 1528.

[179] S. M. Cooper, U. S. P. 1,938,320, Dec. 5, 1933, to Gulf Refining Co.; *A. P. V. M. Abs.*, 1934, **23**, 19; Chem. Abs., 1934, **28**, 1184; *Brit. Chem. Abs.* **B**, 1934, 895.

[180] W. Schmid, *Papier-Fabr., Tech.-Wiss. Teil*, 1931, **29**, 1; *Chem. Abs.*, 1931, **25**, 3165. *Zellstoff u. Papier*, 1933, **13**, 571; *Chem. Abs.*, 1934, **28**, 2529. *J. Hübscher, Seifensieder-Ztg.*, 1921, **48**, 231; *Chem. Abs.*, 1921, **15**, 2177. Freitag, *Oberflächentech.*, 1938, **15**, 190; *Chem. Abs.*, 1939, **33**, 415.

The properties of these materials are shown in Table 11.

Table 11.—Properties of Tall Oil Products.

	Tall Oil	Tall Oil Distillate	Tall Oil Pitch
State	Viscous liquid	Liquid	Solid
Color	Dark brown	Light yellow	Black
Odor	Like rancid lard	Like rancid lard	....
Sediments	Crystalline	Crystalline	....
Index of refraction	$n_D^{15}=0.976$	....	....
Acid number	114.5	151.6	50.3
Saponification number	129.3	162.2	75.5
Unsaponifiable matter	Present	18 per cent	....
Iodine number	....	106.7	....
Specific gravity	....	0.958	....
Drop point	....	....	85° C.

Analysis of tall oil is reported to indicate that it is composed of 2.2 per cent petroleum ether-insoluble material, 12.4 per cent unsaponifiable matter, 30.4 per cent resin acids and 54.9 per cent of "fatty acids."[181] The unsaponifiable material is said to contain 2 per cent[182] phytosterol ($C_{26}H_{44}O$, melting point, 136° C.) and hydrocarbons similar to those in rosin oil. The rosin acid is abietic acid, and the fatty acids are all unsaturated, being mostly oleic, linoleic and linolenic acids.[183]

Tall oil, in the crude state, even when esterified with glycerol is reported to dry very slowly.[184] However, if this material is admixed with drying agents, it is said to dry to a brittle film.[185] Tall oil distillate (acid value of 180), esterified with glycerol, is recommended as a substitute for linseed oil.[186] Tall oil pitch is used in printing inks.[187]

A disadvantage of rosins is their high acid number, which renders the ink likely to liver. To overcome this obstacle it became customary to esterify the rosins with glycerol or ethylene glycol, and these "ester gums" are held to constitute the first artificial resins. Since then many other synthetic resins have been developed which give a variety of outstanding products. They are used either in connection with drying oils or alone as varnishes and can no longer be regarded as substitutes, but are now factors of vital importance.

EMULSIONS

In recent years water-oil emulsions have made much progress because of their inexpensiveness. They are very helpful for certain types of print-

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[181] M. Dittmer, *Z. Angew. Chem.*, 1926, 39, 262; *Chem. Abs.*, 1926, 20, 2072.

[182] W. Schmid, *loc. cit.*

[183] M. Dittmer, *loc. cit.*

[184] H. Reinert, *Farbe u. Lack.* 1936, 461; *Chem. Abs.*, 1937, 31, 5603.

[185] H. Wolff, *Farben-Ztg.*, 1919, 24, 653; *Chem. Abs.*, 1919, 13, 2289.

[186] E. Dörken, German P. 526,491, 1928; *Paint Manuf.*, 1936, 6, 396. H. Reinert, *loc. cit.*

[187] W. Schmid, *Farben-Chemiker*, 1931, 2, 306; *Chem. Abs.*, 1931, 25, 5582. Concerning tall oil, see also: Carleton Ellis, "Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

ing inks and will doubtless come to be used a great deal in the future. Gum arabic,[188] glue and gelatin [189] serve as stabilizers. Emulsions and their applications to printing inks are discussed fully in Chapter 13.

ADDITION OF OTHER MATERIALS

Mixtures of natural oils with grease, proto- and pyroparaffin or wax,[190] waste sulphite cellulose liquors with rosin,[191] stearin or soap,[192] and mineral-oil-free mineral oil alkaline sulphonates [193] have been recommended as inexpensive printing ink vehicles. Also, it has been suggested that the tar fraction (b. 200-300° C.) from peat be neutralized, dewaxed, and mixed with linseed oil to furnish a litho-varnish.[194] However, materials are not always added only in order to keep the price of the ink low. Some ingredients, on the contrary, are rather expensive, particularly certain cellulose ethers and esters,[195] but they impart excellent properties to the vehicle. As overprint varnishes they are often used without drying oils.[196] A type of nitrocellulose completely soluble in methanol has been especially mentioned in this connection.[197] Flexibility and good adhesion of films from cellulose esters or ethers make them useful particularly in tin-printing inks.

The employment of nitrocellulose as the main or essential binder in a printing ink composition is objected to by some, who assert that a paper heavily printed with such an ink is rendered too inflammable for general use. It is suggested that nitrocellulose of low viscosity be admixed with castor oil to form a vehicle.[198]

OTHER VEGETABLE OILS

Records show that consumption of linseed oil for printing ink vehicles is the highest as compared to other materials;[199] but many vehicles consist of different products. Lumbang oil (candlenut oil),[200] resembling

[188] W. Fabrion, *Chem. Umschau*, 1920, **27**, 38, 122; *Chem. Abs.*, 1920, **14**, 2556, 2993. J. R. Geigy, German P. 524,109, 1927; *Chem. Abs.*, 1931, **25**, 3855. J. Maroger, Belgian P. 392,349, 1934, *Chem. Zentr.*, 1935, **106** (2), 3983.

[189] W. G. Dewsbury and A. Davies, U. S. P. 2,014,760, Sept. 17, 1935; *N. P. V. L. Abs.*, 1935, **40**, 212; *Chem. Abs.*, 1935, **29**, 7678. British P. 441,571, 1936; *Chem. Abs.*, 1936, **30**, 4702; *Brit. Chem. Abs.* **B**, 1936, 286.

[190] S. Horii, Japanese P. 90,585, 1931; *Chem. Abs.*, 1931, **25**, 4724.

[191] T. Hynson and F. C. Stephens, British P. 215,824, 1923; *Chem. Abs.*, 1924, **18**, 3484; *Brit. Chem. Abs.* **B**, 1924, 604.

[192] I. S. Andrianov, Russian P. 31,948, 1933; *Chem. Abs.*, 1934, **28**, 3605.

[193] German P. 618,284, 1935, to Twitchell Process Co.; *Chem.-Tech. Ubersicht*, 1935, **59**, 195; *Chem. Abs.*, 1936, **30**, 309.

[194] G. I. Yudas, Russian P. 50,860, 1937; *Chem. Zentr.*, 1938, **109** (2), 428; *Chem. Abs.*, 1939, **33**, 4065; *Rev. Paint, Colour, Varnish*, 1938, **11**, 365.

[195] British P. 311,795, 1928, to I. G. Farbenind. A.-G., *Chem. Abs.*, 1930, **24**, 980. W. Fahrion, *Chem. Umschau*, 1920, **27**, 38, 122; *Chem. Abs.*, 1920, **14**, 2556, 2993. British P. 286,789, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, **23**, 513. Cellulose acetate is dissolved in a mixture of 30 parts of water and 60 parts of glycerol monoformal.

[196] British P. 450,454, 1936, to Celluloid Corp.; *Chem. Abs.*, 1936, **30**, 8434; *Brit. Chem. Abs.* **B**, 1936, 895.

[197] *Am. Ink Maker*, 1936, **14** (9), 37.

[198] French P. 698,639, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, **25**, 3184.

[199] M. J. Hausman, *Am. Ink Maker*, 1937, **15** (17), 16; *Chem. Abs.*, 1937, **31**, 6486.

[200] A. P. West and F. L. Smith, *8d. Bur. Forestry, Philippine Islands*, 1923, Bull. 24; *Chem. Abs.*, 1924, **18**, 477.

linseed oil very closely, is used in the Philippine Islands and the East Indies.[201] Tomato-seed oil is recommended as a drying oil.[202]

Perilla oil, having a higher iodine value and greater drying power,[203] also replaces linseed oil to a certain extent despite the fact that some workers maintain that the latter oil dries faster.[204] Perilla oil is said to have the properties indicated in Table 12.[205] Perilla oil is reported to be superior to linseed oil in the following respects: rate of drying after addition of 0.035 per cent of cobalt drier, rate of bodying on heating to 250° C., rapidity of drying of stand oils, and rate of thickening on blowing with air at 150° C.[206] It is stated that perilla oil when heated has a strong tendency to evolve heat. This property is said to cause rapid temperature rises with attendant fire and explosion hazards.[207] Blown soybean oil [208] is sometimes employed as ink vehicle. Soybean oil is said to be greatly inferior to linseed oil in the following respects: rate of drying after addition of 0.035 per cent of cobalt drier, rate of bodying on heating to 250° C., rapidity of drying of stand oils, and rate of thickening on blowing with air at 150° C.[209] However, soybean oil may be employed together with oiticica oil to prevent gelation.

Table 12.—Properties of Perilla Oil.

Iodine number	198.6	to	202.4
Acid number	0.613	to	0.714
Saponification number	182.15	to	186.62
Index of refraction (at 20° C.)	1.483	to	1.4835
Hexabromide number	54.38	to	59.85
Density (sp. gr. at 20° C.)	0.9348	to	0.9358

A satisfactory drying oil may be produced by rapidly heating together, under pressure, equal quantities of tung and soybean oils until a temperature of 355° C. is attained.[210] The amount of time consumed in this process should be sufficient to secure a substantial reduction in the index of refraction and an increase in the specific gravity, acid number and viscosity, but the time must be sufficiently brief to avoid gel formation. The preferred time is 22 seconds. As soon as a temperature of 355° C. is

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[201] The properties of candlenut oil are reported to be as follows: density 0.935, iodine number 111.4, saponification number 195.8 and free acid as oleic, 1.1 per cent. (G. D. V. Georgi, *Malayan Agr. J.*, 1926, 14, 290; *Chem. Abs.*, 1927, 21, 662.)

[202] M. Brambilla and G. Balbi, *Chimica e Industria*, 1938, 20, 591; *Brit. Chem. Abs.* B, 1939, 76. However this oil is said to produce tacky films, to have small drying power, to have high acidity, and to be unstable in the atmosphere. It may be employed in conjunction with large quantities of linseed oil. Stand oil is made by heating tomato-seed oil at 330° C. for 8 hours.

[203] M. Ogura, *J. Soc. Chem. Ind., Japan*, 1937, 40, *suppl. bind.*, 377B; *Chem. Abs.*, 1938, 32, 1952; *Brit. Chem. Abs.* B, 1938, 298.

[204] H. L. Tchang and C. L. Ling, *Bull. Faculte Sci. Univ., Franco-Chinoise, Peiping*, 1935, 4, 1; *Chem. Abs.*, 1936, 30, 4699.

[205] M. S. Dunin, N. S. Torman, R. M. Erastova and E. A. Buikova, *Trudui Nauch-Issledovatel. Inst. LaKov i Krasok*, 1935, No. 1, 20; *Chem. Abs.*, 1936, 30, 7887.

[206] H. Kemner, *Farbe u. Lack*, 1937, 595; *Chem. Abs.*, 1938, 32, 1494.

[207] Brauer, *Farben-Ztg.*, 1938, 43, 1252; *Farbe u. Lack*, 1938, 535, 545; *Chem. Abs.*, 1939, 33, 1522.

[208] A. J. Lewis and K. S. Markley, *Paint, Oil and Chem. Rev.*, 1938, 100 (22), 8; *Brit. Chem. Abs.* B, 1936, 749. H. Y. Chang and T. H. Chang, *Chemistry* (China), 1935, 2, 206; *Brit. Chem. Abs.* B, 1936, 749; *Chem. Abs.*, 1935, 29, 6443.

[209] H. Kemner, *Farbe u. Lack*, 1937, 595; *Chem. Abs.*, 1938, 32, 1494.

[210] M. F. Taggart, U. S. P. 2,113,358, April 5, 1938; *Chem. Abs.*, 1938, 32, 4364. *Am. Soybean Assoc. 16th Ann. Meeting, Proc.*, 1936, 47; *Chem. Abs.*, 1937, 31, 4518. *Drugs, Oils, and Paints*, 1938, 53, 177; *Chem. Abs.*, 1938, 32, 5645.

attained, the mixture is immediately chilled. The product is said to have excellent drying properties and to lack the disadvantages of the individual oils employed in its manufacture.

"Nonbreak" soy-bean oil is recommended for varnishes.[211] Such an oil is described as one which shows little or no precipitate and which bleaches to a colorless or a very pale yellowish-colored oil, when heated to 600° F. A break oil, on the other hand, is one which develops a dark color and which produces a dark colored precipitate when heated to 600° F. Drying time and Gardner[212] break are proportional to the percentages of phosphatides (phosphorus content expressed as lecithin) in the crude oil.[213] The phosphatides of crude soybean oils are removed in the commercial production of nonbreak oils by acid or alkali refining.

Sunflower-seed oil may be utilized as a drying oil, either as a stand oil or in the form of a dehydrogenated product. Stand oil may be obtained by first removing the break from the raw oil by heating and settling, and then simultaneously blowing with air and heating at 135 to 140° C.[214] Heating of the oil above 350° C. is apt to cause gelation. It is recommended[215] that sunflower-seed oil be admixed with 60 to 70 per cent of linseed oil to produce a satisfactory drying oil.

Dehydrogenated sunflower-seed oil may be manufactured by heating the oil for 4 hours, at a temperature of 320° C. in the presence of 1 per cent nickel and 0.25 per cent mercury.[216] The treated oil is reported to have an iodine value of 144.4 and to possess satisfactory drying properties.

A drying vehicle which is reported to have the properties of soybean oil is safflower oil. It usually is mixed with other drying oils, such as raw perilla, raw linseed or soybean oils.[217] The great advantage of this oil is said[218] to be its low acid number. However, with lead pigments this oil is reported to give a skin which peels off after a short time.[219] The weight increase of this oil from oxidation is stated to be 5.3 to 5.6 per cent.[220] Grapeseed oil is reported[221] to provide a satisfactory substitute for linseed oil in many types of varnish. A stand oil may be prepared by heating the grapeseed oil for 2 hours at 330° C. in a stream of carbon

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[211] R. L. Smith and H. R. Kraybill, *Ind. Eng. Chem.*, 1933, 25, 334; *Chem. Abs.*, 1933, 27, 2053.

[212] See H. A. Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," 7th ed., pp. 747. 751, Inst. of Paint and Varnish Research, Washington, D. C., 1935.

[213] H. R. Kraybill, A. W. Kleinsmith and M. H. Thornton, *Ind. Eng. Chem.*, 1939. 31, 218.

[214] E. Stock, *Farben-Ztg.*, 1938, 43, 134; *Chem. Abs.*, 1938, 32, 4361.

[215] I. Osnos, I. Golovistikov and K. Orlova, *Masloboino Zhirovoc Delo*, 1937, 13 (5), 33; *Chem. Abs.*, 1938, 32, 1951. *Am. Ink Maker*, 1938, 16 (6), 87.

[216] N. Tzonev and V. Yavnel, *Masloboino Zhirovoc Delo*, 1930, No. 62 and 63, 19; *Chem. Abs.*, 1932, 26, 325.

[217] L. L. Carrick and H. K. Nielsen, *Am. Paint J.*, 1938, 22, 12, 14, 43; *Chem. Abs.*, 1938, 32, 8169.

[218] J. S. Remington, *Paint Manuf.*, 1936, 6, 50; *Chem. Abs.*, 1936, 30, 2779.

[219] N. Belyaev, *Masloboino Zhirovoc Delo*, 1930, No. 2, 16; *Chem. Abs.*, 1930, 24, 3667.

[220] J. Tsukervanik, *Univ. Asiac Med. Acta*, 1928, Ser. 6, No. 2, 6; *Chem. Abs.*, 1929, 23, 4585.

[221] M. Brambilla and G. Balbi, *Chimica e industria*, 1938, 20, 591; *Brit. Chem. Abs.* B, 1939, 76. *Chimica e industria*, 1937, 19, 10; *Brit. Chem. Abs.* B, 1937, 257; *Chem. Abs.*, 1937, 31, 3305. *Chimica e industria*, 1936, 18, 353; *Brit. Chem. Abs.* B, 1936, 892.

Table 13.—Properties of Safflower Oil.[222]

Density (sp. gr. at 15° C.)	0.9210		
Refractive index with butyrorefractometer (Zeiss)[223]	77.0	to	75.0
Saponification number	189.53	to	192.77
Iodine number (Hübl)	142.40	to	142.69
Refractive index	1.4744		
Saturated acids	5.93 %		
Unsaturated acids	87.72 %		
Iodine number of unsaturated acids	156		

Composition of Oil	Per cent	Composition of Oil	Per Cent
Oleic acid	25.7	Palmitic acid	4.1
Linoleic acid	65.8	Arachidic acid	0.4
Linolenic acid	0.15	Stearic acid	1.6
Myristic acid	0.04	Lignoceric acid	0.06

dioxide. The heated product is said to have good drying properties, but the acid value is high, rising from 8.97 to 27 during cooking.

Uncooked grapeseed oil is said[224] to have inferior drying qualities. Raw oil dries in 114 hours at 21° C. The oxygen number of the oil boiled with water is 14.1 per cent, while oil not treated with water has an oxygen value of 1.4 per cent.

Table 14.—Properties of Grapeseed Oil.[225]

Acid number	4.72
Saponification number	184.4
Ester number	179.68
Iodine number (Hanus)	123.7
OH Number (Normann)	34.82
Density (sp. gr. at 20° C.)	0.9225
Index of refraction (n_D at 20° C)	1.4765

Composition of Oil	Per Cent	Composition of Oil	Per Cent
Oleic acid	31.00	Stearic acid	2.16
Hydroxy acids	11.78	Palmitic acid	6.17
α-Linoleic acid	36.03	Glycerol radical	4.04
β-Linoleic acid	7.71	Unsaponifiable matter	0.59
Linolenic acid	0.14		

Po-Yoak oil, which is obtained from the seed kernels of *Parinarium sherbroense,* is reported[226] to be a drying oil with properties intermediate between tung and oiticica oil. Its characteristics are given in Table 15.

Table 15.—Properties of Po-Yoak Oil.

Melting point	50 to 70° C.
Density (78° C.)	0.9250
Acid number	1.35
Saponification number	192.0
Index of refraction (18° C.)	1.5209
Index of refraction (48° C.)	1.5110
Index of refraction (70° C.)	1.5018
Iodine number	207 to 208

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[222] G. S. Jamieson and S. I. Gertler, *Oil and Fat Ind.*, 1929, 6 (4), 11; *Chem. Abs.*, 1929, 23, 3363.

[223] N. Belyaev, *Masloboino Zhirovoe Delo,* 1930, No. 2, 16; *Chem. Abs.*, 1930, 24, 3667. For discussion of the Zeiss Butyrorefractometer see: C. R. A. Wright and C. A. Mitchell, "Oils, Fats and Waxes," Charles Griffin Co., London, 1903.

[224] N. Kozin, *Oil and Fat Industry* (Russia), 1928, No. 8, 24; *Chem. Abs.*, 1929, 23, 2587.

[225] C. Otin and M. Dima, *Allgem. Oel u. Fett-Ztg.*, 1934, 31, 107; *Chem. Abs.*, 1934, 28, 6006.

[226] A. Steger and J. van Loon, *Rec. trav. Chim.*, 1938, 57, 620; *Chem. Abs.*, 1938, 32, 6894.

Analysis of the ozonized products of the drying oil are interpreted as indicating the presence of α- and β-eleostearic and α- and β-coupeic acids. The oil is solid at ordinary temperatures.

Cashew nut oil is said to be employed in inks.[227] The properties of this oil are indicated in Table 16. The oil is advocated [229] as a possible substitute for tung oil.

Table 16.—Properties of Cashew Nut Oil.[228]

Iodine number (Hübl)	82.1
Refractive index (40° C.)	1.4609
Saponification number	353
Volatile acids (insoluble)	0.6
Volatile acids (soluble)	3.6

A comparative study of perilla, hempseed, lumbang, sardine, menhaden, poppyseed, rapeseed, soya, walnut, safflower and sunflower-seed oils as substitutes for tung oil indicates [230] that perilla is superior to any of the other oils mentioned above, either raw or kettled. Hempseed and walnut oils are nearly as good as perilla oil. Raw soybean and lumbang oils are satisfactory. Rapeseed oil is valueless as a drying oil, since it apparently never dries.

Stillingia seeds have been used to furnish an oil with drying properties.[231] Properties of oil expressed from seeds obtained in the United States and of a sample imported from China are listed in Table 17.

Table 17.—Properties of Stillingia Oil.

	United States Oil	Chinese Oil
Iodine number	176.1	169.0
Saponification number	211.7	206.2
Thiocyanogen number	102.7	100.7
Oleic acid (%)	7.7	10.4
Linoleic acid (%)	56.3	49.9
Linolenic acid (%)	24.6	25.4
Palmitic acid (%)	4.42	5.89
Stearic acid (%)	1.43	2.64
Arachidic acid (%)	0.34	0.14

SPECIAL TREATMENT OF NATURAL OILS

One of the problems of modern printing ink chemistry (see also Chapter 17) is how to increase the drying speed of the ink. Since the presence of double bonds in the acid radicals in the oil and their position relative to each other are to a great extent responsible for the drying

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[227] W. J. Jenkins, *Imperial Institute Bull.*, 1938, 36 (1), 44; *Rev. Paint, Colour, Varnish*, 1938, 11, 181.

[228] L. Gobert, *Annales des Falsifications et des Fraudes*, 1931, 24, 260; *Chem. Abs.*, 1931, 25, 5052.

[229] H. A. Gardner, *Amer. Paint J.*, 1937, 22 (convention daily), 7; *Oil, Paint, Drug Reporter*, 1937, 132 (19), 47; *Chem. Abs.*, 1938, 32, 811.

[230] *Paint, Oil and Chem. Rev.*, 1935. 97 (24), 12, 14, 16; *Chem. Abs.*, 1936, 30, 4699.

[231] G. S. Jamieson and R. S. McKinney, *Oil & Soap*, 1938, 15, 295; *Chem. Abs.*, 1939, 33, 889.

speed, investigations have been made to attain more double bonds or to effect a rearrangement of their position in the oil molecules. Besides the dehydration of castor oil, as reported above, preparation of drying oils from non-drying oils by action of dehydrogenating metallic catalysts, as nickel or a combination of it with mercury, is described.[232] Catalytic action (at temperatures over 200° C.) of metals, metallic oxides, metallic halides, halogen or inorganic acids on linseed oil, fish oil and others is said to transform them into substances resembling tung oil.[233] Attaching hydroxyl groups to double bonds is reported to have the same effect, the method of preparation being similar; chlorine, hydrochloric acid and permanganate are recommended as catalysts.[234] Treatment with hydrogen sulphide while heating and air-blowing is said to yield a linseed oil substitute.[235] Fish oil fatty acids have been fractionated by distillation and those with high iodine values re-esterified with glycerol.[236] In this way highly unsaturated and therefore readily drying oils are obtained.

It is an established fact, however, that the drying effect rests not only with the double bonds and their position, but that an esterification of the fatty acids with a polyhydric alcohol is necessary for good drying action. Free fatty acids or their esters of monohydric alcohols do not dry to a solid film. Dihydric alcohol esters, such as those of ethylene glycol, show slow drying effects. Real drying is secured with esters of glycerol and can be increased by using higher valent alcohols. Higher alcohols added to the drying oil during the bodying operation partly esterify free fatty acids.[237] Divalent alcohols are also mentioned in this connection.[238]

Combinations of fatty acids with dextrose, mannitol and other polyhydric alcohols have been investigated.[239] Bodying of an ester of quebrachitol (an alcohol of the terpene series) and fatty acids is reported to give a satisfactory vehicle.[240] Although nature provides us with mixed glycerides, *e.g.*, palmito-oleo-linolenic glycerate, nevertheless the formation of uniform triglycerides represents a trend in printing ink research. For the latter purpose it has been suggested to esterify dehydrated ricinoleic acid[241] (see above) or non-frosting compositions consisting of fatty acids from tung oil admixed with those from linseed oil.[242] How-

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[232] T. and N. Yavnel, *Maslob. Jirov Delo*, 1930, 9-10, 19; *Chim. Ind.*, 1932, 27, 146.

[233] J. Scheiber, British P. 338,932, 1929; *Pat. J.*, 1931, 6163; *Chem. Abs.*, 1931, 25, 2580; *Brit. Chem. Abs.* B, 1931, 307. British P. 316,872, 1928; *Chem. Abs.*, 1930, 24, 2315.

[234] J. Scheiber, German P. 520,955, 1928; *Oil. Col. Trades J.*, 1931, 80 (1708), 103; *Chem. Abs.*, 1931, 25, 3502.

[235] K. Hashimoto, Japanese P. 100,422, to Hakodate Seiyu K. K., 1933; *Chem. Abs.*, 1934, 28, 2553.

[236] A. Hill and E. E. Walker, British P. 477,207, 1937, to Metallges, A.-G.

[237] H. Wolf, F. Drexler and H. Beller, German P. 649,108, 1937, to I. G. Farbenind. A.-G.; *Seifen-Ztg.*, 1937, 64, 796; *Chem. Abs.*, 1937, 31, 8964.

[238] Canadian P. 351,671, 1935, to Canadian Industries; *Chim. et Ind.*, 1936, 36 (5), 984.

[239] A. Rheineck, B. Rabin and J. S. Long, U. S. P. 2,077,371, April 13, 1937, to Devoe & Reynolds Co.; *Chem. Abs.*, 1937, 31, 4144. See also L. Rosenthal and W. Lenhard, U. S. P. 1,739,863, Dec. 17, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 980.

[240] British P. 406,738, 1934, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1934, 28, 4922; *Brit. Chem. Abs.* B, 1934, 738.

[241] J. Scheiber, German P. 522,486, 1928; *Chem. Abs.*, 1931, 25, 3184.

[242] C. G. Gauerke, U. S. P. 1,979,260, Nov. 6, 1934, to E. I. duPont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 366; *Brit. Chem. Abs.* B, 1935, 959; *Rev. Paint, Colour, Varnish*, 1935, 8, 18.

ever, an effect similar to the latter is accomplished through ester interchange when these two oils are bodied together. Esterification of polyvalent alcohols, such as sugars, with highly unsaturated fatty acids (aside from color) leads to materials which polymerize too fast for practical purposes, and the same is true for linolenic acid triglyceride.

It is reported[243] that a drying oil may be prepared from cottonseed oil. The raw oil is oxidized by air at 120° C. in the presence of lead and calcium oxides, and pyrolusite.[244] An oil is produced in this manner with an acetyl number of 85. The oil secured by oxidation is dehydrated at 275 to 280° C., in the presence of aluminum oxide and zinc. The final product has an acetyl number of 11.

Drying oils are said to polymerize rapidly by heating them in an atmosphere of sulphur dioxide.[245] It is stated that if a sufficiently large surface is employed or a high concentration of sulphur dioxide is used (*e.g.*, under pressure), the rate of bodying is greater than if hydrogen sulphide, nitrogen, hydrogen, or carbon dioxide is employed under the same conditions. The gas is passed through the oil for 5 hours at a temperature of 290 to 300° C.

Linseed oil and tung oil are modified by treatment with polyhydric-polybasic resins (*e.g.*, glycerol-phthalic resin) for use in printing inks applied to cellulose ester coatings (*i.e.*, book-binding fabrics). An illustrative example of one such vehicle is prepared by heating a mixture of 17.3 parts of glycerol, 55.5 parts of linseed oil acids, and 27.2 parts of phthalic anhydride at 200-225° C. Heating is maintained until an acid number of less than 10 is obtained.[246] Inks prepared from this vehicle are reported to dry tack-free in 12 to 16 hours.

Accelerated production of stand oils by heat polymerization of drying oils may be accomplished by employment of a colloidal solution of heavy metals in an oil-miscible medium.[247] Cobalt, iron, manganese, lead, nickel, chromium, molybdenum or tungsten is dispersed electrically into butyl alcohol, propyl alcohol or turpentine. Approximately 0.01 to 0.05 per cent of the metal in colloidal solution is added to drying oils to be bodied. Electrical heating of the drying oils may be employed.[248]

Hydrogenated cottonseed oil may be employed in a drying oil.[249] The cottonseed oil may also be admixed with a hydrogenated asphaltic oil.[250]

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[243] A. A. Ivanova, *J. Applied Chem.* (*U.S.S.R.*), 1938, 11, 564; *Chem. Abs.*, 1938, 32, 6081.

[244] Pyrolusite is a form of manganese dioxide.

[245] H. I. Waterman and C. Van Vlodrop, British P. 480,677, 1938, to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1938, 1188; *Chem. Abs.*, 1938, 32, 6083; French P. 824,650, 1938; *Chem. Abs.*, 1938, 32, 7294.

[246] D. McBurney and E. H. Nollau, U. S. P. 2,049,507, Aug. 4, 1936, to E. I. duPont de Nemours & Co.; *Chem. Abs.*, 1936, 30, 6586.

[247] W. Krumbhaar, British P. 444,440, 1936, to Beck, Koller and Co.; *Brit. Chem. Abs.* **B**, 1936, 701; *Chem. Abs.*, 1936, 30, 6592.

[248] R. A. Carleton, U. S. P. 1,998,073, April 16, 1935, to National Electric Heating Co.; *Brit. Chem. Abs.* **B**, 1936, 379. I. T. Osnos, Russian P. 48,948, 1929; *Chem. Abs.*, 1931, 25, 1109.

[249] W. N. Blakeman, U. S. P. 1,375,352, April 19, 1921; *Chem. Abs.*, 1921, 15, 2732. U. S. P. 1,375,353, April 19, 1921, and U. S. P. 1,375,354, April 19, 1921; *Chem. Abs.*, 1921, 15, 2733. Carleton Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Company, New York, 1930.

[250] W. N. Blakeman, U. S. P. 1,385,033, July 19, 1921; *Chem. Abs.*, 1921, 15, 3757. U. S. P. 1,385,036, July 19, 1921; *J. S. C. I.*, 1921, 40, 667A.

PETROLEUM DERIVATIVES

Production of printing ink vehicles from petroleum derivatives has been tried successfully.[251] Addition of bitumen to special types of inks,[252] mostly black, is an old custom and provides certain desirable properties, *e.g.*, good adhesion. Newspaper inks have as a vehicle mineral oil, generally blended with rosins. Light mineral oil or wax which is mixed with hard resins sometimes serves as a substitute for boiled linseed oil.[253] Drying oils cannot be used for newspapers[254] because the inks must dry very rapidly by absorption, which is made possible by use of special paper. Naphthenic acids, esterified[255] or as calcium or other soaps,[256] are also said to give good varnishes. Hydrocarbons extracted from crude petroleum by means of selective solvents[257] furnish materials useful as printing-ink vehicles. A similar product is commercially available as "Firnagral."[258] Drying oils are obtained from the liquid products of the petroleum cracking process by polymerization with the catalytic aid of aluminum chloride[259] or various inorganic halides, *i.e.*, one of the Friedel-Crafts type[260] or boron fluoride.[261] Other synthetic drying oils are derived from gaseous petroleum hydrocarbons condensed with phosgene and polymerized with aluminum chloride,[262] iron or metallic oxides.[263] Acid tar residues from sulphuric acid refining of petroleum yield printing-ink vehicles after washing, neutralizing[264] and treatment with sodium plumbite.[265] Heavy distillates which have been recovered from treatment of cracked distillates with a solid absorbent are redistilled while being blown with air. The condensate is reported to be

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[251] M. Ogura, *Gov't. Printing Bur. Tokyo, Research Bull.*, 1937, No. 3, 1; *Chem. Abs.*, 1938, 32, 3988; *Rev. Paint, Colour, Varnish*, 1938, 11, 280.

[252] J. H. Abbott, French P. 728,439, 1931; *Chem. Abs.*, 1932, 26, 5777.

[253] T. P. Sanguinetti, French P. 803,031, 1936; *Chem. Abs.*, 1937, 31, 2842.

[254] W. Fahrion, *Chem. Umschau*, 1920, 27, 38, 122; *Chem. Abs.*, 1920, 14, 2556, 2993.

[255] A. Y. Drinberg, Russian P. 44,253, 1935; *Chem. Zentr.*, 1936, 107 (1), 4218; *Nat. Paint, Varnish Assoc.*, 1936, Circ. 501, 1; *Brit. Chem. Abs.* B, 1936, 648.

[256] M. M. Gurvich, Russian P. 28,415, 1929; *Chim. Ind.*, 1933, 29, 658. Russian P. 26,393, 1928; *Chem. Abs.*, 1932, 26, 6164. V. Ivanov, Russian P. 43,700, 1936; *Farbe u. Lack*, 1936, No. 53, 630; *Rev. Paint, Colour, Varnish*, 1937, 10, 33.

[257] A. H. Batchelder, U. S. P. 2,087,395, July 20, 1937, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1937, 31, 6490.

[258] H. Späth, *Farben-Ztg.*, 1936, 41, 1143; *Chem. Abs.*, 1937, 31, 3249; *Rev. Paint, Colour, Varnish*, 1936, 9, 367.

[259] L. Potolovsky, A. Atalian and V. Buinitskaya, *Azer. Neft. Khoz.*, 1934, 10, 91; *Chim. Ind.*, 1935, 33, 1442; *Chem. Abs.*, 1935, 29, 6080; *Brit. Chem. Abs.* B, 1936, 648. French P. 791,739, 1935, to Bataafsche Petroleum Maatschappij; *Chem. Zentr.*, 1936, 107, (1), 4506; *Chem. Abs.*, 1936, 30, 4344. Dutch P. 38,820, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1937, 31, 3682. British P. 443,679, 1936; *Chem. Abs.*, 1936, 30, 5436; *Brit. Chem. Abs.* B, 1936, 558. M. B. Chittick, U. S. P. 1,891,079, Dec. 13, 1932, to Pure Oil Co.; *Chem. Abs.*, 1933, 27, 2051; *Brit. Chem. Abs.* B, 1933, 755. Carleton Ellis, "Chemistry of Petroleum Derivatives," Chemical Catalog Co., Inc., New York, 1934.

[260] H. Rabe and M. Otto, U. S. P. 2,097,468, Nov. 2, 1937, to I. G. Farbenind. A.-G.; *Nat'l Paint Bull.*, 1937, 1, 14; *Chem. Abs.*, 1938, 32, 348.

[261] L. A. Mikeska and A. H. Gleason, U. S. P. 2,092,889, Sept. 14, 1937, to Standard Oil Development Co.; *N. P. V. L. Abs.*, 1937, 51, 196; *Chem. Abs.*, 1937, 31, 8231.

[262] A. Drinberg, Russian P. 42,647, 1935; *Chem. Ind.*, 1936, 36, 371; *Chem. Abs.*, 1937, 31, 7678.

[263] V. F. Chernishev, Russian P. 47,023, 1936; *Chem. Zentr.*, 1936, 107 (2), 3848.

[264] F. H. Walker and C. E. Sohn, U. S. P. 999,611, Aug. 1, 1911; *Chem. Abs.*, 1911, 5, 3178. B. M. Yaroshewsky, Russian P. 46,315, 1934; *Chem. Zentr.*, 1936, 107 (2), 1256. German P. 617,728, 1935, to N. V. Koninklijke Pharmaceutische Fabr.; *Chem. Abs.*, 1936, 30, 886. L. K. Adalijan, *Neft*, 1933, 4 (20), 9; *Brit. Chem. Abs.* B, 1935, 1030; *Chem. Abs.*, 1935, 29, 2711.

[265] L. K. Adamian, *Neft*, 1936, 7 (7), 32; *Chim. et Ind.*, 1937, 37, 953; *Chem. Abs.*, 1937, 31, 4480.

applicable as a varnish.[266] Distillates of tars obtained in cracking heavy gasoline fractions at 550° C. are converted to drying oils by treatment with sulphuric acid.[267]

Synthetic organic acids can be prepared from petroleum hydrocarbons by air treatment of paraffin oil in the presence of calcium naphthenate. Aluminum salts, and to a minor extent those of cobalt, zinc, lead or barium, of those acids are considered useful for the preparation of synthetic varnishes.[268] Preparation of a synthetic varnish, having a very light color, by fractionating unrefined vapor-phase cracked gasoline is reported by Hyman.[269] A product, similar in properties to linseed oil, is said to formed by heating vapor-phase cracked Mid-Continent naphtha distillate, with air at 7 atmospheres pressure, for 6 hours.[270] Films made with the above product are reported to show cracking after a year's exposure. Treatment of gasoline with gaseous hydrogen chloride in the presence of aluminum chloride and subsequent hydrolysis gives an oil which will dry to a resistant film, particularly if driers have been added.[271]

Drying oils may be manufactured from gas oil (solar oil)[272] distillates. The hydroxy-acids of these distillates are oxidized in air and then washed with hot water. The washed products are converted into drying oil by esterification with glycerol.

Chlorinated hydrocarbons may be dechlorinated in kerosene solution with superheated steam to give unsaturated vehicles.[273] Also, kerosene, lubricating oil, rosin and manganese hydroxide may be boiled together. The liquid produced by this treatment is mixed with cod oil to furnish an ink vehicle.[274] Kerosene containing cycloparaffins is treated with moist chlorine. Subsequently, the chlorinated oil is acidified with acetic acid, and the acid product reacted with metallic zinc. In this manner a drying oil was stated to have been secured.[275]

Mineral oil, from which gasoline and kerosene has been removed, may be converted into a drying oil by ebullition with alcohol.[276] Also, dehydrated vaseline dissolved in benzene is suggested as a vehicle for printing inks.[277]

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[266] A. P. Bjerrogaard, U. S. P. 2,035,455, March 31, 1936, to Gray Processes Corp.; *Chem. Abs.*, 1936, **30**, 3668.

[267] I. F. Bespolov, *Azer. Neft. Khoz.*, 1929, No. 11, 52; *Chem. Abs.*, 1930, **24**, 3105.

[268] A. Y. Drinberg, *So Re Na*, June, 1935; *Olii Minerali*, 1936, **4**, *Peint., Pig. & Vernis*, 1936, **13**, 235.

[269] J. Hyman, U. S. P. 1,919,722 and 1,919,723, July 25, 1933, to Velsicol Corp.; *Chem. Abs.*, 1933, **27**, 4942; *Brit. Chem. Abs.* **B**, 1934, 462.

[270] G. M. Woods, *Petroleum Engr.*, 1936, **8**, 106; *Chem. Abs.*, 1938, **32**, 3592; *Rev. Paint, Colour, Varnish*, 1938, **11**, 270.

[271] S. L. Varshavsky and I. C. Shenfinkel, Russian P. 39,899; *Chem. Zentr.*, 1935, **106** (2), 3016; *Chem. Abs.*, 1936, **30**, 3668.

[272] E. Pyhala, *Erdol u. Teer*, 1928, **4**, 146; *Chem. Abs.*, 1928, **22**, 2049. P. V. Serb-Serbin and A. M. Livshits, *Masloboino Zhirovoe Delo*, 1937, No. 3, 16; *Chem. Abs.*, 1938, **32**, 4361.

[273] H. A. Gardner and E. Bielouss, U. S. P. 1,384,447, July 12, 1921; *Chem. Abs.*, 1921, **15**, 3757; *J. S. C. I.*, 1921, **40**, 667A.

[274] R. C. Bone, U. S. P. 1,347,074, July 20, 1920, to M. A. Esteva; *J. S. C. I.*, 1920, **39**, 605A.

[275] F. C. Thiele, U. S. P. 1,254,866, Jan. 29, 1918; *Chem. Abs.*, 1918, **12**, 769; *J. S. C. I.*, 1918, **37**, 188A.

[276] W. Dyer, U. S. P. 1,256,535, Feb. 19, 1918; *Chem. Abs.*, 1918, **12**, 1002; *J. S. C. I.*, 1918, **37**, 251A. U. S. P. 1,256,536, Feb. 19, 1918; *J. S. C. I.*, 1918, **37**, 251A.

[277] J. Soukup, German P. 321,828, 1918; *Chem. Abs.*, 1921, **15**, 2199.

FISH OILS

Fish oils[278] are considered poor substitutes for linseed oil and should be blended with other oils. Pre-treated fish oils, so-called "winterized" oils, may be bodied to give varnishes.[279] Winterizing consists in storage in a cold place over a long period of time, thereby giving the solid (*i.e.*, mostly saturated) components an opportunity to settle out. These solid parts later are filtered off or decanted, and the percentage of unsaturated acids is thus increased.

Several methods of treating fish oils are recommended.[280] Drying oils may be made from fish oils by replacing fatty acid radicals having slight drying power with fatty acids having greater drying capacity, and by introduction of conjugated double bonds through the medium of halogenation and subsequent dehalogenation. When fish oils are intended for utilization in printing inks,[281] oil may be refined by admixing 3.8 kilograms of fish oil with an aqueous solution containing 90 to 150 grams of sodium bicarbonate and 30 to 90 grams of alum. The whole then is heated at 100 °C. with constant stirring, till most of the water is evaporated. Stearin which precipitates is removed from the liquid vehicle.

Japanese pale sardine oil (iodine value 173 to 174) is said to be polymerized by heating at 290-300° C. in an evacuated vessel (2 to 5 mm. mercury pressure) until a viscosity of 75 to 80 poises (at 20° C.) and an iodine value of 103 is attained. The polymerized product is distilled under a pressure of 1 dyne per square centimeter pressure (.00075 mm. of mercury). The distillation surfaces are of molecular still type (*i.e.*, one in which the distance of separation is less than that of the mean free path of the molecules). The still residue is a brown oil with a viscosity of 385 poises (at 20° C.) and an iodine value of 103 to 104. Films secured with this oil were stated to be clear and fairly hard, and to have a good gloss.[282] Herring and Canadian pilchard oils may be treated similarly.[283]

Drying oils may be obtained by high-pressure hydrolysis of fish oils into high and low iodine value acids.[284] These acids are separated by distillation and the high iodine value acids are esterified with glycerol. Zinc powder and magnesium oxide catalysts may be employed in a similar process.[285] Splitting, when using catalysts, takes place in two hours under pressure of 80 to 92 pounds per square inch.

[278] K. Würth, *Z. Verein Deutscher Ingenieure*, 1935, 1011; *Farben-Ztg.*, 1936, 41 (8), 185.

[279] *Am. Ink Maker*, 1938, 16 (2), 39.

[280] K. Buser, *Farben-Ztg.*, 1938, 43, 803; *Chem. Abs.*, 1938, 32, 8169.

[281] *Farben-Chem.*, 1938, No. 4, 144; *Rev. Paint, Colour, Varnish*, 1938, 11, 179.

[282] E. W. Fawcett and E. E. Walker, U. S. P. 2,128,354, Aug. 30, 1938, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1938, 32, 8808. British P. 442,000, 1936; *Brit. Chem. Abs.* B, 1936, 335. W. Meyer, *Farbe u. Lack*, 1938, 245; *Chem. Abs.*, 1938, 32, 8159. German P. 658,844, 1938, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1938, 32, 6485.

[283] R. Priester, *Verfkroniek*, 1938, 11 (4), 70; *Rev. Paint, Colour, Varnish*, 1938, 11, 184.

[284] British P. 477,207, 1937, to Metallgesellschaft A.-G.; *Chem. Abs.*, 1938, 32, 4364; *Rev. Paint, Colour, Varnish*, 1938, 11, 101.

[285] S. Veno and G. Inagaki, *J. Soc. Chem. Ind., Japan*, 1936, 39, 107B; *Brit. Chem. Abs.* B, 1936, 700; *Chem. Abs.*, 1936, 30, 5437.

Oil of *Sardinella melanostida* may be heated with 20 per cent by weight of rosin at 550 to 570° C. for 4 to 5 hours. The product is dissolved in turpentine.[286] Distillation of raw fish oil yields approximately 70 per cent of polymerized unsaturated acid known as "fish oil-stand oil."[287] The latter material is reported to have properties similar to linseed oil. Some fish oils are said to be converted into drying oils by percolation (in the absence of air and at a temperature of 70 to 100° C.) through a tower packed with granulated iron.[288]

MISCELLANEOUS VEHICLES

Indene-coumarone solvent oils are advocated[289] as possible ink vehicles. Shellac-drying oil varnishes are finding application as vehicles.[290] These oils are prepared by heating shellac, drying oil fatty acids and glycerol at 120 to 140° C. in the presence of aromatic sulphonic acids or aluminum sulphate.

A heat-convertible varnish may be manufactured from a phenol-aldehyde resin, rosin-glycerol ester, linseed oil, cobalt naphthenate driers and chlorinated biphenyl.[291] Such vehicles have been advocated for "cold color" printing. In this process the printing surface is heat-treated after application of the ink.

A non-frosting drying oil with an acid number of 25 is suggested[292] as an ink vehicle. The oil is produced by heating a mixture of equimolar quantities of linseed oil acids and abietyl alcohol in an open vessel at 225° C. for 1.5 hours.

A suggested substitute for linseed oil stand oil is a blend of 21 per cent linseed oil, 16 per cent alkyd resin (containing 75 per cent oil), 12 per cent ester gum, 1 per cent drier and 50 per cent white spirit.[293] The varnish is reported to resemble linseed stand oil in properties.[294]

Printing ink vehicles may be prepared by destructive distillation of old rubber tires with or without subsequent steam distillation.[295] Isoprene and dimethylbutadiene, although polymerizing readily, are consid-

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[286] Y. V. Branke and T. S. Schavski; *Lakokras. Ind.*, 1935, No. 2, 19; *Brit. Chem. Abs.* B, 1936, 846.

[287] G. Kaempfe, *Farben-Ztg.*, 1935, 40, 1009; *Brit. Chem. Abs.* B, 1935, 1054.

[288] W. A. Allsebrook, British P. 122,015, 1918, to O. Wilkins and Co.; *Chem. Abs.*, 1919, 13, 1399.

[289] W. E. Sheehan, H. E. Kelly and W. H. Carmody, *Ind. Eng. Chem.*, 1937, 29, 576; *Rev. Paint, Colour, Varnish*, 1937, 10, 272; *Brit. Chem. Abs.* B, 1937, 866; *Chem. Abs.*, 1937, 31, 4412. W. J. McElroy and J. Clarke, U. S. P. 1,471,746, Oct. 23, 1924; *Chem. Abs.*, 1924, 18, 175.

[290] R. Bhattacharya and B. S. Gidvani, *London Shellac Research Bur.*, *Tech. Paper*, 1938, No. 14; *Chem. Abs.*, 1938, 32, 8171; *Brit. Chem. Abs.* B, 1938, 1192, 1072. *Paint Tech.*, 1938, 3, 189; *Brit. Chem. Abs.* B, 1938, 942.

[291] F. G. Oswald, U. S. P. 2,111,802, Mar. 22, 1938, to John W. Masury and Son; *Chem. Abs.*, 1938, 32, 3992; *Rev. Paint, Colour, Varnish*, 1938, 11, 281.

[292] H. S. Rothrock, Canadian P. 376,207, 1938, to Canadian Industries Ltd.; *Chem. Abs.*, 1938, 32, 8628.

[293] White spirit is a petroleum ether.

[294] *Farben-Ztg.*, 1937, 42 (21), 512; (23), 563; *Rev. Paint, Colour, Varnish*, 1937, 10, 255. E. Rossmann, *Angew. Chem.*, 1937, 50 (5), 113; *Rev. Paint, Colour, Varnish*, 1937, 10, 93.

[295] C. F. P. Millar, British P. 444,683, 1935; *Brit. Chem. Abs.* B, 1936, 608; *Chem. Abs.*, 1936, 30, 6586. French P. 810,299, 1937; *Chem. Abs.*, 1937, 31, 8964. U. S. P. 2,125,683, Aug. 2, 1938; *Chem. Abs.*, 1938, 32, 7754.

ered too volatile to give satisfactory varnishes.[296] However, polymerization of 4-chloro-1,2-butadiene has been stated to yield a drying oil.[297] To prevent excessive polymerization, hydroquinone is added to the chlorobutadiene before reaction. The quinone is said to act as a retarding agent, so that polymerization can be controlled.

Polymers of divinylacetylene,[298] which is made from acetylene,[299] may be employed as printing ink vehicles. The polymers also can be subjected successively to hydrogenation and further polymerization, and the resulting products used as a quick-drying oil.[300] In the latter instance formation of substances insoluble in many types of solvents is prevented by the presence of a small quantity of iodine.[301]

A lacquer for printing may be made by heating under reflux a mixture of 100 parts of phenol, 50 parts of rosin, and 150 parts of tung oil. After ten hours 100 parts of aqueous 40 per cent formaldehyde and 3 parts of aqueous alkali are admixed with the product formed by the boiling described above. The whole is refluxed for 4 to 8 hours further and then is heated at 150° C. until a clear non-tacky tough solid is produced. The solid product is dissolved in 300 parts of turpentine.[302]

Synthetic drying oils are reported [303] to be formed by heating together glycerol, isophthalic acid and linseed oil.

One suggested printing-ink vehicle [304] comprises 10 parts glycerol-phthalate resin, 2 parts butyl alcohol, 12 parts ethyl acetate, 8 parts cyclohexanone, 2 parts linseed oil, 6 parts acetone and 5 parts tricresylic phosphate. Vehicles containing alkyd resins such as the glycerol-phthalate plastic material, have been recommended for utilization in preparing high-gloss inks.[305]

Cellulose ester and rubber solutions are mixed and employed as ink vehicles.[306]

"Grisee oil" is reported [307] to have drying properties. It is heated

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[296] W. Fabrion, *Chem. Umschau*, 1920, 27, 88, 122; *Chem. Abs.*, 1920, 14, 2556, 2993.

[297] O. Nicodemus, H. Lange and O. Horn, German P. 664,458, 1938, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1939, 33, 886.

[298] Canadian P. 366 160, 1937, to E. I. duPont de Nemours & Co.; *Chem. Abs.*, 1937, 31, 5067. A. M. Collins, U. S. P. 1,812,849, June 30, 1931; *Brit. Chem. Abs.* B, 1932, 435; *Chem. Abs.*, 1931, 25, 5048. U. S. P. 1,869,668, Aug. 2, 1932; *Chem. Abs.*, 1932, 26, 5439; *Brit. Chem. Abs.* B, 1933, 556. Both patents to E. I. duPont de Nemours & Co.

[299] See Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935, and "The Chemistry of Petroleum Derivatives," Reinhold Publishing Corp., New York, 1937.

[300] *Journal d'Acetylene*, 1933, 205; *Peintures, pigments, vernis*, 1934, 11, 110.

[301] J. H. Werntz, U. S. P. 2,055,597, Sept. 29, 1936; *N. P. V. L. Abs.*, 1936, 46, 280; *Chem. Abs.*, 1936, 30, 7730.

[302] V. H. Turkington, British P. 324,025, 1927, to Bakelite Corp.; *Chem. Abs.*, 1930, 24, 3387; *Brit. Chem. Abs.* B, 1930, 338. U. S. P. 1,988,615, Jan. 22, 1935; *Brit. Chem. Abs.* B, 1936, 109.

[303] F. Frick, A. Kinsky and E. Pansegrau, German P. 641,269, 1937; *Chem. Abs.*, 1937, 31, 3311; *Rev. Paint, Colour, Varnish*, 1937, 10, 198.

[304] J. H. Frydlender, *Rev. Prod. Chim.*, 1928, 31, 241, 281; *Rev. Paint, Colour, Varnish*, 1928, 1, 84.

[305] R. C. Chandler, *Am. Ink Maker*, 1937, 15 (9), 39; *Rev. Paint, Colour, Varnish*, 1938, 11, 24.

[306] P. Allman, H. N. Morris and L. H. Marlor, British P. 274,968, 1926; *Chem. Abs.*, 1928, 22, 2292; *Brit. Chem. Abs.* B, 1927, 789; *Rev. Paint, Colour, Varnish*, 1931, 4, 51.

[307] A. Stoop, British P. 23,071, 1898; *J. S. C. I.*, 1899, 18, 379. "Grisee oil" is said to be a natural drying oil found at Grisee in Java.

with sodium chloride to remove water. The dehydrated product is purified by distillation.

Synthetic drying oils may be manufactured by five general methods.[308]

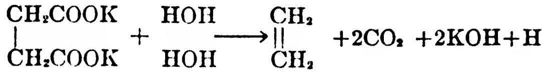
(1) Dehydrogenation as shown in the equation:

$$C_2H_6 \longrightarrow CH_2 = CH_2 + H_2$$

(2) Elimination of water:

$$2CH_3CHO \longrightarrow CH_3CHOHCH_2CHO \longrightarrow CH_3CH = CHCHO + H_2O$$

(3) Electrolysis of dibasic acids:



$$\begin{array}{l}CH_2COOK\\ |\\ CH_2COOK\end{array} + \begin{array}{c}HOH\\ \\ HOH\end{array} \longrightarrow \begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + 2CO_2 + 2KOH + H_2$$

(4) Partial cleavage of high molecular compounds as in gasoline cracking.

(5) Cleavage of halogen compounds into hydrogen halogens is shown below:

$$-CHCl-CH_2- \longrightarrow -CH{=}CH- + HCl$$

Coal-tar fractions, boiling from 150 to 250° C. may be converted to drying oils by treatment with sodium hydroxide and formaldehyde.[309]

Rosin-maleic acid is said to form a satisfactory printing vehicle, if it is dissolved in dilute aqueous ammonia.[310] The solution should contain 40 per cent of the acid, and some castor oil as a plasticizer.

"Filax oil" is reported[310a] to be a satisfactory substitute for linseed stand oil. The vehicle is said to be a mixture of aromatic hydrocarbons and esters with long side-chains. The acid and alcoholic radicals in the esters are both unsaturated. The properties of the oil are indicated in Table 17A. Filax oil is usually mixed with other drying oils.

Table 17A.—Properties of "Filax Oil."

Density (sp. gr.)	0.95
Pour point	Below 10° C.
Stand oil viscosity (20° C.)	3000 centipoises
Viscosity (20° C.)	900 to 1800 centipoises
Flash point	184° C.
Saponification number	40 to 50
Iodine number	180
Acid number	30

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[308] I. Mellan, *National Paint Bulletin*, 1937, 1 (12), 12; (13), 12; 1938, 2 (1), 14: *Rev. Paint Colour, Varnish*, 1938, 11, 183.

[309] J. J. Kessler, U. S. P. 1,616,321, Feb. 1, 1927; *Chem. Abs.*, 1927, 21, 1003.

[310] Carleton Ellis, U. S. P. 2,063,541, Dec. 8, 1936, to Ellis-Foster Company; *Chem. Abs.*, 1937, 31, 894.

[310a] H. Pfanner, *Nitrocellulose*, 1938, 9, 159; *Chem. Abs.*, 1939, 33, 414. *Farben-Chem.*, 1937, 8, 394; *Chem. Abs.*, 1938, 32, 3642. *Farben-Chem.*, 1936, 7, 209; *Chem. Abs.*, 1936, 30, 8657.

STAND OIL KETTLES

The general requirements for the materials of construction of stand oil (heat-treated oil) kettles are:

1. The metal should permit pale resins to be processed without undesirable discoloration, and oil bodies in contact with the metal should remain very light in color.
2. Compounds used as driers should not affect the metal nor should contact with the metal influence the drying characteristics of the varnish.
3. The kettle should be physically strong, even at elevated temperatures, yet easily fabricated.
4. The cost of the kettle, initial plus maintenance charges, should be economical.[311]

Copper was the first metal employed in kettles for bodying (heat-treating) oils. However, some discoloration of the varnish resulted from cuprous salts and Monel metal later replaced copper. Many modern kettles are now made of nickel-coated steel. Nickel is used because it does not influence the drying properties nor color of varnishes.[312]

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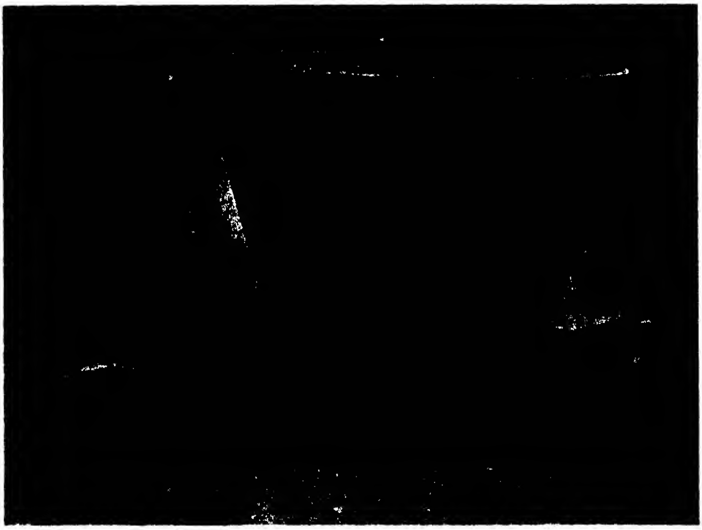
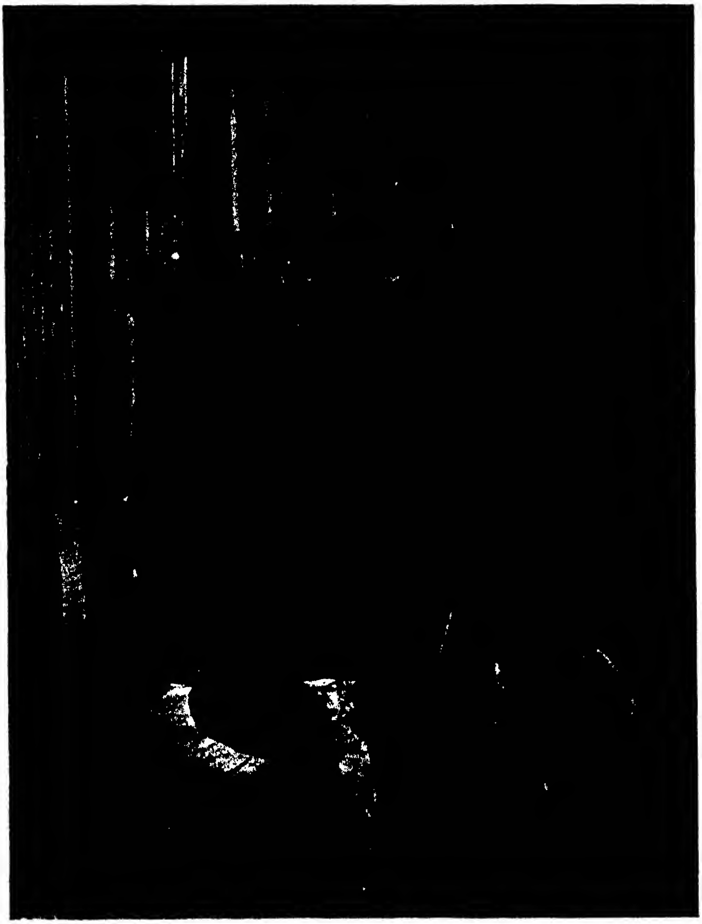
[311] International Nickel Co. Bulletin C-7.

[312] International Nickel Co., *loc. cit.*



Courtesy The International Nickel Company, Inc.

FIGURE 19. Monel Metal Varnish Kettle on Special Type of Truck. Projecting Skirt of Metal Welded to Inside of Truck Ring Prevents Overheating of the Truck Frame by Confining Heat.



Courtesy The International Nickel Company, Inc.

FIGURE 20. Portable Copper Varnish Kettle with Brazed Monel Bottom, Heated by Gas. The Monel Bottom Increases the Useful Life of the Kettle.

For smaller quantities of stand oils portable kettles made of Monel metal are employed. Such a portable kettle is shown in Figure 19. These units are heated over gas or oil-burning radiant heaters with ceramic domes. Figure 20 shows a kettle in place over a heater, and Figure 21 illustrates a battery of such kettles in operation.

Fixed kettles of nickel-coated steel are employed for large quantities of oil. Figure 22 diagrammatically illustrates the construction of the heating unit with the kettle in place. Figure 23 is a photograph of a single fixed kettle and Figure 24 shows a battery of units in operation.

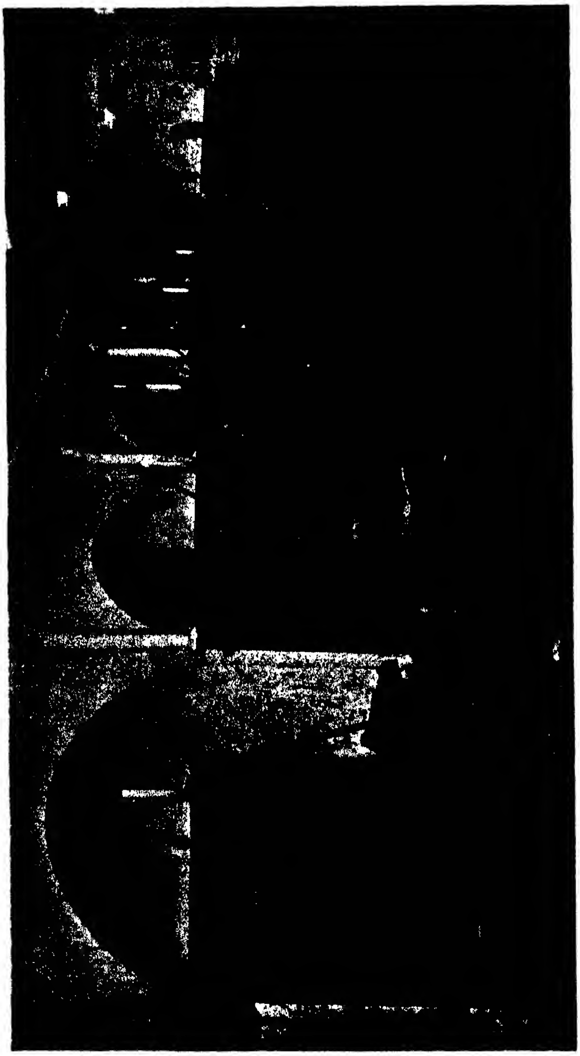
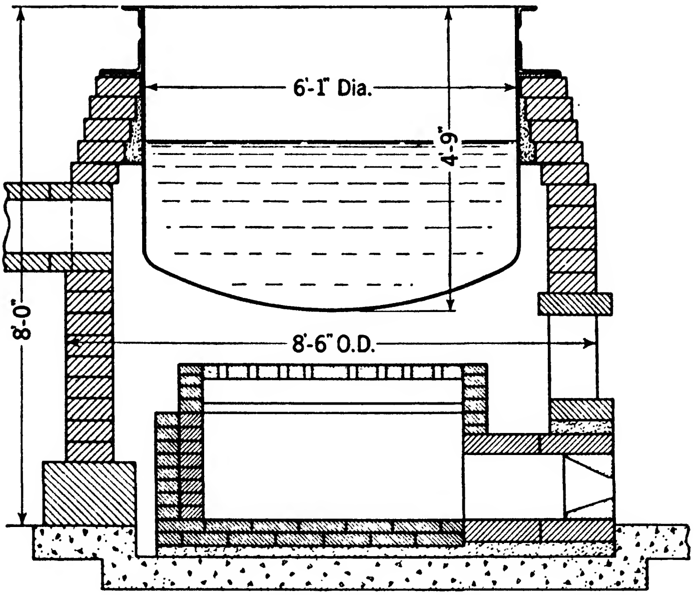


FIGURE 21.

Portable Monel Kettles in Service Cooking Light-colored Lithographic Oils for more than Thirteen Years.

Courtesy The International Nickel Company, Inc.



Courtesy The International Nickel Company, Inc.

FIGURE 22. Section Showing General Construction of a Large Set Kettle and Heater.

Stand oil kettles used in modern practice are reported[313] to possess the following features: absence of condensing surfaces, overflow systems, exclusion of air, and distribution of carbon dioxide and oil by the use of a central cylinder. Figure 25 illustrates the use of carbon dioxide in such a kettle. Figure 26 shows a three hundred gallon high temperature unit fabricated from nickel-clad steel. The latter machine is employed in bodying oils for ink manufacture. Lithographic varnish must be treated carefully during heating in order that the oil may have sufficient fluidity on the press,[314] and hence carbon dioxide, indirect heating, agitation and exclusion of air are employed. Figure 27 illustrates an electrically-heated kettle said to be employed to provide indirect heating in bodying varnish oils.[315]

A careful study of the best type of kettle for bodying linseed oil indicates that such a vessel should have a heated surface which is always proportional to the volume of oil to be heated and also should have a constant ratio of oil volume to the area of oil exposed to the air.[316] Such a kettle has been designed according to mathematical calculations, and

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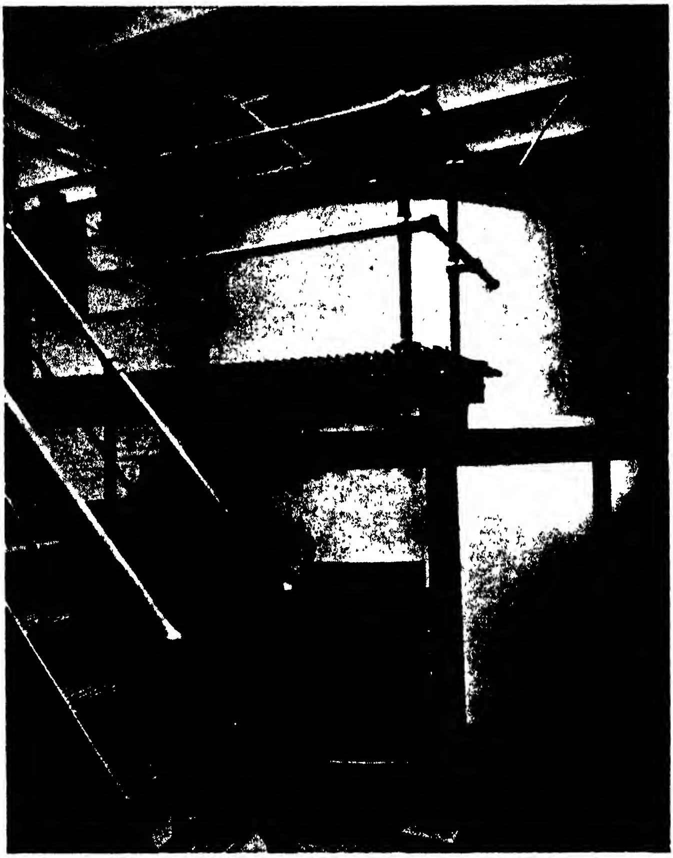
[313] E. Willmeroth, *Farben-Ztg.*, 1936, 41, 278; *Brit. Chem. Abs.* B, 1936, 461.

[314] International Nickel Company, N. Y. Bulletin C-7.

[315] A. P. Gloeckler, *Chemical Age.*, 1921, 29, 381; *Chem. Abs.*, 1921, 15, 3909. Sowers Manufacturing Co., Catalog No. 8.

[316] J. S. Long, J. B. Reynolds and J. Napravnik, *Ind. Eng. Chem.*, 1934, 26, 864; *Chem. Abs.*, 1934, 28, 5688.



Courtesy The International Nickel Company, Inc.

Figure 23. Monel Set Kettle, Equipped with External Ribbon Heating Elements for Electric Heating. Capacity 2400 Gallons.

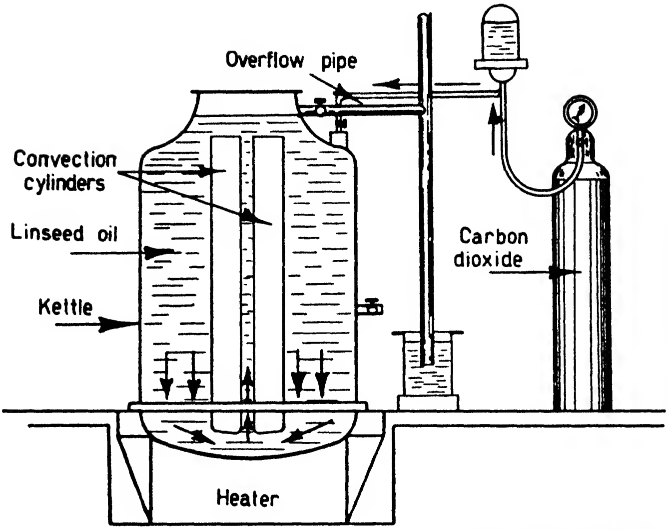
the oil-heating surface shown in Figure 28 demonstrates the application of the surfaces of revolution found. The rate of change of the specific heat of samples of linseed oil with temperature has been indicated (Figure 29). It is recommended that lower temperatures, agitation and indirect heat be used in varnish kettles. Diphenyl or petroleum oils at elevated temperatures may be circulated in jackets surrounding the kettle in order to provide indirect heating. Lower temperatures, on kettle surfaces, serve to prevent skinning, livering and settling. Agitation permits lower temperatures to be employed since bodying is a result of molecular association.

Kettles may last ten years, but some manufacturers find it necessary to replace bottoms twice yearly. It is stated that it is not desirable to

FIGURE 24.

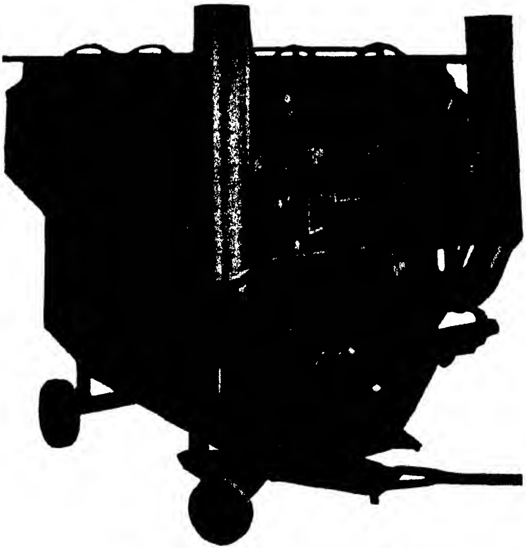
Two Monel 850-gallon Set Kettles for Processing Oils and Resins. The Kettle at the Left Was in Service for Thirteen Years without Rebottoming. The Kettle on the Right Was Rebottomed after Twelve Years' Service.

Courtesy The International Nickel Company, Inc.



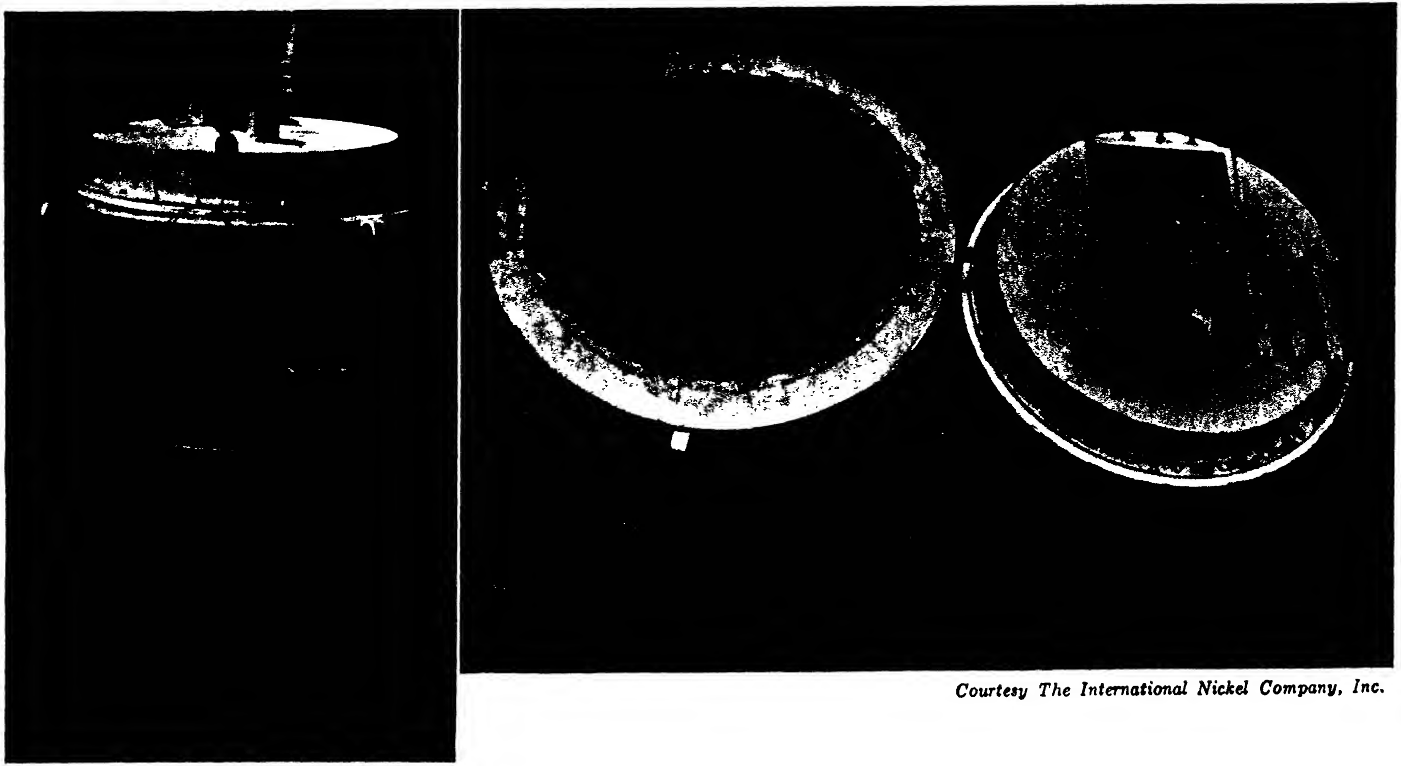
Courtesy Farben-Zeitung

FIGURE 25. Diagrammatic Sketch of Stand Oil Kettle Utilizing Carbon Dioxide (E. Willmeroth).



Courtesy The International Nickel Company, Inc.

FIGURE 26. High-temperature Kettle of Nickel-clad Steel. Capacity 300 Gallons.



Courtesy The International Nickel Company, Inc.

FIGURE 27. Electrically Heated Monel Kettle for Oil Bodying. Assembled Kettle at Left, with Dial Thermometer for Temperature Control. At Right, View of Unit with Kettle Removed, Showing Arrangement of Heating Elements.

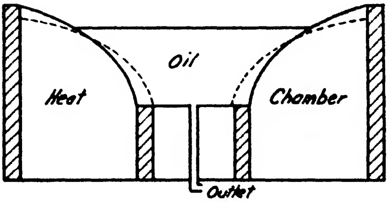
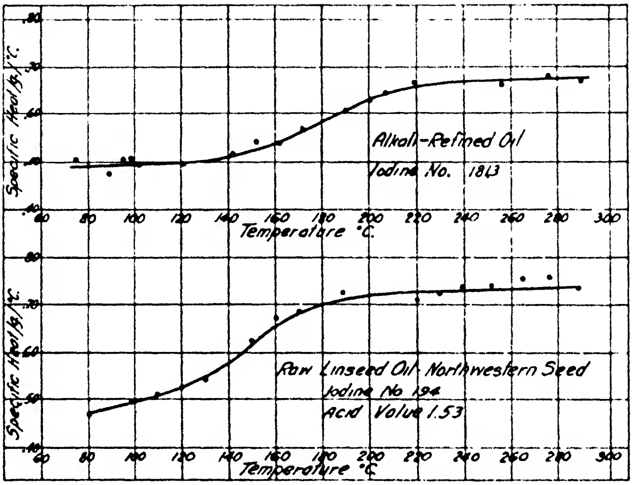


Figure 28.

Diagrammatic Sketch of Oil-heating Furnace with Heated Surface of Oil Always Proportioned to the Volume of Oil Heated (J. S. Long, J. B. Reynolds, and J. Napravnik).

Courtesy Industrial and Engineering Chemistry



Courtesy Industrial and Engineering Chemistry

Figure 29. Specific Heat-Temperature Curves for Linseed Oils (J. S. Long, J. B. Reynolds, and J. Napravnik).

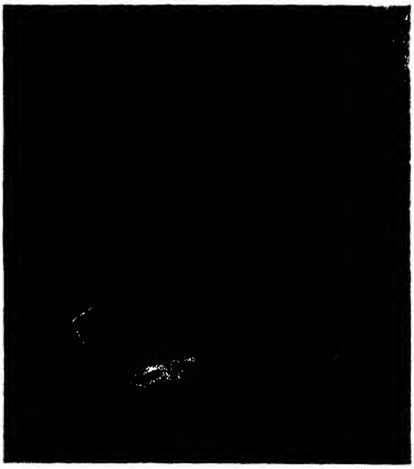


Figure 30.

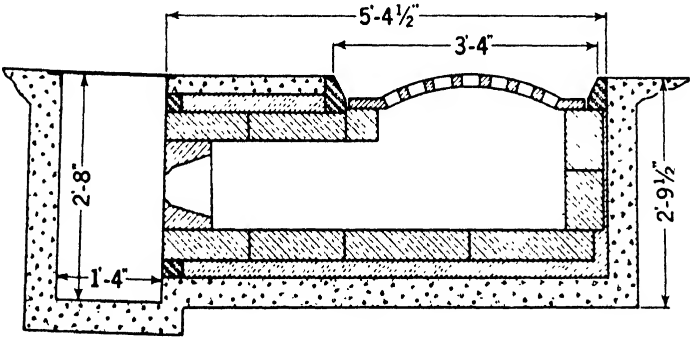
Ceramic Dome of the Type Used on Heaters for Portable Truck Kettles.

Courtesy The International Nickel Company, Inc.

heat these metal units much above 600° F.[317] Mechanical agitation reduces the temperature drop required across the kettle bottom for a given heating rate, and thus the metal is not overheated. Stirring is especially to be desired where metallic driers are employed.

Cleaning of the kettle bottoms involves the removal of caked driers and charred residues. Caked driers have a corrosive influence on the metal, and the accumulation of anything on the bottom may result in a "hot spot" where temperatures well over 1000° F. are produced. Monel and nickel kettles may be safely cleaned with lye solutions.[318]

The heating units employed in stand oil manufacture must provide rapid heating. Gas, oil or coke may be used as fuel. Gas and oil are replacing coke because of better heating control. Ceramic domes providing radiant heat prevent local heating. Figure 30 and Figure 31 show respectively such a dome and heater.



Courtesy The International Nickel Company, Inc.

FIGURE 31. Longitudinal Sectional of Radiant Type Heater Showing Heating Chamber and Perforated Ceramic Dome.

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[317] International Nickel Company, *loc. cit.*

[318] International Nickel Co., *loc. cit.*

Chapter 4

Driers

Drying oils change from the liquid into a solid phase when exposed to air in thin layers, as mentioned in Chapter 3. This process requires a long time, in the case of linseed oil about three weeks, and would be a serious obstacle for application of printing inks and paints, but it can be overcome by the addition of small quantities of "driers," also called "siccatives," which accelerate the film formation very effectively. The induction period is substantially shortened, as are the other stages of drying. It is also concluded, but not proved, that the driers neutralize the antioxidants present in natural oil that cause the induction period.[1]

COMPOSITION OF DRIERS

The catalytic action of certain materials, especially lead salt, has been known for a long time, but only at the end of the last century were studies on catalytic actions started. Cobalt and manganese driers were introduced.[2] The question whether liquid or solid driers should be used arose with their increasing consumption,[3] and the effect of driers on oils[4] and varnishes[5] became subject to thorough investigations. Today, siccatives ordinarily consist of metallic soaps of organic acids, preferably cobalt, lead or manganese, combined with resinic, naphthenic or fatty acids.[6] For example, a precipitated hydroxy metal salt of naphthenic acid such as hydroxy lead, cobalt or manganese naphthenate has been proposed.[7] These salts were stated to be insoluble in water. Also, titanium salts were suggested as siccatives.[8] Thus, titanium tetrachloride and stearic acid were said to interact at 70-110° C. to yield a salt applicable as a drier. Combination of metal with organic acids secures their solubility or at least very fine dispersion in the oil. The metals must be polyvalent, and it is assumed that changes in valence represent the

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[1] *Am. Paint. J., Conv. Daily*, 1932, 16 (53-A), 11; *Am. Paint Varnish Mfrs. Assoc. Tech. Sect. Circ.*, 423; *Paint, Var. Prod. Mgr.*, 1932, 8 (6), Sect. I, 12-9; *Technologie de l'imprimerie*, 1938, 6, 1441; *Rev. Paint, Colour, Varnish*, 1938, 11, 364.

[2] M. Weger, *Z. angew. Chem.*, 1896, 531-6; *J. S. C. I.*, 1896, 15, 728.

[3] H. Amsel, *Z. angew. Chem.*, 1897, 303, 344; *J. S. C. I.*, 1897, 16, 685.

[4] M. Weger, *Z. angew. Chem.*, 1897, 401, 542, 560; *J. S. C. I.*, 1897, 16, 922; *Papier-Ztg.*, 1938, 63, 1307; *Rev. Paint, Colour, Varnish*, 1938, 11, 363.

[5] M. Weger, *Chem. Rev. Fett- u. Harz-Ind.*, 1897, 4 (21), 285; *J. S. C. I.*, 1897, 16, 1024; G. Fearnley, et. al., *Am. Paint J.*, 1938, 23, *Convention Daily* (Oct. 25); *Chem. Abs.*, 1939, 33, 884.

[6] H. Silman, *Am. Ink Maker*, 1936, 14 (12), 18.

[7] A. Minich, U. S. P. 2,116,321, May 3, 1938, to Nuodex Products Co.; *Chem. Abs.*, 1938, 32, 5118; *Rev. Paint, Colour, Varnish*, 1938, 11, 374; *Natl. Paint Bull.*, 1938, 2, 17.

[8] W. W. Plechner, U. S. P. 2,132,997, Oct. 11, 1938, to National Lead Co.; *Chem. Abs.*, 1939, 33, 886.

catalytic action of the siccatives.[9] However, polyvalence is only *one* factor, and not all polyvalent metals act as driers; very similar materials sometimes behave entirely differently. Cerium, for instance, is a valuable promoter of drying, while thorium is not effective.

The action of cobalt driers is shown by the following table:[10]

Linseed oil, heated to 130° C.	Wet after 72 hours
Linseed oil, 1.5% cobalt resinate	Dry after 7½ hours
Linseed oil, 1.5% cobalt linoleate	Dry after 8½ hours
Linseed oil, 1.5% cobalt resinate, fused	Sticky in 8½ hours Dry in 14 hours

Colloidally dispersed metals also can serve as driers, although this method is not used frequently since it is inconvenient. Moreover, their action is slower, for they probably combine with the free fatty acids present in the oil before reacting, thus going into true solution. Metallic oxides have decidedly a similar action. It is reported that semi-drying oils acquire the properties of drying oils when blown with air at 165° C. for two hours in the presence of 1/44 mole of lead, cobalt or manganese oxide to 100 g. of oil.[11]

Preparation of Driers. In the usual preparation of driers an organic acid, such as naphthenic, resinic or a fatty acid, is saponified with an alkali, *e.g.*, sodium hydroxide, to form a water-soluble sodium soap. Subsequently an oxide or a salt of a metal is mixed with the aqueous soap solution and the whole heated. In this manner, an insoluble metal soap is formed as a precipitate. The latter is removed by filtration, washed and dried. The dried salt is ground into an ink vehicle such as linseed oil,[12] benzene,[13] turpentine, naphtha, "white spirit" (petroleum ether),[14] or other varnish solvents. The drier usually is insoluble, or practically so in both water and organic solvents.[15]

Aluminum driers may be made by forming the aluminum soaps of the hydroxy acids resulting from oxidation of petrolatum. The soaps are dissolved or emulsified with a varnish solvent, such as linseed oil or tung oil.[16]

In the preparation of driers the alkalinity of the solution can be controlled by the addition of an acid salt of the metal constituent of the

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[9] A. Mann, *Farbe-u. Lack*, 1933 (2), 19.

[10] T. H. Gant, *J. S. C. I.*, 1925, 44, 191; *Chem. Abs.*, 1925, 19, 1328.

[11] V. Chelinchen, *Masloboino Zhirovoe Delo*, 1929 (5), 49; *Chem. Abs.*, 1930, 24, 3658; *Brit. Chem. Abs.* **B**, 1930, 1037.

[12] R. Priester, U. S. P. 2,128,732, Aug. 30, 1938, to N. V. Industrieele Maatschappij voorheen Noury & Van der Lande; *Chem. Abs.*, 1938, 32, 8807.

[13] L. Roon, U.S. P. 2,113,496, April 5, 1938; *Rev. Paint, Colour, Varnish*, 1938, 11, 294; *Chem. Abs.*, 1938, 32, 4364, and U. S. P. 2,139,134, Dec. 6, 1938; *Chem. Abs.*, 1939, 33, 2355; both to Nuodex Products Co.

[14] A. M. Malamed, Russian P. 43,990, 1935; *Rev. Paint, Color, Varnish*, 1938, 11, 294; *Chem. Abs.*, 1938, 32, 3645.

[15] A. Minich, U. S. P. 2,116,321, May 3, 1938, to Nuodex Products Co.; *Chem. Abs.*, 1938, 32, 5118.

[16] A. Drinberg and V. Varlamov, *Masloboino Zhirovoe Delo*, 1937, 13 (4), 40; *Chem. Zentr.*, 1938, 109 (1), 3116; *Rev. Paint, Colour, Varnish*, 1938, 11, 207.

drier. Thus, when an acid is treated with a basic lead salt in forming a drier compound, a neutral or acid lead salt of an organic acid is said to stabilize the drier compound.[17] Inclusion of small proportions of other substances was said to stabilize the metallic soap drier. About one per cent of a salt resulting from the treatment of a primary, secondary or tertiary substituted ammonium or benzamine derivative, such as triethanolamine, pyridine, or benzamide, with an organic acid, such as salicylic or naphthenic acid, has been suggested for this purpose.[18]

Although, as a rule, driers are incorporated in inks during the milling or mixing process, the additions may be made at any time to vary the ink for special conditions.[19]

ACTION OF DRIERS

The action of driers has been attributed to changes in the valence state of these compounds. It has been stated that the driers absorb oxygen from the air, thereby passing to a higher valence state. The absorbed oxygen subsequently is transferred to the drying oil, and the siccative returns to its lower valence state. This cycle is repeated until the drying oils have been saturated with oxygen. To be acceptable as a drier a metal must, as a rule, have two or more sets of oxides and salts, the lower of which, with respect to valence, is the more stable. The changes of valence may be observed in the case of some of the metals, such as cobalt, manganese, and cerium, by means of variations in the color of the drier, but in the case of lead, because its salts do not exhibit sharp color changes with change of valence, this is not possible.[20] The metals have been arranged in their order of activity as driers by Mackey and Ingle.[21] They claim that the activity of a metal is a function of its position in the periodic table. Cobalt, manganese, nickel, cerium, lead, chromium, iron, and uranium all are metals forming two oxides, of which the higher is less stable. They are here listed in their order of drying power (cobalt, most active). Bismuth, silver, zinc, thorium, mercury and aluminum form but one oxide and are therefore less active. Although sodium forms but one oxide it is quite active.

By experimentation with a calorimeter especially adapted for the purpose, cotton wool soaked in an oil containing a drier has been tested to ascertain the gain in heat taken up by the cotton over a measured

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[17] K. E. Long, U. S. P. 2,102,633, Dec. 21, 1937, to Harshaw Chemical Co.; *Rev. Paint, Colour, Varnish*, 1938, 11, 125; *Chem. Abs.*, 1938, 32, 1499.

[18] P. E. Burchfield, U. S. P. 2,138,087, Nov. 29, 1938, to Harshaw Chemical Co.; *Chem. Abs.*, 1939, 33, 1974. For a discussion of the preparation of driers, see *Chim. Peint.*, 1938, 1, 47; *Rev. Paint, Colour, Varnish*, 1938, 11, 293. A. Foulon, *Allgem. Öl-u-Fett-Ztg.*, 1938, 35, 334; *Chem. Abs.*, 1938, 32, 8805.

[19] L. W. Claybourn, U. S. P. 1,675,695, July 3, 1928; *Rev. Paint, Colour, Varnish*, 1928, 1, 172; *Chem. Abs.*, 1928, 22, 3307.

[20] W. Krumbhaar, "Chemistry of Synthetic Surface Coatings," New York, Reinhold Publishing Corp., p. 45, 1937.

[21] W. McD. Mackey and H. Ingle, *J. S. C. I.*, 1917, 36, 317; *Chem. Abs.*, 1917, 11, 2049; *Seife*, 1921, 7, 228; *Chim. et Ind.*, 1922, 8, 406; *Chem. Abs.*, 1922, 16, 4072.

period of time. The latter was the time in which the temperature of 7 grams of cotton soaked with 14 grams of oil in which was dissolved 2 per cent of a drier would rise from 100° C. to 200° C. The faster the limit of temperature was reached the more active was the metal drier.[22]

The negative radical or organic portion of the siccative also plays some part in the drying action of the compound. It is thought that ester changes occur, and also that the metal radicals change to hydroxides or form intricate complexes, particularly in the presence of resins.[23]

It is necessary for good drier action that the metals should be present in the oil in true solution; if they are only finely dispersed, they tend to go into solution, and the drying process is delayed, as is the case with colloidal metals.

On the other hand the theory of drier action has been explained as a colloidal phenomenon; the particles of drier are said to be colloidal in magnitude. According to Wenzel's law, which states that the greater the absolute surface present, the greater will be the chemical change, the drying reactions will occur rapidly at the surface of the siccatives because their absolute surface areas are great.

The differential action of a lead drier and one containing cobalt or manganese is explained by reference to the orientation theory of the surface molecules in an organic liquid. Lead driers tend to cause a slow thickening of the film, and a final complete hardening, whereas the other driers do not show any action for quite some time and then quickly harden the surface of the film, leaving the lower portions rather tacky. Referring to the orientation theory, it is thought that the molecules arrange themselves so that the most active portions are turned toward the liquid phase. When an addition of manganese or cobalt drier is effected, the surface tension of the ink or paint is raised slightly, but when lead compounds are employed there is a depression in the tension. Therefore it may be assumed that, although the driers are evenly distributed throughout the oil, those inks containing manganese or cobalt driers contain none of the metallic soap in the surface film. The lead drier inks, on the other hand, do contain some of the drier in the surface layer.

When these films are exposed to air, they exhibit different drying properties. Films containing cobalt and manganese driers have for a surface layer a row of inactive vehicle molecules. Therefore a substantial period of time elapses before the oxygen from the atmosphere can penetrate and react with the ink. When the metallic material is finally reached the adsorption of the oxygen is rapid, due to the great adsorptive power of these two metals. In this manner drying occurs quickly, but near the surface of the film. Because the lead is near the surface of the ink film, adsorption is initiated at once, but the process is gradual, with

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[22] W. McD. Mackey and H. Ingle, *J. S. C. I.*, 1916, 35, 454; *Chem. Abs.*, 1916, 10, 2046. For a more complete discussion of the testing methods used, see Chapter 17.

[23] W. Krumbhaar, *loc. cit.*

the result that a more even oxidation occurs throughout the film. In the drying, however, some of the lead soap is forced to the surface and imparts a tacky feel to the surface of the hardened ink.[24]

Changes in valence occur more slowly with manganese driers than with soaps of cobalt, and this is probably the reason for the better action of the latter, which is by far the most efficient siccative.[25] The fact that lead promotes thorough drying, as remarked above, and probably enacts polymerization rather than oxidation, is laid to its ability to attach itself to the double bonds.[26]

Opinions vary on vanadium, which for the most part is not regarded a true drier, although it is sometimes mentioned as having better drying properties than manganese and lead, but as being inferior to cobalt.[27] The action of vanadium is reported to be similar to that of lead, *i.e.*, drying through the whole film.[28] Iron promotes drying at elevated temperatures only, and is used with baking inks.

Cerium naphthenate is an excellent catalyst, but because of its high price and excessive color change when going from the state of high oxidation to that of low valence, its use is very limited in the field of inks and paints. It finds application in the preparation of spar varnishes of the high-grade type. Zirconium soaps do not possess drying properties, but are useful as ingredients of pottery glazes and as anti-chalking agents.[29]

The addition of combinations of driers has proved very advantageous. Mixtures of cobalt, manganese or either one with a lead drier have better properties than either compound alone; lead and cobalt drier, for instance, combine the rapid oxidation of the latter with the drying "from the bottom" of the former. In some instances, the drier combination may be prepared by admixing the separate driers and heating the mixture.[30] Thus a mixed lead-manganese naphthenate is said to be secured by incorporating hydrated manganese naphthenate into a lead salt of the same acid. The temperature of the lead salt is maintained at 120-205° C. during addition. It has been observed that certain metals having no drier effect of their own are able to replace lead in these combinations; zinc particularly,[31] but also calcium, magnesium, aluminum, iron [32] and thorium show this phenomenon. Extensive experiments have shown that the optimum ratios of drier combinations vary with the temperature.[33]

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[24] C. E. Watson, *J. S. C. I.*, 1927, **46**, 436, 457; *Chem. Abs.*, 1927, **21**, 2193. H. C. Boyson, *Paint Manuf.*, 1938, **8**, 115; *Am. Ink Maker*, 1938, **16** (7), 37; *Chem. Abs.*, 1938, **32**, 4805.

[25] *J. Khim. Prom.*, 1933, **10** (4), 22; *Farbe u. Lack*, 1934 (34), 402.

[26] C. A. Knauss, *Am. Ink Maker*, 1937, **15** (4), 16, 39; *Brit. Chem. Abs.* **B**, 1937, 810.

[27] *Vancoram Rev.*, 1931, **2** (1), 4.

[28] J. Alexander, *Paint, Oil, Chem. Rev.*, 1930, **90**, 10.

[29] *Am. Ink Maker*, 1939, **17** (3), 41.

[30] G. M. Fisher, U. S. P. 2,116,884, May 10, 1938, to Socony-Vacuum Oil Co.; *Chem. Abs.*, 1938, **32**, 5003; *Rev. Paint, Colour, Varnish*, 1938, **11**, 374.

[31] C. Müller-Lobeck, *Farben-Chem.*, 1937, **8**, 398; *Chem. Abs.*, 1938, **32**, 3640.

[32] V. S. Kiselev and I. I. Golovistikov, *J. Chem. Ind. Russia*, 1930, **7**, 1348; *Brit. Chem. Abs.* **B**, 1932, 116.

[33] H. Wolff and G. Zeidler, *Farben-Ztg.*, 1934, **39** (35), 897; (36), 921; (37), 945; (39), 993.

The action of the catalysts also depends to a certain degree on the acid radical; the better the solubility it provides, the faster the drying action. Stearates and certain resinates, representing saturated chains, and linoleates representing unsaturated chains, are said to be inferior to naphthenates, which, because of their structure of saturated cyclic compounds, are supposed to dissolve very easily in oils.[34] They are completely stable in concentrated mineral spirit and prevent wrinkling and other troubles in the use of various drier catalysts with phenolic resins.[35]

Better uniformity in metallic content, permanence of solubility and activity are mentioned as further advantages of naphthenate driers.[36] Some investigators, however, state that fused resinates make the most efficient driers,[37] and that an excess of naphthenates gives a plasticizing effect, thus yielding poor films.[38] On the other hand, it is maintained that in moist atmospheres linoleates are more active than resinates.[39] Borates, used frequently in earlier years, are now employed very rarely; they were once considered very useful for half-tone inks.[40] Research is being steadily carried on to find other acids giving salts readily soluble in oils. For example, aliphatic and aromatic keto acids, aromatic alkylated and arylated acids, hydro-aromatic and aliphatic ether acids have been recommended.[41]

Capryloxyacetates and salts of toluic acid in which one hydrogen atom of the methyl group is replaced by a hydrocarbon radical, *e.g.*, amylbenzoate, have especially been mentioned.[42] It seems necessary that the metal be coupled with an acid to facilitate ester interchanges and other processes mentioned above, for lead tetraethyl,[43] cobalt-β-nitroso-α-naphthol and cobalt acetylacetone[44] show no drying effect in spite of excellent solubility. Cobalt pyridine compounds, however, are as active as resinates.

Pigments may influence the action of the catalysts physically and chemically. The main physical source is adsorption, which is observed particularly on carbon blacks, demanding the addition of driers in larger

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[34] C. A. Knauss, *Am. Ink Maker*, 1937, **15** (4), 16, 39; *Brit. Chem. Abs.* **B**, 1937, 810.

[35] C. A. Knauss, *Official Digest Federation Paint & Varnish Production Clubs*, 1934, No. **136**, 158.

[36] G. H. Pickard, *Am. Paint Varnish Mfrs. Assoc. Tech. Sect. Circ.*, 1931, **404**, 542; *Am. Paint J.*, 1931, **16** (9), 7f; *Chem. Abs.*, 1932, **26**, 1140; See also *Am. Ink Maker*, 1938, **16** (12), 41; R. D. Zamplor, et al., *Org. Chem. Ind.* (U.S.S.R.), 1938, **5**, 421; *Chem. Abs.*, 1939, **33**, 884.

[37] W. G. Chase, *Paint, Oil, Chem. Rev.*, 1932, **93** (13), 11.

[38] *Oil, Colour Trades J.*, 1937, **91** (2010), 1290. *Cf.* F. R. Jones and C. R. Watts, *ibid.*, 1937, **91** (1998), 341.

[39] *Am. Ink Maker*, 1934, **12** (3), 13.

[40] H. J. Wolfe, *Paint Manuf.*, 1933, **3** (10), 287.

[41] H. A. Bruson, U. S. P. 1,933,520, Oct. 31, 1933, to Resinous Products and Chemical Co.; *Chem. Abs.*, 1934, **28**, 662. H. A. Bruson and O. Stein, *Ind. Eng. Chem.*, 1934, **26** (12), 1268; *Chem. Abs.*, 1935, **29**, 945. Also, U. S. P. 1,933,521, Oct. 31, 1933; *A. P. V. M. Abs.*, 1934, (23), 29.

[42] H. A. Bruson, U. S. P. 1,920,160, July 25, 1933; *Chem. Abs.*, 1933, **27**, 4942. U. S. P. 1,927,867, Sept. 26, 1933; *Chem. Abs.*, 1933, **27**, 5995. U. S. P. 1,962,478, June 12, 1934: *N. P. V. L. Abs.*, 1934 (29), 239. U. S. P. 1,969,709, Aug. 7, 1934; *N. P. V. L. Abs.*, 1934 (31), 297. U. S. P. 1,880,759, Oct. 4, 1933, to Röhm and Haas Co.; *Chem. Abs.*, 1933, **27**, 1527. All patents except the last to Resinous Products and Chemical Co.

[43] C. A. Knauss, *Am. Ink Maker*, 1937, **15** (4), 16, 39; *Brit. Chem. Abs.* **B**, 1937, 810.

[44] *Am. Ink Maker*, 1934, **12**, (3), 13.

quantities than usually employed.[45] Regarding chemical action, it has been found that dye pigments precipitated on aluminum hydrate (see Chapter 6) substantially decrease the drying effect, whereas those prepared on a blanc fixe base do not influence drying. This behavior is laid to small quantities of phosphate which most of the aluminum hydrates contain and which poison the catalyst.[46] Reaction between aluminum and the metallic radicals as assumed in some instances [47] seems unlikely. Furthermore, pigments prepared by the acetate process (see Chapter 6) retard drying, unlike those made by the nitrate method, because it is impossible to remove the free acetic acid entirely. A similar effect occurs with driers prepared from metal acetates. Small amounts of free acetic acid will hinder or delay the drying action. The stage of valence of the catalysts can be influenced by pigments: zinc oxide usually acts as reducing agent, titanium oxide as oxidizing agent.[48] Lead pigments themselves sometimes act as driers to a certain extent.[49] Aluminum inks, tinted with dyes, require considerable amounts of cobalt.[50]

Siccatives commonly are of a rather dark color; hence, the varnish will be slightly darker after their addition. There is little difference in this respect between the several driers,[51] but the discoloration usually is not very important since only small proportions are added. Annoying, however, is the fact that some white synthetic resin inks tend to yellow due to the presence of the catalyst, especially when alkyd resins are employed, although combinations of driers behave better in this respect than do single driers.[52] Yellowing also occurs upon the addition of lead to pigments containing sulphur.[53] In contrast to the other metals lead causes most of these complications. For example, when it is employed with alkyds, a precipitation of lead phthalates takes place, causing a haze in the film.[54] Resinates do not show this effect as badly as soaps of other acids. The susceptibility of alkyds to lead decreases with increasing molecular weight of the resin. Some phenolics also will be affected by lead. Such driers should be avoided in lithography and tin plate printing because of interreaction between the metals.[55]

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[45] *Mon. Peinture*, 1930, 18, 189; *Farben-Ztg.*, 1938, 43 (51), 1346; *Rev. Paint, Colour, Varnish*, 1939, 12, 18.

[46] C. A. Knauss, *Am. Ink Maker*, 1937, 15 (4), 16; *Brit. Chem. Abs.* **B**, 1937, 810.

[47] L. M. Larsen and A. Grunder, *Am. Paint Varnish Mfrs. Assoc. Tech. Sect. Circ.*, 356, 897. *Chem. Abs.*, 1930, 24, 513.

[48] Montreal Club, *Natl. Paint Varnish Lacquer Mfrs. Assoc. Circ.*, 1936, 523, 351; *Am. Paint J.*, 1936, 21 (8), 7; *Paint, Oil, Chem. Rev.*, 1936, 98 (24), 114.

[49] *Mon. Peinture*, 1930, 18, 189.

[50] *Am. Ink Maker*, 1938, 16 (1), 23.

[51] *Am. Ink Maker*, 1938, 16 (1), 25.

[52] C. A. Knauss, *Am. Ink Maker*, 1937, 15 (4), 16; *Brit. Chem. Abs.* **B**, 1937, 810.

[53] *Am. Ink Maker*, 1938, 16 (1), 25.

[54] C. A. Knauss, *Official Digest Federation Paint & Varnish Production Clubs*, 1935 (145), 156.

[55] G. Haegens, *Tech. d'Imprimerie*, 1937, 5, 1181. For a general discussion of driers, see N. H. Bassett, *J. S. C. I.*, 1934, 53 (23), 504; *Rev. Paint, Colour, Varnish*, 1934, 7, 308; *Chem. Abs.*, 1934, 28, 4921. F. Fritz, *Farben-Ztg.*, 1938, 43, 775; *Chem. Abs.*, 1938, 32, 8168. Ekade, *Papier-Ztg.*, 1938, 63 (12), 208; *Rev. Paint, Colour, Varnish*, 1938, 11, 108; C. Eckmann, *Farben-Chem.*, 1936, 6, 367; *Chem. Abs.*, 1937, 31, 6035. F. J. Sicata, *Can. Chem.*, 1938, 22, 180; *Rev. Paint, Colour, Varnish*, 1938, 11, 293.

DRIER CONCENTRATIONS

Subject to many discussions have been the concentrations in which to apply the catalysts. Although it appears certain that a combination of driers is superior to single siccatives, the exact amount and ratio is unknown. Incidentally, despite the prevailing experience, a few experts warn against the use of mixtures of driers.[56] Employment of excessive amounts of driers results in grave drawbacks in respect to the quality of the ink,[57] for such practice [58] causes picking, wrinkling and skinning, particularly with cobalt; but by addition of zinc this usually can be straightened out, presumably through a lowering of the surface tension.[59] In the lithographic and offset processes especially, an excess of drier tends to cause what is called, "filling-up" of the plates, which means that the non-printing areas of the plate are covered by a partially-dried film of ink and this spoils the effect of the printed sheet. In extreme cases, the tack of the ink is lowered to such a degree that it is not lifted off the plate by the offset blanket.[60] However, printing inks, intended to dry as quickly as possible and not exposed to certain conditions as paints are, usually stand a much higher amount of siccatives than the latter. Beyond a maximum in concentration, drier action does not improve, but comes to a standstill or may even be retarded. A linseed oil-titanium oxide paint containing cobalt drier was investigated by measuring weight increases in pure oxygen, and showed increasing drying power up to an end point, above which there was no change. The acid radical of the catalyst (resinates or naphthenates) was reported to have little effect.[61] From experience the most advantageous quantities are known for use of siccatives and their ratios of combination in linseed oil, but no scientific background supports these rules. Winiker [62] recommends a ratio of 7.5 parts of lead to 1 part of manganese and states that this is the best proportion to obtain the maximum drying speed. If it is necessary to keep the drier concentration lower, a proportion of 6:1 is suggested. Lead-cobalt combinations are reported to have best activity in proportions of 5:1 If less cobalt is added, the drying time decreases sharply. However, addition of more cobalt does not yield a substantial increase in drying time. For quickest action, a combination of lead, manganese and cobalt in a proportion of 0.5:0.05:0.1 is suggested, which causes an oil to dry within 1.75 hours. Workers reporting that perilla oil does not dry as quickly as linseed oil (customarily the contrary statement is maintained) recommend the addition of larger amounts of catalysts, preferably

[56] *Farben-Ztg.*, 1931, **36** (34), 1576; *Chem. Abs.*, 1931, **25**, 4722.

[57] *Paint Manuf.*, 1934, **4** (7), 203.

[58] *Deutscher Drucker*, 1937, **44** (518), 78.

[59] C. A. Knauss, *Official Digest Federation Paint & Varnish Production Clubs*, 1935 (145), 156.

[60] C. F. Geese, *Nat. Lith.*, 1938, **45** (3), 47; *Rev. Paint, Colour, Varnish*, 1938, **11**, 192.

[61] D. G. Nicholson and C. E. Holley, *Ind. Eng. Chem.*, 1938, **30**, 114.

[62] K. Winiker, *Farben-Ztg.*, 1933, **38**, 504, 534; *Chem. Abs.*, 1933, **27**, 1771.

resinates, and state that 0.5-1.0 per cent of cobalt gives best results.[63] Oiticica oil also requires more drier when serving as substitute for tung oil; in this case a combination of lead and cobalt is considered best.[64] The catalytic effect of lead and manganese driers on tung oil is indicated in Figure 32 and Figure 33.[64a] It is advisable to investigate the suitable amount of siccative for every kind of ink and not merely to apply the quantities used for linseed oil. This is particularly true for synthetic resin inks since not all resins are compatible with every drier, as intimated above, and in every case the miscibility, best combination and correct quantity should be subjected to careful examination.

Attempts have been made to set up drier standards, one suggested unit of drying power, called "aridyne," being defined as the drying power equivalent to 0.064 oz. of lead. A liquid drier containing 6.4 oz. of oil-soluble lead per gallon would be called "100 proof" on this basis. However, the establishment of the aridyne value in the drying power of linseed oil met with considerable difficulty,[65] and it is stated that only a

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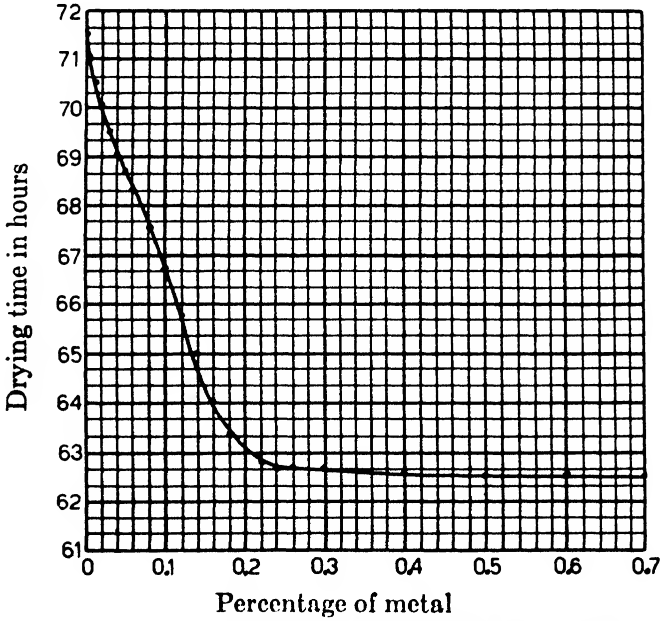
[63] H. L. Tchang and C. L. Ling, *Bull. faculté sci. univ. franco-chinoise, Peiping*, 1935 (4), 1; *Chem. Abs.*, 1936, 30, 4699.

[64] *Am. Ink Maker*, 1936, 14 (9), 35.

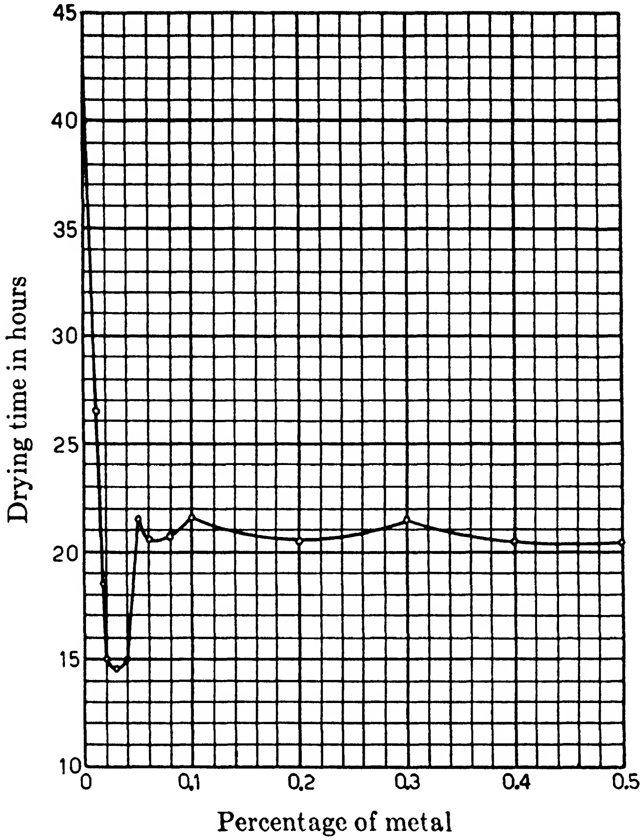
[64a] G. E. Ludwig, *Ind. Eng. Chem.*, 1925, 17, 1160.

[65] C. F. Carrier, *Am. Paint J.*, 1930, 14 (33), 70; *Chem. Abs.*, 1930, 24, 3660. *Am. Paint J.*, 1930, 14 (52-D), 25; *Paint, Oil, Chem. Rev.*, 1930, 90 (17), 71; *Oil, Paint, Drug Rep.*, 1930, 118 (19), 58; *Chem. Abs.*, 1931, 25, 221. *Am. Paint Varnish Mfrs. Assoc. Tech. Sect. Circ.*, 1931, 404, 635; *Paint, Oil, Chem. Rev.*, 1931, 92 (24), 52f; *Am. Paint J.*, 1931, 15 (51-E), 18f; *Chem. Abs.*, 1932, 26, 1140.



Courtesy Industrial and Engineering Chemistry

FIGURE 32. Catalytic Effect of Litharge on Drying of Tung Oil (G. E. Ludwig).



Courtesy Industrial and Engineering Chemistry

FIGURE 33. Catalytic Effect of Manganese Borate on Drying of Tung Oil (G. E. Ludwig).

standard established for the drying power of raw linseed oil under uniform conditions is worth considering.[66] The plan of drier standardization seems to have been discontinued, for nothing has been noted in the more recent literature. Certain specifications and methods of determination of the metallic content are given by a German manufacturers' league, but no real standardization of drying power is attempted.[67]

NON-METALLIC DRIERS

The transfer of oxygen into the ink is effectively supported by turpentine, depending on its content of peroxides. Other materials show similar

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[66] W. G. Chase, *Paint, Oil, Chem. Rev.*, 1932, 93 (13), 11.
[67] W. Meyer, *Farbe-u. Lack*, 1931, 36 (31), 359 (32), 373.

tendency, *e.g.*, dipentene, menthol[68] and certain other terpenes, but the presence of metallic driers is compulsory in all these cases. Small amounts of phenol ethers such as isosafrole or anethole, and aromatic ketones, aldehydes or their derivatives promote drying; acetophenone, benzaldehyde and salicylaldehyde are examples of the latter accelerators.[69]

Small quantities of ozone cause the inks to dry much faster, but larger quantities destroy them, decomposing the fatty acids at the double bonds.[70]

Drier compounds are obtained through the reaction of vinylacetylene with hydrogen in the presence of hydrogenation catalysts. The oily products having more than four carbon atoms per molecule are isolated and may contain varying proportions of polymeric acetylenes.[71] The paper or other surface to be printed may be conditioned by treatment with ozone before it is printed, thus accelerating hardening of the ink.[72]

Rapid film formation occurs when oils, either drying, semi- or non-drying or an oil such as cashew nut shell oil, are exposed to the vapors of sulphur monochloride. Drying oils react faster because in the other oils more substitution takes place, requiring a certain time. However, even non-drying oils solidify in thin layers within a few seconds. This effect seems due to oxidation, since in thicker layers only the surface solidifies. The exact mechanism has not yet been established, but the reaction can be followed quantitatively.[73] Subjected to higher temperature, the sulphur monochloride probably decomposes before being able to react because no such effect could be observed with high temperatures.[74]

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[68] A. Castiglioni, *Ann. chim. applicata*, 1936, 26, 249; *Chem. Zentr.*, 1936, 107 (2), 3017.

[69] K. K. Honen Seiyu, Japanese P. 99,478 and 99,977, 1933; *Chem. Abs.*, 1934, 28, 2553.

[70] C. Denzler, *Helv. Chim. Acta*, 1933, 16, 807; *Chem. Abs.*, 1933, 27, 4696.

[71] French P. 820,286, 1937, to I. G. Farbenind. A.-G.; *Rev. Paint, Colour, Varnish*, 1938, 11, 186; *Chem. Abs.*, 1938, 32, 3177.

[72] R. Wiche, German P. 599,859, 1934, to Siemens & Halske Akt.-Ges.; *Rev. Paint, Colour, Varnish*, 1935, 8, 26; *Chem. Abs.*, 1934, 28, 7561.

[73] H. P. Kaufmann, J. Baltes and P. Mardner, *Fette u. Seifen*, 1937, 44, 337, 390; *Chem. Abs.*, 1938, 32, 815, 816.

[74] V. Chelinchen, *Masloboino Zhirovoe Delo*, 1929 (5), 49; *Brit. Chem. Abs.* B, 1930, 1037; *Chem. Abs.*, 1930, 24, 3658.

Chapter 5

Printing Ink Modifiers

Printing inks can be widely modified by addition of a variety of materials [1] in order to impart certain properties to the inks or to inhibit undesirable ones. Elimination of offset,[2] change in drying speed, reduction of excessive tack and other factors [3] are influenced by modifiers. Much progress has been made in this respect, many new materials have been developed and old-fashioned ones improved. However, many inks do not contain modifying agents, since the purpose for which they are used does not always require such agents.

WETTING AND DISPERSING AGENTS

The fact that some pigments offer considerable resistance to the grinding process while others are worked into the vehicle quite easily is known to every ink maker. In earlier years this was taken as a matter of fact, but in later times scientists began to investigate the phenomenon and its causes. It was known that air-bodied heavy varnishes, particularly those which tend to liver, were incorporated with pigments more easily than light varnishes. Thus, it was not going very far to ascribe the better wetting action to the presence of comparatively large quantities of free fatty acids in heavy-bodied varnishes. We know now that wetting is accomplished by so-called polar compounds, *i.e.*, substances composed of molecular groups having different ends. Metal soaps are example of such compounds and, in fact, are employed frequently as wetting agents, as will be mentioned later on. The molecules of these polar compounds surround the pigment particles in monomolecular layers and have the property of decreasing the interfacial tension between pigment and vehicle. Use of wetting agents thus either shortens the grinding time or provides finer dispersion of the pigment.[4]

It is obvious from the foregoing that only small amounts of dispersing agents are necessary.[5] Moreover, too large a quantity may have deleterious effects, *e.g.*, causing livering (particularly by employment of fatty

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[1] For a review on materials added to inks see also *Chem. Trade J.*, 1935, 97, 221.

[2] By offset is meant here the occasional detachment from or smearing of the wet ink on the printed sheet while handling the latter after it has come out of the printing machine.

[3] R. F. Bowles, *Am. Ink Maker*, 1937, 15 (4), 25.

[4] J. L. Burton, *Am. Ink Maker*, 1937, 15 (3), 21; *Chem. Abs.*, 1937, 31, 4141; *Brit. Chem. Abs.* B, 1937, 589.

[5] *Am. Paint J., Conv. Daily*, 1934, 18 (53A), 15; *Natl. Paint Varnish Lacquer Assoc. Circ.*, 1934, 471, 313; *Paint, Oil, Chem. Rev.*, 1934, 96 (22), 74.

acids), attacking the pigment or delaying the drying time. On the other hand, if incorporated in appropriate proportions, usually varying from 1/4 to 1 per cent of the ink, the compound may prevent the ink from livering. Experience has shown that different wetting agents are necessary for various pigments. Carbon black requires a larger quantity because of its comparatively high oil absorption power. Induline oleate has been suggested as a wetting agent for carbon black,[6] also sulphonated castor oil. On the other hand, sulphonated mineral oils or the sulphonated condensation product of an aromatic hydrocarbon and a fatty acid of high molecular weight[7] (*e.g.*, stearic) are more effective for lithopone.[8] Carbon black may also be dispersed with the aid of copper salts, such as resinates, stearates, oleates or naphthenates. However, even inorganic salts, such as nitrates and chlorides, are reported to be helpful.[9] Zinc naphthenates and lecithin are very useful for wetting titanium oxide pigments.[10] Titanium oxide is also readily wetted by zinc oleate and lead compounds.[11]

Grinding of pigments with the aid of nitrocellulose is not very common because of the fire hazard involved. However, cellulose esters may be employed for this purpose, especially if they are blended with castor oil and, if necessary, dissolved in a hydrocarbon solvent.[12] Nitrocellulose, emulsified with water by means of castor oil and an emulsifying agent, has also been recommended as a dispersing agent.[13] The fire hazard is avoided if nitrocellulose is replaced by methylcellulose.[14] Fluidity of the ink is said to be improved by adding as a dispersing agent a sulphonic acid of phenol-aldehyde or naphthalene-aldehyde condensation products, alkyl naphthalene-sulphonic acids, sulphonated mineral oils or alkylated (*e.g.*, isopropylated) derivatives of the latter.[15]

Sulphonated higher alcohols (particularly of the C_{18} series) promote wetting action.[16] The same holds true for mahogany sulphonate.[17] This

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[6] M. P. Volarovich and V. S. Borinevich, *Kolloid-Z.*, 1936, 77, 93; *Chem. Abs.*, 1937, 31, 560; *Brit. Chem. Abs.* B, 1936, 1217.

[7] This product is known as the Twitchell reagent: E. Twitchell, *J. A. C. S.*, 1900, 22, 22. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," New York, Reinhold Publishing Corp., 1934.

[8] *Am. Paint J., Conv. Daily*, 1934, 18 (53A), 21; *Natl. Paint Varnish Lacquer Assoc. Circ.*, 1934, 471, 329; *Paint, Oil. Chem. Rev.*, 1934, 96 (22), 87; *Chem. Abs.*, 1935, 29, 361; *Brit. Chem. Abs.* B, 1935, 32; *Rev. Paint, Colour, Varnish*, 1934, 7, 467.

[9] *Am. Ink Maker*, 1938, 15 (6), 37.

[10] *Natl. Paint Varnish Lacquer Assoc. Circ.*, 1935, 495, 376; *Paint, Varnish Production Mgr.*, 1935, 13, 40; *Paint, Oil, Chem. Rev.*, 1935, 97 (23), 81.

[11] D. W. Robertson, *Am. Ink Maker*, 1936, 14 (11), 18; *Chem. Abs.*, 1937, 31, 1232.

[12] E. H. Bucy, U. S. P. 1,911,104, May 23, 1933, to Brevolite Lacquer Co.; *Chem. Abs.*, 1933, 27, 4107; *Brit. Chem. Abs.* B, 1935, 109. French P. 758,068, 1934; *Chem. Abs.*, 1934, 28, 3254.

[13] R. T. Hucks and G. R. Maker, U. S. P. 2,114,713, Apr. 19, 1938, to E. I. duPont de Nemours & Co.

[14] Hercules Powder Co., *Drugs, Oils, & Paints*, 1936, 51, 247; *Chem. Abs.*, 1937, 31, 4141; *Brit. Chem. Abs.* B, 1936, 751. For wetting and settling of pigments see also V. G. Jolly, *J. Oil Col. Chem. Assoc., Ann. Conference Report*, 1937, 55; J. C. Smith, *Paint Manuf.*, 1935, 5, 37, 93; *Chem. Abs.*, 1935, 29, 3535. C. K. Sloan, *Am. Ink Maker*, 1937, 15 (2), 16.

[15] C. Hollins and E. Chapman, British P. 279,968, 1926; *Chem. Abs.*, 1928, 22, 3055; *Brit. Chem. Abs.* B, 1928, 203.

[16] British P. 318,610, 1928, to H. T. Böhme A.-G.; *Chem. Abs.*, 1930, 24, 2257; *Brit. Chem. Abs.* B, 1931, 290.

[17] H. Heckel, British P. 360,075, 1930, to Twitchell Process Co.; *Chem. Abs.*, 1933, 27, 615. U. S. P. 1,906,961 and 1,906,962, May 2, 1933; *Chem. Abs.*, 1933, 27, 3627; *Brit. Chem. Abs.* B, 1934, 157.

material is obtained from the oil layer after treatment of mineral oil with sulphuric acid or sulphur trioxide. It is separated from the oil by alcoholic solvents and distillation.[18] Salts of naphthenic acids which have proved useful as driers (as stated in Chapter 4) are also advantageously used as wetting and dispersing agents,[19] but for the latter purpose other metallic radicals usually are employed, especially zinc.[20] The precipitate formed by neutralization of sodium aluminate with phosphoric acid has been suggested as a wetting agent.[21] A compound consisting of olive oil, sandarac and stearin is also reported to work satisfactorily as a dispersing medium.[22] Particularly good action is secured with compounds containing substituted ammonia radicals. Sulphuric esters of amides which are substituted in the ammonia radical by fatty acids [23] are effective, especially if the acids are unsaturated. Combination of triethanolamine with eleostearic acid yields a satisfactory dispersing agent.[24] Instead of triethanolamine, cyclohexylethanolamine likewise has been used.[25] Other substituted amides include heterocyclic aromatic bases which are hydrogenated, *e.g.*, piperidine.[26]

An amine having no hydroxyl group and containing at least one alkyl radical is said to be useful. It may be condensed with soap-forming carboxylic or sulphonic acids or their derivatives (*e.g.*, ricinoleic acid).[27] The five-valent, substituted nitrogen atom is generally held responsible for the excellent action of these compounds and also that of lecithin briefly mentioned above.

It has also been suggested to use solutions of certain resins (such as ascaroid, dammar, colophony, gum lac or a synthetic resin) as dispersing agents, especially after they have been treated with aqueous alkaline solutions.[28]

An examination of the efficacy of a number of dispersing agents has been made.[29] Using standardized vehicles, the ease of wettability of representative pigments was determined for each agent. It was stated that zinc naphthenate and lecithin were effective dispersing agents in the

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[18] Carleton Ellis, "The Chemistry of Petroleum Derivatives," Vol. II, New York, Reinhold Publishing Corp., 1937, p. 1029.

[19] Carleton Ellis, "The Chemistry of Petroleum Derivatives," Vol. II, New York, Reinhold Publishing Corp., 1937, p. 1117.

[20] C. A. Knauss, *Am. Ink Maker*, 1937, 15 (4), 16; *Chem. Abs.*, 1937, 31, 4835.

[21] W. D. Patten, U. S. P. 1,035,229, Aug. 13, 1912; *Chem. Abs.*, 1912, 6, 3333.

[22] H. Lesne and M. Lapierre, French P. 451,452, 1912; *Chem. Abs.*, 1913, 7, 3549.

[23] British P. 318,542, 1928, to H. T. Böhme A.-G.; *Chem. Abs.*, 1930, 24, 2257; *Brit. Chem. Abs.* B, 1931, 433.

[24] A. Chwala, British P. 445,701, 1936; *Chem. Abs.*, 1936, 30, 6968; *Brit. Chem. Abs.* B, 1936, 652; French P. 780,799, 1935; *Chem. Abs.*, 1935, 29, 6081; cf. *Farben-Ztg.*, 1936, 41, 679.

[25] W. Kritchevsky. U. S. P. 2,089,212, Aug. 10, 1937; *Chem. Abs.*, 1937, 31, 6773.

[26] British P. 224,882, 1924, to H. T. Böhme A.-G.; *Chem. Abs.*, 1925, 19, 1952; *Brit. Chem. Abs.* B, 1925, 588.

[27] British P. 469,559, 1936, to United Color and Pigment Co., Inc.: *Brit. Chem. Abs.* B, 1938, 410.

[28] H. Kurz and K. Albert, French P. 43,145, 1934; *Chem. Abs.*, 1934, 28, 5262; Add. to French P. 711,613, 1931; *Chem. Abs.*, 1932, 26, 1810. For a review of wetting of pigments see also G. A. Campbell, *J. Intern. Soc. Leather Trades Chem.*, 1937, 107; *Rev. Paint, Colour, Varnish*, 1937, 10, 273.

[29] A. O. Allen, *et. al.*, *Am. Paint J.*, 1935, 19, *Convention Daily*, 14 (Oct. 31); *Paint Varnish Production Mgr.*, 1935, 13, 40 (Nov.); *Paint, Oil and Chem. Rev.*, 1935, 97 (23), 81; *Chem. Abs.*, 1936, 30, 630.

greatest number of cases. The remainder of the agents, in the order of decreasing efficiency, were: "Twitchell Base No. 265" (a sulphonated compound), ester gum, oleic acid, "Emulsifier A" (a sulphonated compound), salicylic acid, and nitrobenzene. The following compounds were said to exhibit no dispersing action under the conditions of experiment: butyl stearate, benzaldehyde, triethanolamine, ethylene glycol and the ethyl ether of diethylene glycol.

EMULSIONS AND EMULSIFYING AGENTS

To promote and to improve dispersion of pigments and to produce certain other desirable properties in printing inks, vehicles for the latter are frequently emulsified. As is well known, an emulsion can be made with two immiscible liquids, one of which forms the continuous or outer phase, and the other is the disperse or inner phase. In printing inks the two liquids are often a drying oil and water or a dilute aqueous solution of some substance to be incorporated with the ink. In place of the drying oil other organic liquids immiscible with water, *e.g.*, hydrocarbons or mineral oils, may be employed. Emulsification is usually effected in the presence of an emulsifying agent which may serve also as a pigment-wetting agent.

The action of emulsifiers[30] may be explained by their adsorption on the surface of drops of the dispersed liquid, which thus receive an electric charge from the emulsifier, the latter being a polar compound. Also, emulsifying agents may decrease the interfacial tension between the two phases, thus facilitating dispersion of one in the other. Explanation of the pigment-dispersing effect of emulsions is that selective wetting of the pigment is effected by the phase with which it exhibits the lower interfacial tension.[31] Emulsifying agents which produce a fine subdivision of the insoluble coloring matter have been obtained by mixing a solution of a gel-forming substance, *e.g.*, glue, gelatin or water-soluble gums, with an alkali salt of an organic sulphonic acid, such as the sodium-sulphonate of isopropylnaphthalene.[32] In place of the alkali sulphonate, neutralized and concentrated cellulose sulphite waste liquor,[33] or trihydroxyethylamine may be substituted.[34] Sulphonated oils, especially turkey red oil (sulphonated castor oil), have been employed for this purpose for a long time.

Since soaps are good dispersing and wetting agents, water-wet pigments may be emulsified with a lithographic varnish in the presence of a

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[30] A. von Buzagh, "Colloid Systems," London, The Technical Press, Ltd., 1937.

[31] J. Alexander, "Colloid Chemistry," Vol. III, New York, The Chemical Catalog Co., Inc., Reinhold Publishing Corp., 1934, Chapter 3. See also *Witcombings*, 1939, June, 11.

[32] British P. 258,551, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1927, 21, 3095; *Brit. Chem. Abs.* B, 1928, 152.

[33] British P. 258,551, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1927, 21, 3095.

[34] British P. 270,293, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1928, 22, 1418; *Brit. Chem. Abs.* B, 1928, 704.

soap as dispersing agent. Dispersion of the pigment in the varnish is facilitated by addition of a mineral salt (such as barium chloride or magnesium sulphate). The latter cause precipitation of the wetting agent, thus breaking the emulsion. The water then separates from the oil-pigment mixture, and the latter is ready for use.[35]

Lecithin and particularly the substituted amines coupled with fatty acids, as noted above, are good emulsifying agents. Another amine of cyclic structure is morpholine (tetrahydro-1,4-oxazine), fatty acid soaps of which are used as emulsifying agents. Due to their low volatility, emulsions with morpholine soaps can be produced at a relatively high temperature (90° C.). Upon drying of the ink film, morpholine gradually evaporates, leaving the fatty acid as a residue and thus rendering the dried films more resistant to water and less apt to re-emulsify.[36] Morpholine is also reported to aid in the formation of wax emulsion.[37]

Printing ink vehicles may be admixed with viscous emulsions obtained from raw rubber, gutta percha or balata. By working these latter substances (in a rubber mixing mill) with naphtha or petroleum hydrocarbons, then passing the mass through a high-speed colloid mill, a viscous liquid is obtained. This product may be incorporated in a proportion up to 20 per cent in drying oils of the type of linseed or tung oil to furnish lithographic varnish.[38]

Proteins [39] and glutinous materials, except gum and casein,[40] are other emulsifying agents. Mahogany sulphonates, noted above as wetting agents, are stabilizers for emulsified printing ink vehicles.[41]

Salts of N-alkylated aminocarboxylic acids,[42] particularly sodium *p*-diethylaminobenzoate, and also casein together with borax and ammonia may serve as emulsifying agents.[43] Besides the stabilizers mentioned, pectins, tannins, gums and vegetable mucus may be used. To eliminate the usual dampening of paper in lithographic work, an oil emulsion of an aqueous solution of one or more deliquescent salts, such as calcium chloride or borax, is incorporated in the ink.[44] For the same purpose a mixture of glycerol or other polyhydric alcohol, calcium chloride, potassium

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[35] British P. 452,556, 1936, to International Printing Ink Corp.; *Chem. Abs.*, 1937, 31, 1234; *Brit. Chem. Abs.* B, 1936, 1109.

[36] A. L. Wilson, *Ind. Eng. Chem.*, 1935, 27, 867; *Chem. Abs.*, 1935, 29, 6571; *Brit. Chem. Abs.* B, 1935, 893.

[37] *Am. Ink Maker*, 1938, 16 (5), 35. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," Vol. II, Reinhold Publishing Corp., New York, 1937, 583.

[38] A. Davies, British P. 421,820, 1933; *Chem. Abs.*, 1935, 29, 3874; *Brit. Chem. Abs.* B, 1935, 241; *Rev. Paint, Colour, Varnish*, 1935, 8, 46.

[39] British P. 9,663, 1908, to Chem. Fabrik Electro Co., Ltd.; *Chem. Abs.*, 1909, 3, 2492; *J. S. C. I.*, 1909, 28, 533.

[40] Danish P. 38,262, 1927, to Aktieselskabet Sadolin & Holmblad; *Chem. Abs.*, 1928, 22, 3056.

[41] H. Heckel, British P. 360,948, 1930; *Chem. Abs.*, 1933, 27, 1216; *Brit. Chem. Abs.* B, 1932, 234.

[42] Swiss P. 188,298, 1937, to Soc. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1937, 31, 6776.

[43] British P. 409,009, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 6003; *Brit. Chem. Abs.* B, 1934, 593.

[44] W. P. Price, British P. 236,614, 1924, to Schuck, Maclean & Co., Ltd.; *Brit. Chem. Abs.* B, 1925, 770; Canadian P. 275,513, 1927, to Horace Cory & Co.; *Chem. Abs.*, 1928, 22, 1244; U. S. P. 1,817,522, Aug. 4, 1931; *Chem. Abs.*, 1931, 25, 5584.

phosphate with a gum solution, and phenol may be added.[45] In other instances, an aqueous solution of an alkali salt, such as soda, in glycerol, emulsified with resin oil, may be added to the lithographic varnish.[46]

To improve brushing qualities and to inhibit running of stencil pastes, emulsified false-bodying agents[47] are incorporated. Such emulsions are made of a drying oil-modified or a drying oil-fatty acid-modified alkyd resin with a solution of metallic soaps in water, mineral spirits or alcohol. Soaps of calcium, magnesium and other bivalent metals, *e.g.*, calcium oleate, in conjunction with alkali metal soaps, such as ammonium stearate, are found to be most effective.[48]

TACK AND VISCOSITY

Greasy substances are often added to inks to overcome excess of tack. Petrolatum, also called petroleum jelly or Vaseline, serves this purpose, and at the same time softens and extends the ink.[49] The most applicable kind for printing inks is that of high viscosity and a melting point of 115-120° F.[50] Use of Vaseline in printing inks has been known for a long time and was reported as early as 1890.[51] It may be replaced by wool fat,[52, 53] natural or synthetic waxes[54] or paraffin wax. The latter together with a resin, in some instances, may be dispersed in a concentrated aqueous solution of alkali (*e.g.*, caustic soda or soda ash) before incorporation into the ink.[55]

Addition of these substances lowers the viscosity of the ink. As little as 5 per cent of paraffin wax decreases the viscosity by about 50 per cent. Viscosity relations of mixtures of petrolatum and linseed oil varnishes have been indicated.[56] Potassium soap was incorporated into inks in earlier years. It is now substituted by non-drying metallic soaps such as palmitates, stearates or oleates of aluminum, zinc, magnesium or calcium,[57] or by resinates (particularly those of aluminum).[58] These soaps are added to prevent settling of pigments and, in some instances, to produce "short" inks.

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[45] F. C. Fitzgerald, U. S. P. 1,406,837, Feb. 14, 1922; *Chem. Abs.*, 1922, 16, 1875. Canadian P. 215,783, 1922; *Chem. Abs.*, 1922, 16, 1512. British P. 159,809, 1920; *Chem. Abs.*, 1921, 15, 2199.

[46] S. Wechsler, German P. 236,338, 1909; *Chem. Abs.*, 1911, 5, 3632.

[47] These are agents which impart the property of thixotropy to the ink.

[48] J. W. Iliff, P. Robinson and W. Whitescarver, U. S. P. 2,011,898, Aug. 20, 1935, to E. I. duPont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 6770; *Brit. Chem. Abs.* B, 1936, 895; *Rev. Paint, Colour, Varnish*, 1936, 9, 315.

[49] E. Meyer, *Am. Ink Maker*, 1934, 12 (4), 13; *Brit. Chem. Abs.* B, 1934, 463.

[50] *Paint Varnish Production Mgr.*, 1935, 12, 26.

[51] W. G. Fuerth, British P. 16,689, 1890; *J. S. C. I.*, 1891, 10, 136.

[52] W. Obst, *Allgem. Öl-Fettztg.*, 1929, 26, 579; *Chem. Abs.*, 1930, 24, 741.

[53] A. J. Gautsche, U. S. P. 2,018,060, Oct. 22, 1935; *Chem. Abs.*, 1936, 30, 309; *Brit. Chem. Abs.* B, 1936, 1109.

[54] G. Schneider and R. Folgner, *Chem. Umschau*, 1932, 39, 175; *Chem. Abs.*, 1932, 26, 6170.

[55] K. Sonder, British P. 463,187, 1937; *Chem. Abs.*, 1937, 31, 5906. For a review on waxes used in printing inks see J. J. Deeney, *Am. Ink Maker*, 1930, 8, 25; *Chem. Abs.*, 1930, 24, 4646.

[56] R. F. Bowles, *Am. Ink Maker*, 1937, 15 (4), 25.

[57] *Am. Ink Maker*, 1936, 14 (8), 25.

[58] J. H. Caughlan, U. S. P. 1,578,582, March 30, 1926; *Chem. Abs.*, 1926, 20, 1723. British P. 265,787, 1926; *Chem. Abs.*, 1928, 22, 505; *Brit. Chem. Abs.* B, 1927, 305.

Spreading and setting properties of an ink are said to be improved by addition of a composition consisting of petrolatum, magnesium carbonate and sodium silicate.[59] Clogging of the printing machine is said to be prevented if the ink is modified with manganese dioxide.[60] Silica[61] or Bologna chalk also are mixed into inks, inhibiting sticking to the tympan sheet.[62] Chalk also increases opacity and "taking power" when printed on non-absorbent surfaces such as Cellophane, metal foil or parchment.[63] Barium sulphate, also employed as a substrate for dyes, lowers oil absorption (particularly of carbon blacks)[64] and increases covering power (for lead pigments).[65]

In offset printing the ink occasionally may mix with the dampening water and thus become thin. Addition of a small proportion of magnesia and starch in such instances is reported to give the ink a firmer body.[66] Addition of starch also prevents offset after printing but decreases the gloss of the ink.[67] However, some investigators report that offset is increased by starch and that resistance to rubbing is diminished when the ink is printed on glazed paper.[68] Mixtures of gum arabic, gum tragacanth, water and alcohol are often used to overcome offset,[69] as well as compositions of mutton tallow, starch, paraffin oil and citronella oil.[70] Other compounds serving the same purpose consist of mixtures of calcium carbonate, zinc oxide, barium sulphate and rapeseed oil.[71] Beeswax or wool fat are employed especially for overprint inks.[72] It is reported that the color of the print may be intensified and better permanency secured by addition of starch, water and formic acid to a printing ink. Formic acid may be replaced by oxalic, phosphoric or silicic acid.[73]

Many types of materials have been proposed as agents to increase the viscosity of printing inks. One example comprises a mixture of approximately 45 per cent petrolatum, 10 per cent oil of turpentine, 35 per cent naphtha, and 10 per cent paraffin wax. The formation of clear and durable prints is reported when this product is incorporated to an extent of from 30 to 50 per cent by weight in ink.[74] Rosins from the

[59] W. N. Haas and H. C. Young, U. S. P. 1,273,361, July 23, 1918; *Chem. Abs.*, 1918, 12, 2056.

[60] British P. 270,671, 1926, to Chem. Fabrik auf Aktien vorm. E. Schering; *Chem. Abs.*, 1928, 22, 1696; *Brit. Chem. Abs.* **B**, 1928, 24.

[61] H. N. Potter, U. S. P. 908,132 and 908,133, Dec. 29, 1908, to G. Westinghouse; *Chem. Abs.*, 1909, 3, 960. M. Wolff, British P. 4,419, 1914; *Chem. Abs.*, 1915, 9, 2155.

[62] The sheet of paper or cloth placed between the impression surface (platen or cylinder) and the paper to be printed.

[63] *Deutscher Drucker*, 1937, 44, 78; *Rev. Paint, Colour, Varnish*, 1938, 11, 24.

[64] H. Wolff and G. Zeidler, *Farben-Chem.*, 1935, 6, 127; *Chem. Abs.*, 1935, 29, 8363; *Brit. Chem. Abs.* **B**, 1935, 561.

[65] K. Würth, *Farben-Ztg.*, 1938, 43, 279; *Rev. Paint, Colour, Varnish*, 1938. 11, 84.

[66] *Lith. Offset Print.*, 1937, 33, 140; *Rev. Paint, Colour, Varnish*, 1937, 10, 341.

[67] R. E. Hunt, *Am. Ink Maker*, 1934, 12 (11), 27; *Rev. Paint, Colour, Varnish*, 1934, 7, 456.

[68] *Papier-Ztg.*, 1938, 63, 99; *Rev. Paint, Colour, Varnish*, 1938, 11, 107.

[69] R. A. Habermaier, U. S. P. 2,101,999, Dec. 14, 1937, to The De Vilbiss Co.; *Am. Ink Maker*, 1938, 16 (2), 37; *Chem. Abs.*, 1938, 32, 1023. Canadian P. 367,893, 1937; *Chem. Abs.*, 1937, 31, 7152.

[70] C. H. Rackle, U. S. P. 1,272,092, July 9, 1918; *Chem. Abs.*, 1918, 12, 2056.

[71] L. L. Farkas, U. S. P. 1,439,623, Dec. 19, 1922; *Chem. Abs.*, 1923, 17, 888.

[72] E. A. Kilheffer, *Am. Pressman*, 1938, 48 (2), 19; *Rev. Paint, Colour, Varnish*, 1938, 11, 109. For overprint varnishes see Chapter 14.

[73] M. Hasler, Swiss P. 74,852, 1917; *Chem. Abs.*, 1917, 11, 3450.

[74] A. Vecchioni, Italian P. 285,531, 1929; *Chem. Zentr.*, 1936, 107 (2), 1806; *Rev. Paint, Colour, Varnish*, 1936, 9, 816.

Siberian larch are also used. Pulverized oil cakes or extraction residues are said to be employed as thickening agents after freeing them from sand, alkali, and husks.[75]

Chlorinated biphenyls have also found application as materials to increase viscosity. These compounds, mainly 2- and 4-chlorobiphenyl, and closely-related substances, the "Arochlors" (chlorinated phenyl compounds) are non-drying and show no appreciable tendency to oxidize in the air. An increase in chlorine content results in higher viscosity and a darkening in color from water-white to amber.[76]

Dispersions of water-insoluble higher alcohols, such as cetyl or hexadecyl alcohol, in water serve also as thickening agents.[77] Stability of the dispersions is secured by addition of salts of fatty carboxylic or sulphonic acids. The viscosity of carbohydrate ethers may be reduced to make them applicable as thickening agents for inks. The ethers are treated with a substance containing molecular oxygen, such as air or an agent which yields oxygen in the nascent form, such as potassium permanganate, chlorate or nitrate, or hydrogen peroxide.[78]

Plasticizers. In some cases, addition of certain materials to the ink is necessary to increase flexibility and adhesion. This is particularly important for metal coatings. Castor oil has been used for this purpose for a long time, as well as other non-drying oils. Mixtures of soft resins with solvents (preferably turpentine), mineral oil, and driers may be used as plasticizers.[79]

Numerous other organic compounds, mostly esters, have been introduced as plasticizing agents. Examples are tricresyl phosphate and butyl lactate. Also, utilization of esters of maleic acid, such as dimethyl-, diethyl-, and dibutylmaleate has been proposed.[80] Dibutylmaleate has a low vapor pressure, and is a solvent for cellulose acetate. These properties make the dibutyl ester applicable as a plasticizer in printing inks containing the above cellulose derivative. Some investigators employ glycerol, which also may be substituted by sorbitol or its dehydrated products.[81] Certain of the terpenic ethers have been proposed as plasticizers. The ethers are synthesized by heating an alcohol, such as methanol or ethylene glycol, with p-toluenesulphonic acid, benzenesulphonic acid or phenolsulphonic acid, and an unsaturated terpene, such as α-pinene, α-terpinene or dipentene. After the synthesis has taken place, (usually in from 30 to 70 hours), the product is washed with water to remove the unreacted alcohol. Two layers result, one containing the

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[75] W. G. Leitess, Russian P. 48,131, 1935: *Chem. Zentr.*, 1937, 108 (2), 296; *Rev. Paint, Colour, Varnish*, 1937, 10, 262.

[76] C. H. Penning, *Ind. Eng. Chem.*, 1930, 22, 1180; *Chem. Abs.*, 1931, 25, 561.

[77] French P. 776,477, 1935; *Chem. Abs.*, 1935, 29, 3430; British P. 443,365, 1936; *Brit. Chem. Abs.* B, 1936, 492; *Rev. Paint, Colour, Varnish*, 1936, 9, 170; *Chem. Abs.*, 1936, 30, 5333. Both patents to Kammgarnspinnerei Stöhr & Co. A.-G.

[78] H. F. Oxley, E. B. Thomas, and J. Downing, British P. 479,445, 1938; *Chem. Abs.*, 1938, 32, 5001.

[79] A. M. F. Antonio, German P. 620,976, 1935; *Chem. Zentr.*, 1936, 107 (1), 1726.

[80] *Am. Ink Maker*, 1938, 16 (7), 37.

[81] J. H. Frydlender, *Rev. prod. chim.*, 1937, 40, 129; *Chem. Abs.*, 1937, 31, 4012; French P. 705,428, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 5179.

original terpene and the other the terpenyl methyl or ethyl ether with traces of other compounds.[82]

Usually a small percentage of a plasticizing agent will produce the desired effect, although in some cases a relatively large proportion, compared with the plasticizable substance, is added. In printing on foils, films, or other surfaces made of cellulose derivatives, the required amount of plasticizer incorporated in inks containing a cellulosic or resinous plasticizable base, such as cellulose acetate or a phenol-aldehyde resin, is reported to be at least 5 times, and in some cases 10 to 20 times the weight of plasticizable substance.[83]

ANTISKINNING AGENTS AND ANTIOXIDANTS

A drying oil, on standing for a certain time with access of air to its surface, undergoes a change which begins with the formation of a skin on the surface and finally results in the gelatinizing and subsequent hardening of the whole body of the oil. This phenomenon, *i.e.*, the film formation or "drying" of the oil, although not yet fully understood, may be explained by polymerization processes, involving certain degrees of oxidation.[84] The final consistency and the time of drying depend upon the molecular structure of the oil, to a great extent upon the treatment of the latter (primarily refining and bodying processes) and upon its content of certain catalysts incorporated to promote or to retard drying. It has been shown that drying is accompanied by decrease of the iodine value [85] and usually by an increase in refractive index. Changes in these properties therefore afford an indication of the rate of oxidation.

Although the formation of a solid film is the purpose for using drying oils in printing-ink vehicles, skinning and gelation of inks are very undesirable phenomena when they take place during storage of the ink. As mentioned above, drying may be promoted or retarded by the addition of certain catalyzers. To accelerate drying, oxidation catalysts or driers [86] (usually metallic soaps) are incorporated in the oil. Retardation is secured by catalysts which inhibit oxidation for a certain time or by solvents which exert a dispersing effect [87] on a newly formed skin of oil. The latter types of compounds are known as antioxidants or antiskinning agents, respectively. Solvents having a dispersing effect on solidifying oil surfaces include methylcyclohexanol and dipentene.[88]

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[82] French P. 818,787, 1937, to the Hercules Powder Co.; *Rev. Paint, Colour, Varnish*, 1938, 11, 206; *Chem. Abs.*, 1938, 32, 2653.

[83] W. H. Moss, British P. 456.898, 1936, to British Celanese Ltd.; *Brit. Chem. Abs.* B, 1937, 159; *Chem. Abs.*, 1937, 31, 2457; See also Chapter 14 for special inks used in printing on Celluloid, Cellophane and other analogous cellulosic material.

[84] T. F. Bradley, *Ind. Eng. Chem.*, 1937, 29, 440; *Chem. Abs.*, 1937, 31, 5184.

[85] J. Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 5th Ed., Macmillan and Co., Ltd., London, 1914.

[86] These are discussed in Chapter 4.

[87] L. Light and T. Barry, *Official Printing Ink Maker*, 1934, 4 (3), 10; *Chem. Abs.*, 1934, 28, 3916; *Paint Manuf.*, 1933, 3 (12), 346; *Rev. Paint, Colour, Varnish*, 1933, 6, 322.

[88] L. Light and T. Barry, *loc. cit.* H. A. Gardner and G. G. Sward, *Am. Paint Varnish Mfr's. Assoc. Circ.* No. 400, 1931; *Chem. Abs.*, 1932, 26, 607; *Brit. Chem. Abs.* B, 1932, 153; *Rev. Paint, Colour, Varnish*, 1931, 4, 271.

The use of antioxidants in printing inks and other compositions containing drying oils is relatively new. Those substances which exhibit antioxidative properties in most instances are phenolic or amino- bodies or their derivatives. Intensive study of such compounds began with that on the inhibiting effect of hydroquinone upon the oxidation of acrolein.[89] The effect of antioxidants on certain drying oils and on some of the semi-drying and non-drying oils has been determined by various methods. The latter depend in some instances upon observing changes in the physical and chemical properties of the oil occurring during oxidation, as, for example, decrease in iodine value and increase of refractive index.

Wagner and Brier [90] utilized the changes in these properties to evaluate the effect of certain phenols and aromatic amines on the oxidation of linseed oil. The phenolic substances used in these experiments were hydroquinone, resorcinol, pyrogallol, and α- and β-naphthol. The experimental procedure consisted in blowing carefully dried air through raw linseed oil, with and without various concentrations (0.00001 to 0.02 per cent by weight) of the dissolved antioxidant. The tests were carried out at approximately room temperature (30° C.) and at 100° C. They found that an extremely low concentration (0.00001) of hydroquinone did not prolong the induction period [91] at 100° C., but effectively inhibited oxidation at 30° C. in extending the induction period from 315 to 486 hours (see Table 18). A minimum concentration of 0.0001 per cent of hydroquinone was necessary at 100° C. to retard oxidation effectively, apparently due to the higher normal rate of oxidation at this temperature, *i.e.*, the rate at which linseed oil is oxidized without an antioxidant. At

Table 18.—Induction Period as a Function of the Proportion of Hydroquinone in Linseed Oil at 30° C.

	Proportion of Antioxidant Present in Linseed Oil									
	None		1:100,000		1:25,000		1:10,000		1:1000	
Time (hours)	Iodine No.	Refr. Index	Iodine No.	Refr. Index	Iodine No.	Refr. Index	Iodine No.	Refr. Index	Iodine No.	Refr. Index
0	184.5	1.477	182.5	1.477	182.4	1.477	183.0	1.477	182.3	1.4785
315	184.0	1.4795	182.0	1.4799	183.2	1.479	183.0	1.477	182.9	1.479
382	171.3	1.4795								
406	165.4	1.4805								
486	138.8	1.4857	181.0	1.479	[b]		[b]		[b]	
542	122.3[a]	1.4882[a]	175.2	1.4805						
645			146.1	1.4852						
695			130.2[a]	1.4873[a]	183.0	1.479				
972					156.7	1.4835				
987					156.2[c]	1.4838[c]	183.5	1.478		
3000							183.9[c]	1.4795[c]	183.0	1.4795
5250									182.1[d]	1.4801[d]

[a] Samples gelled.
[b] No apparent change.
[c] Samples consumed by repeated withdrawals for testing.
[d] Sample discontinued.

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[89] C. Moureu and C. Dufraisse, *Compt. rend.*, 1922, 174, 258; G. E. Greenbank and G. E. Holm, *Ind. Eng. Chem.*, 1934, 26, 243.

[90] A. M. Wagner and J. C. Brier, *Ind. Eng. Chem.*, 1931, 23, 40, 662; *Chem. Abs.*, 1931, 25, 1105, 3852; *Brit. Chem. Abs.* B, 1931, 401, 727; *Rev. Paint, Colour, Varnish*, 1931, 4, 15, 186.

[91] The initial period of drying, during which no perceptible physical or chemical changes take place in the oil.

higher concentrations the duration of the induction period varied directly within certain limits with the proportion of antioxidant in the oil. The proportionateness was found to be nearly quantitative at concentrations of between 1:10,000 and 1:800 as regards hydroquinone, at 100° C. Within this range, after the end of the induction period, the rate of oxidation, it was noted, rises almost abruptly to that of the oil without inhibitor, and the oxidation curves (change of iodine number with time) become very nearly parallel to that of linseed oil containing no antioxidant. Further, in this instance, the influence of temperature on the rate of oxidation can be seen from the fact that while at 100° C. a 1:1000 concentration of hydroquinone caused an induction period of about 10 hours, at 30° C. with the same concentration this period was prolonged to more than 8 months.

At 100° C. pyrogallol effectively inhibited oxidation at a concentration of 1:1000, as did also α-naphthol, 1 part in 250. Resorcinol was found to have only slight effect, and β-naphthol to be ineffective at 100° C. The rate of oxidation immediately after the induction period increased in the same manner as noted in the tests with hydroquinone, except in the case of samples containing α-naphthol. In the latter instances an exceedingly high rate of oxidation was observed. This was probably due to gradual evaporation of the antioxidant from the oil during the induction period.

From a comparison of the relative effects of the phenols studied these antioxidants can be arranged in the following order of decreasing effect: hydroquinone, pyrogallol, α-naphthol.

Investigations by Wagner and Brier on aromatic amines showed that diphenylamine, α-naphthylamine and phenyl-β-naphthylamine do not produce an induction period at 100° C. even at a concentration of 1:100. The oxidation curves with the amines parallel those of non-inhibited linseed oil, although the iodine numbers corresponding to same periods of air-blowing are shifted toward somewhat higher values.

m- and *p*-Phenylenediamine were found to be very effective antioxidants at 100° C. at a concentration of 1:100. The effect is reported greater than that of an equal concentration of hydroquinone.

A difference in activity appeared when antioxidants were added after the termination of the induction period instead of being present in the oil prior to oxidation. Under such conditions hydroquinone inhibited oxidation at 30° C. but not at 100° C. On the other hand, *m*- and *p*-phenylenediamine were effective at 100° C. only. Other antioxidants, except α-naphthylamine, which produced a slight retarding effect at 100° C., and phenyl-β-naphthylamine, somewhat effective at 30° C., did not bring about any change in the rate of oxidation after the end of the induction period.

The fact that hydroquinone inhibited oxidation at a lower temperature, although not as effectively as when added before the induction period was started, indicates that if a velocity of oxidation above a critical value has been reached, antioxidants do not exert an inhibiting effect. The behavior of *m*- and *p*-phenylenediamine in the last-mentioned tests shows that decomposition products of the latter compounds are effective. This opinion is substantiated by the tarry black color imparted to linseed oil containing phenylenediamine and subjected (at 100° C.) to blowing with air. No similar occurrence of color was observed at a considerably lower temperature.

By oxidizing a mixture of raw linseed oil (with an iodine number of about 190), partially oxidized oil, and an antioxidant, a shortening of the induction period was observed. The proportion in which the duration of the induction period decreased was dependent upon the prior treatment given the partially oxidized linseed oil, the percentage of the latter in the mixture and the proportion of antioxidant present.

Greenbank and Holm[92] investigated the effect of di- and trihydric phenols, certain other aromatic compounds and aliphatic acids, and of certain natural pigments (occurring in plant and animal fats) on cottonseed oil. The experimental method consisted of storing the oil, after adding 0.01 per cent of the antioxidant, for 10 days, then adding potassium iodide to the sample acidified with acetic acid dissolved in trichloromethane and titrating the liberated iodine with a solution of sodium thiosulphate. In this manner they determined the amount of peroxides formed in the oil.

The antioxidant has been characterized by the "protective factor," *i.e.*, the proportion of millimoles of peroxide per kilogram in untreated oil to that in the oil containing an antioxidant. No inhibiting action is designated by a protective factor of 1.

Of the phenols studied, hydroquinone, and pyrocatechol, pyrogallol, and hydroxyhydroquinone have been found effective, the respective protective factors being 3.7, 2.0, 3.6, and 3.6. Resorcinol and phloroglucinol exhibited protective factors of only 1.1 and 1.0, respectively, or, in other words, no antioxidative effect in accordance with the results obtained by Wagner and Brier. The authors give the explanation that *o*- and *p*-dihydric and 1,2,3- and 1,2,4-trihydric phenols are capable of forming quinones, thus building up oxidation-reduction systems at the expense of the peroxides formed by the oil. Phenol was studied also, but no oxidation-inhibiting effect was observed.

Phthalic acid is reported to be an effective antioxidant as well as maleic acid, but not the stereoisomeric form of the latter, fumaric acid. The effect of maleic acid has been investigated with various oils. The results are not very different, with a protective factor of 3.0 for linseed

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[92] G. E. Greenbank and G. E. Holm, *Ind. Eng. Chem.*, 1934, 26, 243; *Chem. Abs.*, 1934, 28, 2205; *Brit. Chem. Abs.* B, 1934, 411.

oil and 3.1 for cottonseed oil. However, for corn oil a protective factor of 5.3 was obtained, probably due to the smaller tendency of this oil to undergo autoxidation.

Of the natural pigments studied, quercitin, a flavone derivative, showed some activity as an antioxidant.

An extensive research on antioxidants, by Tanaka and Nakamura,[93] involved the action of phenols and derivatives, aromatic amines (also with driers present), antioxidants for rubber, aniline and some of its derivatives, alcohols, ethers, ketones, and terpenes on linseed oil. The results obtained with phenols also showed that pyrogallol, hydroquinone and pyrocatechol are good inhibitors. However, the effect of pyrogallol proved stronger than that of hydroquinone (in a concentration of 1:100). Cresols also have been found effective, though their effectiveness decreases in the order, *o*-, *p*- and *m*-cresol. The three isomeric mononitrophenols exhibited almost equal activities. With regard to chlorophenols, *o*-monochlorophenol was observed to exert a slight inhibiting effect. The experimental method in each instance comprised determination of the iodine value of the oil, with and without dissolved inhibitor, after exposing it to sunlight for about 39 hours.

The activity of α- and β-naphthol at various temperatures has been studied[94] by the same method but in absence of ultraviolet rays. Concentration of the antioxidant in linseed oil was varied from 0.5 to 5 per cent. With α-naphthol the iodine value remained unchanged at room temperature for a period of 78 days. Under the same condition β-naphthol was slightly less effective. At higher temperatures, particularly at 100° C. and 150° C., the difference between the action of these two naphthols was still more conspicuous. At these temperatures, however, the effectiveness of either one is not permanent, probably on account of their volatility.

It has been reported that oxidation-inhibiting and promoting effects of certain compounds are closely related, depending on experimental conditions.[95] This is indicated by the observations that aniline, xylidine, *p*- and *o*-toluidine and *p*- and *o*-chloroaniline showed both anti- and pro-oxidative effects. *m*-Toluidine proved an effective antioxidant and *o*-nitroaniline a less active inhibitor for linseed oil. The tests were made by determining specific gravity, refractive index, viscosity and iodine value of linseed oil before and after exposure to sunlight, the concentration of the antioxidant tested being 0.01 mol in 100 grams of oil.

The influence of phenolic ethers and ketones, of terpenic alcohols and ketones, and of some aromatic acids has also been investigated.[96] Deriva-

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[93] Y. Tanaka and M. Nakamura, *J. Soc. Chem. Ind., Japan*, 1930, 33, 126; *Chem. Abs.*, 1930, 24, 3388; *Brit. Chem. Abs.* B, 1930, 776.

[94] Y. Tanaka and M. Nakamura, *J. Soc. Chem. Ind., Japan*, 1930, 33, 107; *Chem. Abs.*, 1930, 24, 2906; *Brit. Chem. Abs.* B, 1930, 776.

[95] Y. Tanaka and M. Nakamura, *J. Soc. Chem. Ind. Japan*, 1931, 34, 405; *Chem. Abs.*, 1932, 26, 862; *Brit. Chem. Abs.* B, 1932, 29.

[96] Y. Tanaka and M. Nakamura, *J. Soc. Chem. Ind. Japan*, 1932, 35, 81; *Chem. Abs.*, 1932, 26, 2610; *Brit. Chem. Abs.* B, 1932, 1125.

tives of dihydric phenols such as eugenol, isoeugenol and safrole (the latter after being exposed to air), acted as strong antioxidants. Benzoic and salicylic acid slightly accelerated oxidation.

Various antioxidant preparations used for rubber have been found effective in inhibiting oxidation of linseed oil.[97] Antioxidative action was measured by determining the increase in weight of linseed oil. For example, the preparations V.G.B. (acetaldehyde-α-naphthylamine) and Neozone Standard (a mixture of phenyl-α-naphthylamine, *m*-toluenediamine and stearic acid) showed strong activity.

The opinion has been advanced that antioxidative effect is due more to certain arrangements in the molecule of differently active groups of atoms than to the proportion of inhibitor employed. These groups, which may be classified as antioxidant, include such radicals as phenyl-, naphthyl-, hydrazine and cyanide and those designated as auxoantioxygenophoric, such as the amino-, hydroxyl-, alkyl-, methoxy- and carboxyl groups. Oxidation is promoted by oxygenophore groups, *e.g.*, chloro- and nitro- combinations.

It is reported that antioxidants effectively counteract driers, although the action of the latter is not entirely overcome. Experiments with fatty-acid soaps or resinates of lead or manganese as driers (0.2 per cent metal content in linseed oil) and pyrocatechol, α-naphthol and β-naphthylamine as antioxidants (0.5 per cent),[98] showed an extended induction period as compared with that for driers alone. The order of activity was found to be the same with and without driers, namely, β-naphthylamine, pyrocatechol and α-naphthol, in decreasing effect. Similar results were obtained by Hilpert and Niehaus.[99] They studied the action of phenol, thymol, cresols and β-naphthol on linseed and tung oil films during drying in the absence and presence of cobalt, manganese and lead driers. The amount of antioxidant was found to diminish gradually during drying. Moore's researches [100] on the effect of antioxidants upon oxidation of linseed oil confirm the previously mentioned results regarding the effect of α- and β-naphthol (the former having the stronger effect) and toluidines (the meta-compounds being the most active), as well as that of nitraniline. Similarly, the action of driers was not completely destroyed by the antioxidant.

It has been suggested that skinning during storage of coating compositions containing a drier can be prevented by incorporating creosol (2-methoxy-4-methylphenol) in a concentration of about 1/3 to 1 per

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[97] Y. Tanaka and Sabuo Nakamura, *J. Rubber Soc., Japan*, 1930, **2**, 176; *Chem. Abs.*, 1931, **25**, 3852; *Brit. Chem. Abs.* **B**, 1931, 1105; Y. Tanaka and M. Nakamura, *J. Soc. Chem. Ind., Japan*, 1930, **33**, 129; *Chem. Abs.*, 1930, **24**, 3388; *Brit. Chem. Abs.* **B**, 1930, 776.

[98] Y. Tanaka and M. Nakamura, *J. Soc. Chem. Ind., Japan*, 1930, **33**, 127; *Chem. Abs.*, 1930, **24**, 3388; *Brit. Chem. Abs.* **B**, 1930, 776.

[99] R. S. Hilpert and C. Niehaus, *Angew. Chem.*, 1934, **47**, 86; *Chem. Abs.*, 1934, **28**, 2549; *Brit. Chem. Abs.* **B**, 1934, 333.

[100] C. L. Moore, *Dyer*, 1934, **72**, 651; 1935, **73**, 18; *Chem. Abs.*, 1935, **29**, 2621; *Brit. Chem. Abs.* **B**, 1935, 1003; *Rev. Paint, Colour, Varnish*, 1935, **8**, 225; *Chem. Zentr.*, 1935, **106** (1), 2105.

cent.[101] Secondary amines produced by the reaction of 2,4-diphenyl aniline or its hydrochloride with a phenol or alcohol have antioxidant properties. Among the alcohols and phenolic substances which may be used are α- and β-naphthol, phenol, chlorophenol, cresol, methanol, ethanol, propanol and benzyl alcohol.[102]

Induction period of various fats was prolonged about 1.7 times by lecithin prepared from soybeans. A more prolonged induction could be obtained after the lecithin was purified by precipitating it with acetone.[103]

A mixture of an anti-gelling agent, such as dipentene, and an antioxidant, *e.g.*, hydroquinone, is said to be more effective than an antioxidant alone.[104]

The rate of oxidation of films of linseed oil containing an antioxidant was measured directly by Stern and Puffett.[105] Their method of obtaining a thin oil film was to dip a piece of iron gauze into the oil. Afterwards the gauze coated with the oil film was exposed at about 100° F. to an enclosed atmosphere of humid oxygen. The absorption of oxygen was estimated by the decrease in pressure as indicated by a mercury manometer.

The kinetics of drying of oils was studied by Lederer.[106] From his results he concluded that the effect of antioxidants is proportional to their concentration, up to a certain limit, above which their activity decreases with an increase in proportion. However, the quantity of absorbed oxygen at the end of the oxidation is said to be independent of the length of time required for complete oxidation.

LIVERING

Apparently little is known concerning the actual causes of the phenomenon known as "livering," which is the flocculation and coagulation of inks and paints as a result of the gelatinization of the vehicle. Some investigators claim that the acid value of the varnish oil has no bearing on the tendency of ink to liver, while others contend that the tendency is directly proportional to the acid number of the vehicle. Wolfe [107] points out that all acids but sulphanilic (*p*-aminobenzenesulphonic acid) cause livering; sulphanilic acid retards livering of inks, as do calcium hydrox-

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[101] J. K. Hunt and G. H. Latham, U. S. P. 1,948,582, Feb. 27, 1934; *Brit. Chem. Abs.* **B**, 1934, 1070. Canadian P. 329,223, 1933; *Chem. Abs.*, 1933, 27, 1530.

[102] M. M. Levine, U. S. P. 2,111,863, March 22, 1938, to Monsanto Chemical Co.; *Chem. Abs.*, 1938, 32, 3667; *Rev. Paint, Colour, Varnish*, 1938, 11, 294.

[103] E. W. Kochenderfer and H. G. Smith, *Proc. Iowa Acad. Sci.*, 1932, 39, 169; *Chem. Abs.*, 1934, 28, 6583; *Brit. Chem. Abs.* **A**, 1935, 43; *Rev. Paint, Colour, Varnish*, 1934, 7, 466.

[104] L. Light and T. H. Barry, *Official Printing Ink Maker*, 1934, 4 (3), 10; *Chem. Abs.*, 1934, 28, 3916; *Paint Manuf.*, 1933, 3, 346; *Rev. Paint, Colour, Varnish*, 1935, 8, 122.

[105] H. J. Stern and W. Puffett, *Trans. Inst. Rubber Ind.*, 1932, 8, 216; *Chem. Abs.*, 1933, 27, 2060; *Brit. Chem. Abs.* **B**, 1933, 79; *Rev. Paint, Colour, Varnish*, 1933, 6, 32.

[106] E. L. Lederer, *Petroleum Age*, 1935, 31 (44), 1; *Chem. Abs.*, 1936, 30, 2734; *Brit. Chem. Abs.* **B**, 1936, 10; *Öle, Fette, Wachse*, 1936 (1), 5; *Chem. Abs.*, 1936, 30, 4703; *Brit. Chem. Abs.* **B**, 1936, 27; *Farben-Ztg.*, 1935, 40, 1144; *Rev. Paint, Colour, Varnish*, 1935, 8, 531.

[107] H. J. Wolfe, *Am. Ink Maker*, 1934, 12 (8), 13; *Rev. Paint, Colour, Varnish*, 1934, 7, 376; *Chem. Abs.*, 1934, 28, 7559.

ide, heavy-bodied mineral oils, petroleum jelly, and Venice turpentine. Water absorbed by the vehicle increases the livering tendency. Experiments by Wolfe showed that triethanolamine and calcium and manganese gluconates are unsatisfactory as retarding agents.

Those who do not admit the importance of the acid value of the vehicle in livering claim that the formation of soaps is partially the cause of thickening. However, more emphasis has been placed upon the structure, electric charge, and surface activity of the pigment particles and their power of solvation. The presence of silicic acid is thought to cause livering to some extent.[108] Addition of aluminum naphthenate as drier was stated to increase stability of inks and decrease occurrence of livering.[109]

If a coating of a salt or an organic substance is formed on each pigment particle, the livering tendency is stated to be reduced. Oxalic acid, tannin, albumin, calcium glycerophosphate, phosphoric acid, various phosphates, and aluminum sulphate are some of the materials which have been suggested.[110] Livering of basic pigments in the presence of alkyd resins is said to be reduced by addition of malic acid.[111] Inks can be prevented from livering and livered inks brought back to workable conditions when linseed fatty acids are incorporated with these materials.[112]

The density of an ink may be lowered by incorporation of small quantities of water-soluble aliphatic compounds having a specific gravity below 1. Acetone and methanol have been utilized for this purpose.[113] A thinner applicable to printing inks consists of kerosene containing rosin, varnish and a double silicate of magnesium and nickel.[114] Other thinners are terpineol or terpinyl acetate (especially for rotogravure, offset and collotype [115] inks). They are said to prevent discoloration of white pigments, in contrast to many other thinning agents.[116] Terpenic ethers, formed by reaction of unsaturated terpenic alcohols with ethylene glycol in the presence of a sulphonic acid (*e.g.*, benzene- or phenolsulphonic acid), are solvents and act as softening agents.[117]

Special types of resins may be employed as modifiers when "dull" inks are required. A new type of "flat gum" [118] is reported to have been

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[108] S. W. Jakubowicz and S. W. Kirsamowa, *Kolloid-Z.*, 1933, 65 (3), 333; *Rev. Paint, Colour, Varnish*, 1934, 7, 14; P. E. Marling, *Am. Paint Varnish Mfrs. Assoc. Sci. Sec. Circ.*, 1927, 319, 535; *Rev. Paint, Colour, Varnish*, 1928, 1, 7; *Chem. Abs.*, 1928, 22, 2069; J. Mattiello and L. T. Work, *Natl. Paint, Varnish, Lacquer Assoc. Circ.*, 1936, 502, 37; *Rev. Paint, Colour, Varnish*, 1936, 9, 164; *Chem. Abs.*, 1936, 30, 3665; L. J. Venuto, *Official Digest Federation Paint & Varnish Production Clubs*, 1936, 8 (158), 256; *Rev. Paint, Colour, Varnish*, 1936, 9, 358; H. Wagner, *Kolloid-Z.*, 1932, 60 (3), 307; *Rev. Paint, Colour, Varnish*, 1932, 5, 256; *Chem. Abs.*, 1932, 26, 6161.

[109] A. R. Thornton, *Am. Ink Maker*, 1935, 13 (5), 19; *Chem. Abs.*, 1936, 30, 3665; *Brit. Chem. Abs.* B, 1935, 684.

[110] A. Chwala, French P. 788,001, 1935; *Chem. Abs.*, 1936, 30, 1594.

[111] C. Bogin, U. S. P. 2,092,300, Sept. 7, 1937, to Commercial Solvents Corp.; *N. P. V. L. Abs.* 1937, 51, 167; *Chem. Abs.*, 1937, 31, 8, 8232.

[112] T. F. Bradley, U. S. P. 1,478,017, Dec. 18, 1923; *Chem. Abs.*, 1924, 18, 759.

[113] French P. 788,383, 1935, to Encres Antoine; *Chem. Abs.*, 1936, 30, 1595.

[114] J. E. Rhodes, U. S. P. 1,553,914, Sept. 15, 1925; *Chem. Abs.*, 1925, 19, 3605.

[115] For description of the various printing processes, see Chapter 1.

[116] British P. 472,938, 1937, to Kemitype Ltd.; *Chem. Abs.*, 1938, 32, 1955; *Brit. Chem. Abs.* B, 1938, 693.

[117] French P. 818,787, 1937, to Hercules Powder Co.; *Chem. Abs.*, 1938, 32, 2653.

[118] *Am. Ink Maker*, 1938, 16 (1), 25.

developed for this purpose. Hiroe dammar, a fossil Borneo resin, is also applicable for matte inks.[119] This resin also is said to provide adhesion, especially in nitrocellulose vehicles.

Adhesion. Good adhesion of inks on surfaces such as Cellophane, Glassine, Celluloid and other non-absorbent surfaces may be accomplished by addition of materials which have some solvent powers on such surfaces, *e.g.*, a small quantity of a Celluloid solvent is incorporated in the ink.[120] Materials which roughen the surface, *e.g.*, acetone or amyl alcohol, also are recommended.[121] The scratch resistance of ink is said to be improved by the addition of butyl stearate[122] and also by the use of a solid finely ground hydro- or oxy-cellulose in the ink.[123]

Additive Agents Accelerating Drying. Besides the drier catalysts as discussed in Chapter 4 some modifying agents are reported to increase the drying power of inks. A mixture of stearin, white wax, lard, boiled together and incorporated in boiled oil and potassium bromide is recommended.[124] By incorporating semi-liquid, higher alcohols in drying-oil inks, the weathering resistance of the latter is reported to be increased. The higher alcohols may be obtained by oxidizing solid or liquid paraffins of high molecular weight or by reducing high-molecular fats.[125] An addition of sodium amyl sulphate, in a proportion of about 0.25 per cent by weight, is said to prevent smearing and to minimize the tendency of ink to accumulate on type plates and rollers. Also this sulphate has been reported to increase speed of drying.

Miscellaneous Compounds

A compound of sebates or oleates of organic colors with alkali salts of sulphonated aromatic benzyl bases is reported to "shade off" printing inks. The compound, which is soluble in water, benzene, fats and oils, but not in ether, is obtained by mixing the water-insoluble dyestuff-salt with an alkali salt of the sulphonic acid of an aromatic benzyl compound.[126] In addition to the usual constituents, *i.e.*, a drying oil and oil-soluble resinous matter, with or without driers, a small proportion of an oil-swellable organic salt, *e.g.*, a soap of a metal of the magnesium, alkaline earth or earth metal group is added to glossy overprint varnishes.

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[119] H. Kemner, *Farben-Ztg.*, 1936, 41, 586; *Chem. Abs.*, 1936, 30, 6220; *Brit. Chem. Abs.* B, 1936, 751.

[120] G. Pundsack, Canadian P. 343,266, 1934; *Chem. Zentr.*, 1935, 106 (2), 443. For discussion of printing on cellulosic surfaces, see Chapter 14.

[121] *Papier-Ztg.*, 1937, 62, 1142.

[122] *Chem. Trade J.*, 1933, 93, 156.

[123] German P. 527,453, 1926, to Ferdinand Sichel Komm.-Ges.; *Chem. Abs.*, 1931, 25, 4724; *Rev. Paint, Colour, Varnish*, 1931, 4, 231.

[124] P. Brownsey, G. Madders, J. A. Grimshaw and H. Redfearn, British P. 322,873, 1928; *Chem. Abs.*, 1930, 24, 2903; *Brit. Chem. Abs.* B, 1930, 338.

[125] H. Wolf, F. Drexler and H. Beller, German P. 610,600, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 6083; *Rev. Paint, Colour, Varnish*, 1935, 8, 196; German P. 649,108, 1937, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, 31, 8964; *Rev. Paint, Colour, Varnish*, 1937, 10, 405.

[126] B. Homolka and J. Erber, U. S. P. 839,590, Dec. 25, 1906, to Farbweke vorm, Meister, Lucius & Bruning; *Chem. Abs.*, 1907, 1, 657.

Also oil-swellable zinc salts or soaps may be used.[127] To prevent the removable of sulphur from the rubbered cloth of offset machines,[128] a liquid consisting of a solution of sulphur in aniline or its homologs has been recommended, to which furfural may be admixed. This mixture is added to the ink.[129] Opacity, smoothness and durability of an ink may be improved by addition of titanium dioxide coalesced with sulphate particles.[130] A medicated ink contains nutgall, fir balsam, extract of hemlock, beeswax, pine balsam and carbolated Vaseline in addition to varnish and pigment, and may be used for printing on paper towels.[131] Objectionable odors of inks are difficult to remove. Exposure to as much fresh air as possible has been recommended.[132] Scheiber [133] suggests the use of a vehicle consisting of or comprising odorless residues from the vacuum distillation of castor oil. Small quantities of materials with pleasant odors, *e.g.*, perfumes, are sometimes admixed with the inks.

Printing ink vehicles may be extruded after mixing with collagen,[134] polymerization products of distillates derived from unvulcanized rubber,[135] creosote oil with rosins [136] or tar oil dispersions of coal, wood, straw, cotton, peat or mixtures of these materials.[137] Pulped peat, with or without other black pigments, is reported to be useful in low-priced inks. The peat is prepared by boiling it with a viscous solution of sodium silicate or other alkaline substance, which causes the peat fibers to separate. A vegetable black may be admixed during the latter procedure. The separated and pulped peat is then filtered and the residue incorporated with a vehicle of a drying oil and resin.[138]

The "crawling" of ink on a glass or ceramic surface is stated to be prevented by the addition of approximately 0.01 per cent of benzene-azo-benzene-azo-β-naphthol to an oil vehicle such as perilla oil.[139]

By incorporating sodium diisopropylnaphthalenesulphonate in ink, the surface tension of both the ink and the paper to be printed upon is reported to be lowered without affecting the durability of either.[140]

[127] British P. 434,450, 1935, to Chemische Fabrik Halle-Ammendorf Gebr. Hartmann; *Chem. Abs.*, 1936, 30, 886; *Brit. Chem. Abs.* B, 1935, 1056. See also Chapter 14 for overprint varnishes.

[128] See Chapter 1.

[129] J. Scheiber, German P. 608,383, 1935; *Chem. Zentr.*, 1935, 106 (1), 3722; *Chem. Abs.*, 1935, 29, 2632.

[130] L. E. Barton and H. A. Gardner, U. S. P. 1,283,455, Nov. 5, 1918, to The Titanium Alloy Manufacturing Co.; *Chem. Abs.*, 1919, 13, 196; *J. S. C. I.*, 1919, 38, 46A.

[131] W. T. Billings, U. S. P. 1,233,962, July 17, 1917; *Chem. Abs.*, 1917, 11, 2619.

[132] *Paint Var. Prod. Mgr.*, 1935, 47, 221.

[133] J. Scheiber, German P. 522,277, 1928; *Chem. Abs.*, 1931, 25, 3184.

[134] W. G. Dewsbury and A. Davies, British P. 441,571, 1936; *Chem. Abs.*, 1936, 30, 4702; *Brit. Chem. Abs.* B, 1936, 286. *Cf.* British P. 425,049, 1935; *Chem. Abs.*, 1935, 29, 5690; *Brit. Chem. Abs.* B, 1935, 476.

[135] A. Davies, British P. 360,934, 1930; *Chem. Abs.*, 1933, 27, 1217; *Brit. Chem. Abs.* B, 1932, 237.

[136] E. Evensen and O. Haugan, Norwegian P. 58,648, 1937; *Chem. Abs.*, 1938, 32, 2378.

[137] H. Teichmann, British P. 166,117, 1921, to Rütgerswerke A.-G.; *Chem. Abs.*, 1922, 16, 351; *J. S. C. I.*, 1922, 41, 559.

[138] H. Sureties, British P. 14,245, 1913; *Chem. Abs.*, 1915, 9, 158; *J. S. C. I.*, 1914, 33, 798.

[139] F. Scofield, *Natl. Paint, Varnish, Lacquer Assoc., Sci. Sect., Circ.* 1937, 541, 213, *Am. Ink Maker*, 1938, 16 (8), 37; *Chem. Abs.*, 1938, 32, 4805.

[140] German P. 590,279, 1934, to H. T. Böhme A.-G.; *Chem. Zentr.*, 1934, 105 (1), 1722; *Rev. Paint, Colour, Varnish*, 1934, 7, 119.

The phenomena of silking, sagging, flooding and floating may be minimized by the addition of 5 to 7 per cent by weight of tricalcium phosphate or bismuth phosphate suspended in an oil vehicle.[141] A composition suggested for improving drying and tack of ink consists of a mixture of Venice turpentine, a drying oil such as linseed, a solvent (*e.g.*, turpentine), a mineral oil and a drier, as for example, lead resinate.[142]

RESINS AS INK MODIFIERS[143]

Natural and synthetic gums and resins are frequently used in inks as bodying agents and in some instances as vehicles. Of the natural gums, rosin, dammar, copal, tragacanth, kauri and elemi often find application as ink constituents. Many synthetic products, such as the alkyd, coumarone, ester gum, and phenolic resins and modifications of these substances are employed as bodying agents, protective colloids, and binding media for inks. Drying resins are synthesized by incorporating an oil such as linseed or tung in a resin-forming reaction mixture. The product possesses some of the properties of the oil and resin. For example the modified resin is oil-soluble, air- or heat-hardening, and plastic.

Apparently, few natural resins are entirely satisfactory when employed in inks because the properties of natural resins are not uniform. On the other hand the solubility, durability, viscosity, and other chemical and physical properties of synthetic resins may be controlled during manufacture. Some synthetic resins, such as those obtained by polymerization of petroleum fractions and rosin, have been utilized in inks because slight variations in the treatment used to produce the resins modify their qualities to such a degree that many types of inks may be prepared from these substances.

A gum may be prepared from the albumin of locust beans by removing the skins and embryos and crushing the remainder of the bean. Subsequently 15 parts of naphthalenesulphonic acid are added to 100 parts of ground beans and the whole ground with water to form a paste. The latter has been advocated to body inks.[144] The sodium salt of formaldehydesulphoxylic acid and the sodium salt of benzylsulphanilic acid find application as stabilizers for gum tragacanth in inks that contain glycerol, potassium hydroxide and a pigment.[145]

The utilization in printing inks of resinous materials from extracts secured from solvent extraction of petroleum distillates has been suggested.[146] Such extracts generally contain asphaltenes, paraffin wax and

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[141] C. J. Borger, U. S. P. 2,147,083, Feb. 28, 1939, to Interchemical Corp.; *Chem. Abs.*, 1939, 33, 4064.

[142] A. Marzio, British P. 482,489, 1938; *Chem. Abs.*, 1938, 32, 7294.

[143] See Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935. *Am. Ink Maker*, 1939, 17 (5), 31.

[144] A. Müller, U. S. P. 1,749,833, March 11, 1930, to Sigismund Neuman; *Chem. Abs.*, 1930, 24, 2258.

[145] Swiss P. 147,416, 1930, to Soc. pour l'ind. Chim. a Bâle; *Chem. Abs.*, 1932, 26, 2332.

[146] E. H. Crawley, U. S. P. 2,114,796, April 19, 1938; *Rev. Paint, Colour, Varnish*, 1938, 11, 300; *Chem. Abs.*, 1938, 32, 4691.

resinous bodies. The extract may be agitated with propanol, butanol, hexanol or other wax and asphaltene precipitants, to secure a resin-forming liquid. Thus, amyl alcohol may be mixed with crude petroleum extract and the whole agitated for 12 to 24 hours at a temperature of about 70° F. to precipitate wax and asphaltenes. The precipitated impurities are separated by filtration or centrifuging. The alcohol is removed by distillation and the solvent-free liquid remaining is vacuum-distilled to remove the lower fractions. The residue from distillation has a boiling point higher than 500° F. and an iodine number of approximately 35. It is a brown liquid with a wide range of viscosity (from 40 seconds Saybolt at 100° F. to 1000 seconds at 210° F.). The resin-forming liquid is compatible with usual drying oils and other resins, and is soluble in nitrocellulose solutions, carbon tetrachloride, carbon disulphide, naphtha (86° C. boiling point), acetone, turpentine, chloroform, and benzene.

Acid resins resulting from the treatment of crude petroleum with sulphuric acid may be extracted from the acid sludge with various solvents. Fractional washing with alcohol, acetone, or chlorinated hydrocarbons effects separation of the resins, which are used for bodying inks.[147]

By heating natural resins to a temperature above 250° C., polymerization is effected and a semi-artificial resin obtained which may be utilized as a binding agent. An ink is made by mixing 72 parts of the resin with 20 parts of carbon black and 8 parts of linseed oil.[148] One difficulty found with natural rosin and other resins is their tendency to crystallize. This tendency may be tested by one of several methods, such as keeping the rosin at a temperature of about 100° F. and noting the time required to form crystals. The natural resin may be dissolved in an equal volume of a vegetable or mineral oil and the time required for crystallization noted; also, lumps of rosin may be placed in a test-tube with acetone and time of crystal formation noted. Any crystallization will occur in less than an hour by this third method, whereas a much longer period is needed in the two former procedures.[149]

The action of sulphuric acid upon rosin also causes polymerization. The rosin is dissolved in a solvent, such as a halogenated aromatic compound, which is stable in the presence of sulphuric acid. The concentrated acid causes polymerization and is separated afterwards from the resin formed. The solvent is evaporated and the polymerized rosin is obtained.[150]

[147] L. Singer, British P. 109,270, 1917 (application not accepted, no patent issued); *Chem. Abs.*, 1918, 12, 93.

[148] V. Szidon, French P. 825,800, 1938; *Chem. Abs.*, 1938, 32, 6484.

[149] S. Palkin and W. C. Smith, *Oil & Soap*, 1938, 15 (5), 120; *Am. Ink Maker*, 1938, 16 (8), 35; *Chem. Abs.*, 1938, 32, 5236. E. Mayfield, *Official Digest Federated Paint Varnish Production Clubs*, 1936 (155), 164; *Chem. Abs.*, 1936, 30, 4946. For a study of the viscosity of solutions of gum dammar in various solvents, see C. L. Mantell and A. Skett, *Ind. Eng. Chem.*, 1938, 30, 417; *J. Inst. Petroleum Tech.*, 1938, 24, 264A; *Chem. Abs.*, 1938, 32, 4362.

[150] A. L. Rummelsburg, U. S. P. 2,108,928, Feb. 22, 1938; *Chem. Abs.*, 1938, 32, 3178; U. S. P. 2,136,525, Nov. 15, 1938; *Am. Ink Maker*, 1939, 17 (3), 41; *Chem. Abs.*, 1939, 33, 1526. Both patents to Hercules Powder Co.

Of the thousands of synthetic resins produced and used commercially, only a few apparently are available for printing ink use.[151] A resin to be applicable must possess certain properties, as mentioned above, *i.e.*, solubility, durability and plasticity. Some synthetic resins are not soluble in the ordinary ink solvents such as turpentine, linseed oil, benzene, or naphtha. Many resins are far too brittle and would not produce a tough film in the dried ink. There are, however, a number of plastics which do find application in printing inks, and they are used to produce inks whose qualities are widely divergent.

Specific ink properties may be varied by addition of a resin. Ester gums add tack, in proportion to their acid values, without a corresponding reduction in length. Maleic acid resins, being more viscous than the ester gums, increase both the length and tack of ink, as do the phthalic resins. Tung oil-modified phenol resins produce an increase in length without a change in tack. These compounds are produced by heating a mixture of 1 part of resin in 2½ parts of oil at 175 to 260° F. for 30 minutes and immediately cooling the mixture. Some resins react with the ink pigments. In such instances the latter have to be protected with additions of organic acids to the ink.[152]

Ester gum is adaptable for ink vehicles and overprint varnishes[153] because of its low cost and complete solubility with relatively low viscosity in solvents such as petroleum ether and other organic liquids (with the exception of ethyl alcohol). The gum is completely compatible with drying oils and nitrocellulose lacquer vehicles.[154]

Rosin-modified alkyd resins are hard and quite friable and possess excellent heat and light resistant qualities. Their solutions are more viscous than those of ester gum and have the characteristic of releasing the solvent from the film with rapidity. These resins may be cooked with drying oils to produce varnishes. Some varieties of the resin are soluble in petroleum ethers, while others require the addition of ethyl alcohol or coal tar naphtha to increase their solubility.[155]

Basic alkyd resins are adaptable for special types of ink, but do not find a wide range of use. These resins may vary from hard solids to viscous liquids which are very clear and colorless. Some varieties are fairly compatible with cellulose acetate, with which few other synthetic resins will mix.[156] Rezyl 110, one type of alkyd resin, when present in ink with carbon black, causes an increase in viscosity during storage.[157]

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[151] J. McE. Sanderson, *Paint, Oil Chem. Rev.*, 1935, 97 (12), 22, 45; *Chem. Abs.*, 1935, 29, 6775; *Rev. Paint, Colour, Varnish*, 1935, 8, 402. J. McE. Sanderson, *Am. Ink Maker*, 1938, 16 (4), 21. For a general discussion of resins as applied to printing ink, see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935; *Printing Equip. Eng.*, 1938, 55 (5), 18; *Rev. Paint, Colour, Varnish*, 1938, 11, 107. C. E. Willis, *Am. Ink Maker*, 1935, 13 (3), 13; *Rev. Paint, Colour, Varnish*, 1935, 8, 208; *Chem. Abs.*, 1935, 29, 4607.

[152] J. G. Hall, *Oil Colour Trades J.*, 1938, 93, 579, 811; *Am. Ink Maker*, 1938, 16 (6), 37; *Chem. Abs.*, 1938, 32, 3641, 8988; *Brit. Chem. Abs.* B, 1938, 942.

[153] See Chapter 14, on overprint varnishes.

[154] J. McE. Sanderson, *Am. Ink Maker*, 1938, 16 (4), 21.

[155] J. McE. Sanderson, *loc. cit.*

[156] J. McE. Sanderson, *loc. cit.*

[157] *Am. Paint. J.*, 1932, 17 (5), 12; *Rev. Paint, Colour, Varnish*, 1932, 5, 304.

A typical alkyd resin is produced by heating together glycerol, linseed oil, phthalic anhydride and colophony. When the resin is formed it may be ground with Lithol Fast Scarlet R and the resulting mixture dissolved in a vehicle with the addition of driers and plasticizers.[158]

Saturated fatty acid-modified alkyd resins frequently are used with nitrocellulose lacquers because the modified alkyd resins exhibit no drying qualities by themselves. They are compatible to a limited extent with drying-oil vehicles and with petroleum ethers. They are soluble in many of the organic ester solvents used in lacquers (amyl acetate, butyl acetate), and find application where "drying" is accomplished by penetration of the printed material.[159]

Alkyd resins modified with drying oils have wide application in printing inks. They combine the characteristic resin qualities of hardness and gloss with those of drying oils, *i.e.*, toughness and tack. There are exceptionally pale-colored resins in this group. These are utilized with light-colored pigments. A printing ink with a viscosity of from 25 to 60 seconds is made by incorporating a resin produced by the reaction of glycerol, phthalic anhydride, and a drying oil. The latter comprises approximately 40 to 55 per cent by weight of the resin. The resin is dissolved in a volatile solvent and driers and a pigment are added.[160]

Addition of phenol to alkyd resins increases the water resistance of the latter. However, the modified resins are somewhat darker than ordinary alkyd resins.[161]

Urea-formaldehyde resins are applicable for printing inks, although to a rather limited degree. They are thermosetting and when it is possible to effect drying of the printed matter at about 225° F., these resins may be employed. They are soluble in many organic solvents, especially in a mixture of xylene and butanol.[162] Aminotriazineformaldehyde resins are closely allied to the urea type of product and find application in inks. The speed of hardening may be regulated by the addition of accelerators. Materials such as kaolin and lithopone act as fillers for the resin when printing pastes are made.[163]

Among polymerization products which are adaptable as ink binders, polystyrene[164] and polymerized unsaturated aliphatic acids, such as acrylic acid,[165] serve as examples. The polystyrene resins are soluble in reduced naphthalenes or in mixtures of the latter with esters of high boiling point, such as phthalates and stearates.

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[158] British P. 337,199, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2011. See also L. Lilienfeld, British P. 171,661, 1920; *Chem. Abs.*, 1922, 16, 1301. German P. 591,456, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 2553; *Rev. Paint, Colour, Varnish*, 1934, 7, 196. British P. 373,233, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3627. French P. 700,892, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3855.

[159] J. McE. Sanderson, *loc. cit.*

[160] E. H. Callahan, Canadian P. 332,858, 1933, to the Canadian Industries, Inc.; *Chem. Abs.*, 1933, 27, 4428.

[161] J. McE. Sanderson, *loc. cit.*

[162] J. McE. Sanderson, *loc. cit.*

[163] British P. 480,816, 1938, to Soc. pour l'ind. Chim. à Bâle; *Chem. Abs.*, 1938, 32, 5965.

[164] German P. 592,661, 1934, to I. G. Farbenind. A.-G.; *Chem. Zentr.*, 1934, 105 (2), 519; *Rev. Paint, Colour, Varnish*, 1934, 7, 294.

[165] British P. 351,508, 1932, to I. G. Farbenind. A.-G.; *Rev. Paint, Colour, Varnish*, 1932, 5, 166.

Synthetic copal resins are easily prepared and possess qualities such as freedom from stickiness, rapid drying, and uniformity of properties, as compared with natural resins. Certain varieties of copals have been suggested for light-colored inks.[166]

Coumarone resins are not satisfactory *per se* as binders for ink because they produce brittle and non-durable films through the oxidation of their paraindene content and the polymerization of the paracoumarone constituent. However, when these resins are modified with drying oils, much the same as the alkyds, satisfactory printing inks are reported to be produced. Such inks possess high gloss.[167]

Alcohols obtained from the reduction of natural resins are fused at 120 to 150° C. with an organic or inorganic acid and a mono- or polyhydric alcohol. Among the acids used are boric, phosphoric, lactic, lauric, laevulinic, salicylic, oxalic, adipic and phthalic. The resins resulting have been advocated as binders for ink.[168]

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[166] E. Fonrobert, *Kunststoffe*, 1931, 21, 145, 178; *Chem. Abs.*, 1931. 25, 5583; *Paint Manuf.*, 1931, 1 (6), 160; (7), 196; *Rev. Paint, Colour, Varnish*, 1931, 4, 247, 281. W. Schwedler, *Seifensieder-Ztg.*, 1932, 59 (19), 301; *Rev. Paint, Colour, Varnish*, 1932, 5, 174.

[167] J. Marcusson, *Chem.-Ztg.*, 1919, 43, 93, 109, 122; *Chem. Abs.*, 1919, 13, 2607.

[168] Austrian P. 146,509, 1936, to Deutsche Hydrierwerke; *Chem. Zentr.*, 1936, 107 (2), 3208; *Rev. Paint, Colour, Varnish*, 1936, 9, 396.

Chapter 6

Pigments

Printing-ink pigments may be defined as substances or mixtures of substances which impart color and opacity to inks; also, pigments serve to some degree in increasing the body of the ink.

Printing inks may be divided into three general classes, planographic, intaglio and typographic inks.[1] For lithographic inks, pigments must be completely free from acids, and insoluble in water. Pigments containing acidic substances would cause continued etching of the stone or plate during the printing operation with consequent blurring of the printed impression. Further, lithographic and offset printing are effected by utilization of the principle that oil and water do not mix.[2] For this reason it is necessary that the pigments be insoluble in water. Otherwise bleeding of the pigment into non-printing areas would occur, causing a blurred impression on the final printing surface.[3] Also pigments employed for planographic printing must have great color strength. This is particularly true in offset printing, where a thin film of ink is transferred from the plate to a rubber blanket and then to the final printing surface.[4] Pigments employed in offset printing should contain no compounds which would react with the printing plates. Thus, sulphur-containing pigments generally are avoided when zinc is employed in the printing plates.

Pigments intended for use in intaglio inks must be soft and nonabrasive.[5] Otherwise, the inks would scratch the printing plates when the doctor blade was run over the latter to remove excess ink. Also, as with planographic inks the pigments should be free from substances which might react with the printing plates. Color strength is not as important in intaglio printing as in planographic work, since relatively large bodies of ink are carried in the former operation, as compared with the thin films required in planographic printing.

The requirements for pigments intended for typographic inks are somewhat less stringent than for the two types mentioned previously. Almost all pigments will serve for letter-press inks. To prevent offset high concentrations of pigment in ink generally are employed. There-

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[1] T. M. Tyson, *Oil and Colour Chem. Assoc.*, 1918, 1 (5); *J. S. C. I.*, 1918, 37, 742A; *Chem. Abs.*, 1919, 13, 1158.

[2] For description of planographic printing, see Chapter 9.

[3] H. Hadert, *Paint Manuf.*, 1933, 3, 5; *Chem. Abs.*, 1933, 27, 1526; *Rev. Paint, Colour, Varnish*, 1933, 6, 25. See also W. Van Wüllen-Scholten, Farben-Chem., 1937, 8, 337, 368, 406; *Rev. Paint, Colour, Varnish*, 1938, 11, 83.

[4] E. G. Jones, *Oil Colour Trades J.*, 1932, 81, 906; *Rev. Paint, Colour, Varnish*, 1932, 5, 90.

[5] For a description of intaglio printing, see Chapter 10.

fore inks which have a low oil absorption, *i.e.*, require small amounts of oil vehicle, usually are utilized. Other considerations, such as color strength, must be considered, so that the quality of low oil absorption is not absolutely necessary in all instances.

Other properties are required for coloring agents used for special purposes. Thus, inks with which tin printing is effected should have heat-resistant pigments. When printed matter is to be covered with varnishes containing alcohol, the pigments employed should be non-bleeding in this solvent. Also inks for printing soap-wrappers should be inert to alkalies.

Colored pigments other than blacks may be classified according to structure as mineral (or inorganic) and organic colors (produced from natural or synthetic dyes).[6] Since inorganic pigments comprise many different types of chemical compounds, these coloring agents have been classified in this text according to color. Also, extenders have been included under the heading of inorganic pigments, since extenders are inorganic compounds, though not true coloring agents. Organic colors have been grouped according to chemical constitution and properties. A section has been devoted to carbon black, the backbone of the printing-ink industry.

INORGANIC OR MINERAL COLORS

Red, which has been termed the liquid fire of the ink fountain, has many desirable qualities which have given it a dominating position in the printing industry.[7] For example, red has its maximum strength at a position midway between black and white, and although some other colors also have this characteristic, red is much stronger than these. For this reason, red was said to be an ideal color for accenting a black and white printing job. Further, most reds are reported to be resistant to the reactions encountered in printing, such as fading, bleeding and heat-changes.

The psychological reactions to color are of great importance and have been used in the layout and planning of various work. Thus, red has been employed to symbolize valor, danger, fire and anger and also to attract attention. It may be intense, vital and exciting in mood, and is capable of great refinement when used discreetly.

Inorganic red pigments which have been utilized in the printing-ink industry include vermilion, cadmium red, molybdate orange, and iron oxide reds. All have characteristics which make them effective in certain types of printing. These properties, together with the limitations, indicate to some extent the possible applications of such pigments.

Vermilion. The bright red sulphide of mercury known as vermilion

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[6] For discussion of dyestuffs in inks, see L. M. Larsen and F. A. Weymouth, *Paint, Oil and Chem. Rev.*, 1937, 99 (17), 20; *Chem. Abs.*, 1937, 31, 7673.

[7] See *The Official Printing Ink Maker*, 1934, 4, (3).

was employed as a pigment as early as 400 B.C.[8] Two processes have been used in the preparation of this material.[9] In the wet process, mercury and sulphur were ground together under water. When the elements had formed an apparently homogeneous mixture, the whole then was stirred with a solution of sodium hydroxide or sodium sulphide. In this manner, black mercury sulphide was converted to brilliant scarlet mercuric sulphide. The dry process comprises agitating mercury and sulphur together until an amorphous black powder is secured. The latter then is sublimed and washed with a hot solution of sodium hydroxide. Sublimation of the black mercuric sulphide results in conversion of the latter to the red form.

Pure vermilion was reported to be insoluble in water, oil, alcohol, hot paraffin, acetone and benzene. It shows a low oil absorption, which means that a small quantity of oil vehicle is necessary to disperse the pigment. As a result the hiding power of the resulting ink is good. For this reason vermilion has been employed in lithographic printing, and to some extent, in printing on tin. However, it was said to be somewhat unsuited for tin printing since heat causes a darkening of the color.[10]

In preparing dispersions of a pigment such as vermilion, the latter may be ground into a paste with water.[11] The paste subsequently was emulsified with a solution of asphalt and xylene. The water which separated from the mixture was withdrawn and the residue distilled to remove the remaining water.

Cadmium Red. Coprecipitation of a mixture of cadmium sulphide, cadmium selenide and barium sulphate, followed by calcination of the precipitated mass, produces the pigment called cadmium red.[12] The redness of this coloring agent depends upon the cadmium selenide content, and increases as the proportion of the latter becomes greater.[13] Cadmium red was stated to be insoluble in water, oil, hot paraffin, acetone, benzene, alcohol, and dilute aqueous acids.[14] Also, the hiding power of cadmium reds has been reported to be about three times as great as that of vermilion, but the former is somewhat duller in tone. The principal utilization of cadmium reds apparently has been in lithographic and tin printing.

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[8] *Cf.* H. J. Wolfe, "The Manufacture of Printing and Lithographic Inks," New York, MacNair-Dorland Co., Inc., 1933.

[9] S. L. Karpeles, A. B. Portman and P. Thomasset, *Am. Ink Maker*, 1936, **14** (5), 39; *Brit. Chem. Abs.* **B**, 1936, 702; *Chem. Abs.*, 1937, **31**, 4141; *Rev. Paint, Colour, Varnish*, 1936, **9**, 242. C. Eckmann, *Farben-Chem.*, 1935, **6**, 365; *Chem. Abs.*, 1936, **30**, 2408; *Rev. Paint, Colour, Varnish*, 1935, **8**, 483.

[10] H. Wilson, *Ind. Mineral Rocks*, 1937, 493; *Chem. Zentr.*, 1938, **109** (1), 1465; *Rev. Paint, Colour, Varnish*, 1938, **11**, 83.

[11] H. Cajar, Austrian P. 127,824, 1931, to Kast and Ehringer G. m. b. H.; *Chem. Abs.*, 1932, **26**, 4486.

[12] W. J. O'Brien, *Paint Varnish Production Mgr.*, 1931, **5** (5), 8; *Rev. Paint, Colour, Varnish*, 1931, **4**, 113, W. H. Droste and W. Wildensee, *Verfkroniek*, 1938, **11**, 158; *Brit. Chem. Abs.* **B**, 1938, 1326; *Chem. Abs.*, 1938, **32**, 8167.

[13] S. L. Karpeles, *Lith. Offset Print.*, 1931, **27**, 208; *Rev. Paint, Colour, Varnish*, 1931, **4**, 250.

[14] S. L. Karpeles, A. B. Portman and P. Thomasset, *Am. Ink Maker*, 1936, **14** (5), 39; *Chem. Abs.*, 1937, **31**, 4141; *Brit. Chem. Abs.* **B**, 1936, 702; *Rev. Paint, Colour, Varnish*, 1936, **9**, 242.

Molybdate Orange. Mixtures of lead chromate, lead molybdate and lead sulphate which have been precipitated together give an orange pigment said to be fast to light and insoluble in water, oil, hot paraffin, and dilute aqueous acids and alkalies.[15]

There has been some question as to whether presence of lead sulphate is essential to preparation of molybdate orange.[16] It was reported that molybdate orange could be prepared with lead chromate and lead molybdate without lead sulphate, although the reaction was somewhat more difficult to control. That is, lead sulphate is of value in maintaining the crystal form (tetragonal) of the chromate which is formed in conjunction with lead molybdate. However, the borate, perborate, silicate, cyanide, nitroprusside, ferricyanide, chloride or carbonate of lead have been employed in place of lead sulphate without affecting ease of manufacture or color of the product. Indeed it was stated that molybdate orange prepared with a ferricyanide of lead was more brilliant, and much faster to light than any of the colors prepared with lead sulphate.

Molybdate orange has been utilized in lithography and tin printing and in conjunction with red toners to produce brilliant, opaque reds especially for printing on transparent surfaces.[17]

Orange Mineral, Red Lead. Oxidation of metallic lead by heating in a current of air is employed to effect conversion of the metal to red lead, or as it once was termed, minium. Also, this pigment can be secured by heat treatment of white lead (basic lead carbonate).[18] Orange mineral was said to be fairly resistant to light. However, in common with other lead pigments, it reacts with hydrogen sulphide fumes to form lead sulphide, which is black. Also, it shows a tendency to react with drying oils, particularly those of a highly unsaturated character. This causes the ink to body rather quickly and leads to livering of the ink. Orange mineral has been said to have a high specific gravity and low oil absorption, indicating good hiding qualities. In combination with red toners, red lead yields brilliant opaque inks that are applicable for printing on transparent surfaces.[19]

Indian Red or *Venetian Red* includes the naturally-occurring iron-oxide pigments. The oxide is the active coloring agent in these sub-

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[15] E. R. Allen, *Official Digest Federation Paint and Varnish Production Clubs*, 1931, 104, 409; *Rev. Paint, Colour, Varnish*, 1931, 4, 108.

[16] A. Linz, *Am. Ink Maker*, 1938, 16 (9). 51. *Schultze, Ann.*, 1863, **126**, 52. F. M. Jaeger and H. C. Germs, *Z. anorg. allgem. Chem.*, 1921, 119, 145, 169; *Chem. Abs.*, 1922, **16**, 1190. E. Lederle and H. S. Grimm, U. S. P. 1,926,447. Sept. 12, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 5994. German P. 574,379 and 574,380, 1933; *Chem. Abs.*, 1933, **27**, 3626. German P. 595.473. 1934; *Chem. Abs.*, 1934, **28**, 4255. German P. 615,147, 1935; *Chem. Abs.*, 1935, **29**, 6445. U. S. P. 2,030,009, Feb. 4, 1936; *Chem. Abs.*, 1936, **30**, 2028. H. Wagner, R. Haug and M. Zipfel, *Z. anorg. allgem. Chem.*, 1932, **208**, 249; *Chem. Abs.*, 1933, **27**, 34. U. S. P. 2,063,254, Dec. 8, 1936; *Chem. Abs.*, 1937, **31**, 893. A. Linz, Belgian P. 327,250, 1937.

[17] *Cf.* H. Zimmer, French P. 696,423, 1930; *Chem. Abs.*, 1931, **25**, 2865.

[18] See *Chemical Age*, 1932, **26**, 424; *Rev. Paint, Colour, Varnish*, 1932, 5, 114. *Cf. Farben-Ztg.*, 1935, **40**, 559; *Rev. Paint, Colour, Varnish*, 1935, **8**, 306. K. Würth, *Farben-Ztg.*, 1936, **41**, 185; *Z. des Vereins Deutscher Ingenieure*; *Rev. Paint, Colour, Varnish*, 1936, **9**, 92.

[19] For a survey of theories advanced to explain pigment characteristics, see H. Grohn, *Farben-Chem.*, 1931, **2**, 200; *Brit. Chem. Abs.* **B**, 1932, 117; *Rev. Paint, Colour, Varnish*, 1931, **4**, 110. See also H. Hadert, *Farbe u. Lack*, 1926, 457; *Chem. Abs.*, 1927, **21**, 181.

stances, which generally contain other materials as impurities. The amount and nature of the impurities determines the hue of the pigment. The latter range in color from a purplish brown to light red.

Hematite was the source of iron oxide pigments for centuries. The ore was mined, ground, screened and washed to prepare it for use as pigment. More recently, utilization of by-product ferrous sulphate from the iron industry as raw material has been practiced.[20] The waste sulphate liquor is treated with calcium hydroxide and the mixture calcined in reverberatory furnaces or rotary kilns. The calcined pigment generally contains about 40 per cent ferric oxide, the rest being calcium sulphate. Also, iron oxide pigments may be secured from copperas (ferrous sulphate). The latter is heated to convert the sulphate to ferric oxide by removal of sulphur trioxide.

Iron oxide pigments are fast to light, alkalies, oils, water and alcohol. Venetian reds are slightly soluble in acids.

Because of their grittiness, iron oxide pigments generally are used only in poster inks and in stamping and plate inks. For these purposes, the permanency and low oil absorption of Venetian reds make the latter acceptable.

Yellow, the inspirational note, is one of the lightest of all colors, and is of great strength.[21] It is symbolic of wisdom and inspiration, and is well suited to express gaiety and merriment because of its active and stimulating effect. It may be contrasted with black to obtain good visibility, or with purple-blue shades.

Cadmium Yellow. Cadmium sulphide, generally known as cadmium yellow, is prepared by bubbling hydrogen sulphide gas through an aqueous solution of cadmium chloride or cadmium sulphate to which a small proportion of free acid has been added.[22] The resulting opaque yellow precipitate is washed, filter-pressed and dried in a current of warm air. Different shades of yellow can be obtained by altering the temperature and acidity of the aqueous cadmium chloride or sulphate solution and the rate of flow of hydrogen sulphide.

Cadmium sulphide is light-resistant and is not affected by hydrogen sulphide or aqueous alkalies.[23] It does not bleed in alcohols or hot paraffin, but does bleed in aqueous acid solutions. The pigments are easily ground but have a tendency to pile up on the press unless admixed with an extender.[24]

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[20] J. W. Ayers, *Paint, Oil, and Chem. Rev.*, 1930, 90 (10), 10; *Chem. Abs.*, 1930, 24, 5170.

[21] *The Official Printing Ink Maker*, 1934, 4 (3), 8. N. Heaton, *J. Oil Colour Chem. Assoc.*, 1931, 14, 373; *Chem. Abs.*, 1932, 26, 1806; *Brit. Chem. Abs.* B, 1932, 436; *Rev. Paint, Colour, Varnish*, 1932, 5, 2.

[22] F. W. Weber, *Drugs, Oils & Paints*, 1930, 46, 237; *Rev. Paint, Colour, Varnish*, 1931, 4, 6.

[23] C. Eckmann, *Farben-Chem.*, 1935, 6, 365; *Chem. Abs.*, 1936, 30, 2408; *Rev. Paint, Colour, Varnish*, 1935, 8, 483.

[24] S. L. Karpeles, A. B. Portman and P. Thomasset, *Am. Ink Maker*, 1936, 14 (5), 39; *Brit. Chem. Abs.*, B, 1936, 702; *Chem. Abs.*, 1937, 31, 4141; *Rev. Paint, Colour, Varnish*, 1936, 9, 242. P. Kluckow, *Farben-Ztg.*, 1932, 38, 380; *Chem. Abs.*, 1933, 27, 855; *Rev. Paint, Colour, Varnish*, 1933, 6, 3.

Preparation of cadmium yellow pigments in cellulose derivatives has been proposed.[25] In one instance methylcellulose was incorporated in an aqueous solution of cadmium sulphate. Aqueous ammonium acid sulphide was added to the mixture to precipitate cadmium sulphide and the whole then warmed to coagulate the methylcellulose. In this manner a dispersion of finely divided pigment in the cellulose ether was reported to be secured.

Chrome Yellow. The lighter shades of chrome yellow, primrose and lemon, usually are made by coprecipitation of lead chromate and lead sulphate from an aqueous solution of lead nitrate or acetate. Medium chrome yellow contains lead chromate alone and is produced in the same manner as the primrose and lemon shades, except that no lead sulphate is present. The deeper, more orange shades contain mixtures of lead chromate and basic lead chromate, and the deepness of the shade depends on the basic salt content.[26] Chrome yellows obtained by coprecipitation of lead and barium chromates were stated to be no more resistant to light than the pure lead salt.[27]

Chrome yellow is a rather opaque coloring agent, with high specific gravity, soft grinding properties and low oil absorption.[28] When used alone in planographic printing, chrome yellow shows some tendency to form a scum on the press. This undesirable characteristic was said to be overcome by admixture of Hansa yellow with the chrome pigment. Also, since Hansa yellow has high oil absorption powers, the quantity of vehicle required in preparing the ink was reported to be increased. Chrome yellow has been said to be fast to varnish oils, water, alcohol and hot paraffin. However it is affected by alkali and soap, the color changing from yellow to red.

A suggestion has been made that chrome yellows be given names which correspond more nearly to the shade of the pigment.[28a] One proposed classification was:

Old Name	New Name	% Lead Sulfate Content
Primrose	Extra Light	50
Lemon	Light	11
Light	Medium	33
Medium	Dark	None

Zinc Yellow. Mixtures of hydrated zinc chromate and potassium chromate are known as zinc yellow. The pigment usually is obtained by adding potassium chromate to a suspension of zinc oxide in zinc sulphate

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[25] A. Weihe, German P. 554.174, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, **26**, 5220.

[26] V. N. Shultz, F. P. Ivanovskii and V. A. Klevke, *J. Chem. Ind.* (*Moscow*), 1930, **7**, 760; *Chem. Abs.*, 1932, **26**, 2331; *Rev. Paint, Colour, Varnish*, 1931, **4**, 4. *Farbe u. Lack*, 1931, **36**, 8; *Rev. Paint, Colour, Varnish*, 1931, **4**, 4. H. Wagner, *Paint Manuf.*, 1931, **1**, 186; *Rev. Paint, Colour, Varnish*, 1931, **4**, 264.

[27] G. Draeger, *Farbe u. Lack*, 1932, **37**, 173, 185, 199; *Brit. Chem. Abs.* **B**, 1932, 561; *Chem. Abs.*, 1932, **26**, 3122; *Rev. Paint, Colour, Varnish*, 1932, **5**, 116.

[28] S. L. Karpeles, A. B. Portman and P. Thomasset, *Am. Ink Maker*, 1936, **14** (5), 39; *Chem. Abs.*, 1937, **31**, 4141; *Brit. Chem. Abs.* **B**, 1936, 702; *Rev. Paint, Colour, Varnish*, 1936, **9**, 242.

[28a] T. P. Brown, *Am. Ink Maker*, 1939, **17** (12), 23.

solution. Zinc yellow is reported not to darken on exposure, and to be unaffected by sulphides. However it is said to be somewhat difficult to work in inks. Also the yellow bleeds both in water and alcohol, which render it somewhat unsuited for printing that later may be exposed to these substances.[29]

Incorporation of pigments such as zinc yellow in oil vehicles may be somewhat difficult because of the water content of the coloring agent. To overcome this, it was suggested that the pigment be wetted with an alcohol or ketone that is miscible both with water and the oil vehicle.[30] Subsequently the wetted pigment may be dispersed in the vehicle, and the whole heated to 50-60° C. to remove the wetting agent.

Iron Yellow is the name given to the yellow oxides of iron. Apparently these pigments have not found wide application in the printing-ink industry because of their dull color and poor working qualities. However the pigments are resistant to light and non-bleeding.

Ochre or ochery earth has been defined as a natural mineral pigment composed largely of clay permeated with hydrated iron (ferric oxide).[31] The color of the pigment is regulated by the amount of impurities present. The varieties of ochre have been classed according to color as cream, gray white, golden, green, red and ochre.

The yellow form of ochre is found principally in Spain, Italy and France. The crude material is washed to remove sand. The washed coloring agent then is levigated to separate the particles into fractions according to size. Use of ochre in printing ink generally is restricted to plate and stamping inks. In these instances the natural pigment frequently is fortified by incorporation of a chrome yellow or yellow lake.[32]

Ochre is insoluble in water, alcohol, varnish oils and dilute alkali.[33] However acids dissolve the iron oxide content of the pigments, leaving a residue of clay and impurities.

The red varieties of ochres, called siennas, are produced to a great extent in Italy. In composition sienna is very similar to ochre, the red hue of the former being caused by presence of small amounts of anhydrous red iron oxides and manganese compounds in the pigment.[34] In some instances siennas are calcined to yield burnt sienna. In this process the hydrated iron oxides are converted to anhydrous red iron oxide. Thus a more opaque and richer pigment is secured.[35]

Natural and burnt siennas are insoluble in water, varnish oils, alcohol and dilute alkalies. However acids act upon these coloring agents in the

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[29] R. Schwarz, *Farbe u. Lack*, 1934, 39, 342; *Rev. Paint. Colour, Varnish*, 1934, 7, 263.

[30] British P. 207,275, 1922, to Plauson's (Parent Co.) Ltd.; *Brit. Chem. Abs.* B, 1924, 103; *Chem. Abs.*, 1924, 18, 1209. Cf. H. Hadert, *Paint Manuf.*, 1933, 3, 5; *Chem. Abs.*, 1933, 27, 1526.

[31] R. M. Santmyers, *Bur. of Mines*, 1929, Circ. No 6132; *Chem. Abs.*, 1929, 23, 3819

[32] H. N. Morris, *Brit. Plastics*, 1930, 1; *Synthetic and Applied Finishes*, 1930, 1, 4; *Rev. Paint, Colour, Varnish*, 1930, 3, 197.

[33] E. S. Greigov, *Peintures, pigments, vernis*, 1935, 12, 212; *Chem. Abs.*, 1936, 30, 2777.

[34] H. E. Tuffs, *Drugs, Oils and Paints*, 1920, 36, 144; *Chem. Abs.*, 1920, 14, 3802.

[35] J. D. Johnson, *Chem. Age (London)*, 1935, 32, 293.

same manner as upon ochre, dissolving out the iron and leaving a residue of clay. Both types of sienna are employed in plate and stamping inks.

Umber is a brown species of ochre, the brown hue being caused by presence of manganese oxides in the pigment.[36] The earth is mined and prepared for utilization as pigment by washing and grinding. Burnt umber is produced by calcining the natural material. In this manner a deeper and richer shade of brown pigment is stated to be secured.

Umbers are resistant to alcohol, water, varnish oil and dilute alkalies. However acids act upon these coloring agents to dissolve out the iron.

Employment of umbers in printing inks has been most extensive in the field of plate and stamping inks. Also the brown pigments are used in finer grades of ink to produce permanent brown tints.[37]

Blue, the badge of sincerity, is characteristic of calmness and expansiveness, and can be employed in various shades to represent moods ranging from peacefulness and sincerity to reverence and solemnity. Inorganic blues comprise one of the most important groups of pigments utilized in the manufacture of printing inks both because of their inexpensiveness and the wide range of pigments with which they can be mixed.

Iron Blue. The pigments known as Bronze, Milori, Chinese and Prussian blue are species of iron ferric ferrocyanide and all are included under the generic name, iron blue. These blues are secured by adding an aqueous solution of potassium or sodium ferrocyanide to an aqueous solution of ferrous sulphate.[38] Also use of ferric chloride in place of ferrous sulphate has been proposed.[39] During adjunction of the ferrocyanide the temperature of the sulphate or chloride solution is maintained at 20-40° C. when Prussian blue is desired. In this manner a light blue precipitate of ferrous ferrocyanide is formed. To convert the latter to ferric ferrocyanide, the whole then is heated for several hours with hydrochloric or sulphuric acid and sodium bichromate or chlorate.[40] The duration of the latter operation depends upon the shade of blue desired. When oxidation is complete the pigment is washed, filter-pressed and dried. In instances where sodium ferrocyanide is used to precipitate the ferrous ferrocyanide, ammonium sulphate or ammonium chloride is added to the ferrous sulphate or chloride solution. The ammonium salt is said to aid in brightening and strengthening the final color of the pigment. Alteration of the acidity, concentrations, temperature, and time of oxidation cause variations in the shade of iron blue secured. A flow sheet

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[36] R. M. Santmyers, *Bur. of Mines*, 1931, Information Circ. 6504; *Chem. Abs.*, 1931, **25**, 5778. F. Richter, *Farbe u. Lack*, 1931, 305; *Chem. Abs.*, 1931, **25**, 4721.

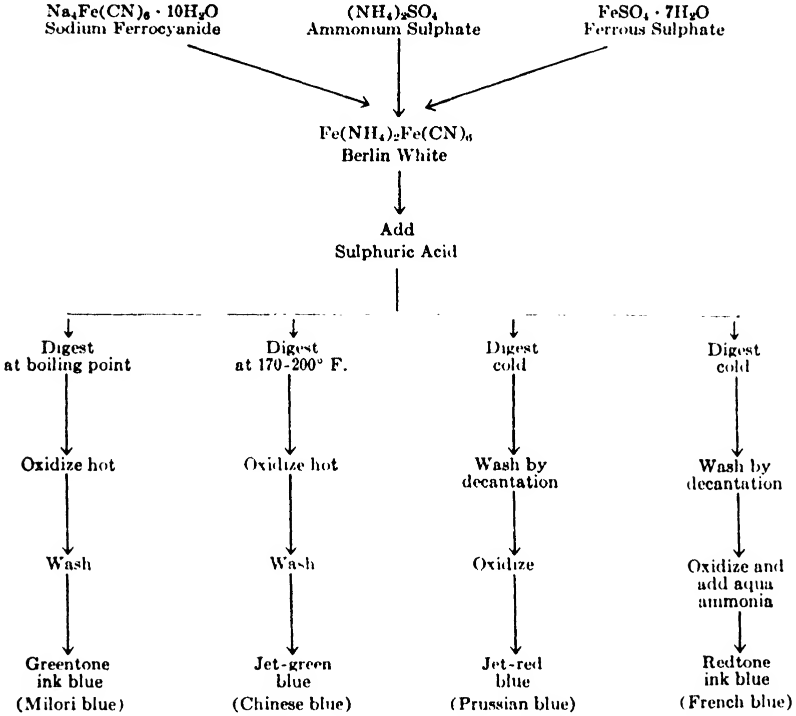
[37] For discussion of chemical and microscopic examination of umbers, see H. Wagner and G. Hoffmann, *Veroffentlichungen des Fachausschussess für Anstrichtechnik*, 1931, No. 8, 28; *Farben-Ztg.*, 1931, **36** (33), 1470; *Rev. Paint, Colour, Varnish*, 1931, **4**, 114.

[38] W. van Hoogstraaten, *Farbe u. Lack*, 1930, **35**, 209, 223; *Rev. Paint, Colour, Varnish*, 1930, **3**, 94. *Farbe u. Lack*, 1930, **35**, 232, 244; *Chem. Abs.*, 1930, **24**, 3659.

[39] G. Zerr, *Farbe u. Lack*, 1933, **38**, 533, 544; *Brit. Chem. Abs.* **B**, 1934, 71; *Chem. Abs.*, 1934, **28**, 915; *Rev. Paint, Colour, Varnish*, 1933, **6**, 291.

[40] D. Davidson, *J. Chem. Education*, 1937, **14**, 277; *Chem. Abs.*, 1937, **31**, 5290; *Brit. Chem. Abs.* **A** (1), 1937, 422; *Rev. Paint, Colour, Varnish*, 1937, **10**, 318.

which indicates the shades of blue secured by variations in the manufacturing procedure is shown in Figure 33A.[40a] It is interesting to note that in this instance the iron blue pigments have been designated by the shade characteristics as well as by the names usually associated with these coloring agents. This was stated to be a step toward clarification of nomenclature for these compounds.



Courtesy American Ink Maker

FIGURE 33A. Manufacturing Flow Sheet for the Four Common Iron Blues (T. P. Brown).

The iron blues are characterized by marked tinctorial strength, resistance to light, metallic sheen on printing, and stability in water, alcohol, oil vehicles, hot paraffin and weak acids.[41] However, alkalies of any concentration destroy the color, as do strong acids. Iron blues generally are resistant to baking temperatures of approximately 250° F., though there may be some change in shade, but are destroyed at somewhat higher temperatures. Also, the ferric ferrocyanides are crystalline in nature, and for this reason may be somewhat difficult to grind.

[40a] T. P. Brown, *Am. Ink Maker*, 1939, 17 (12), 23.

[41] See *Farben-Ztg.*, 1933, 38, 1781; 1934, 39, 14; *Rev. Paint, Colour, Varnish*, 1934, 7, 1, 69.

To secure dispersion of iron blues, it has been suggested that the pigment be admixed with water-wet cellulose nitrate and water.[42] The whole then was agitated while adding an aqueous emulsion of castor oil and triethanolamine oleate. When the mixture was homogeneous, citric acid was incorporated to break the emulsion. Filtration of the resulting mass was reported to give a fine dispersion of pigment in the cellulose derivative. In place of triethanolamine oleate, substances such as soya lecithin, sodium oleate or ricinoleate, glyceryl oleate or glycol stearate may be employed.

Removal of the reddish cast from iron blues was stated to be effected by incorporating 1-10 parts of zinc oxide and 40 parts of blown castor oil in 100 parts of the iron blue.[43]

Ultramarine Blue. Mixtures of finely ground soda ash or sodium sulphate with clay, sulphur and carbon are calcined in closed crucibles out of contact with air to furnish the pigment known as ultramarine blue.[44] Three principal species of blue are secured by employment of different concentrations of raw materials:

(1) Sulphate ultramarines, prepared from sodium sulphate and alum.
(2) Soda ultramarines of somewhat high silica and sulphur content. The shades secured range from a rich, true blue to violet, and the pigment is characterized by fairly high resistance to alum.
(3) Soda ultramarines of relatively low silica and sulphur content. These possess a bright color and are the pigments usually preferred for printing inks. Because of the relatively small percentage of silica these pigments have better working qualities than the other ultramarines.[45]

Also, reduction of the amount of sulphur present in the pigment tends to render it less corrosive to metal surfaces. This is important, particularly in intaglio printing from copper plates.[46]

Ultramarine blues are stated to have a low tinting strength. However, it was pointed out that the method of grinding the pigment into a vehicle has a direct bearing upon this property.[47] Differences in tinting strength of as much as 30 per cent have been reported between inks in which the blue was rubbed slowly into the vehicle and those in which the incorporation was accomplished by vigorous grinding. Also, ultramarine blue is said to be light-resistant. Although it may become slightly duller and redder upon exposure, apparently it does not fade appreciably for some time. The blue is insoluble in water, varnish oil, alcohol, hot

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[42] R. T. Hucks and G. R. Maher, U. S. P. 2,114,713, April 19, 1938, to E. I. duPont de Nemours & Co.; *Chem. Abs.*, 1938, 32, 4806; *Am. Ink Maker*, 1938, 16 (6), 41; *Rev. Paint, Colour, Varnish*, 1938, 11, 260.

[43] R. T. Hucks, U. S. P. 2,118,511, May 24, 1938, to E. I. duPont de Nemours & Co.; *Chem. Abs.*, 1938, 32, 5648.

[44] S. L. Karpeles, A. B. Portman and P. Thomasset, *Am. Ink Maker*, 1936, 14 (5), 39; *Brit. Chem. Abs.* B, 1936, 702; *Chem. Abs.*, 1937, 31, 4141; *Rev. Paint, Colour, Varnish*, 1936, 9, 242.

[45] See, for example, *Paint Exp.*, 1930, 3, 40; *Rev. Paint, Colour, Varnish*, 1930, 3, 1.

[46] *Farbe u. Lack*, 1937, 163; *Rev. Paint, Colour, Varnish*, 1937, 10, 173.

[47] H. Muck, *Farbe u. Lack*, 1930, 35, 591; *Rev. Paint, Colour, Varnish*, 1931, 4, 5.

paraffin and is unaffected by mild alkalies. The resistance of ultramarine blue to action of alkalies has been utilized in preparation of inks which must be alkali-proof. Because of its relative coarseness, it is usually admixed with other blue pigments.

Green, nature's favorite dress, is a particularly efficient color for creating an atmosphere of coolness and tranquility. Light greens give a refreshing effect and dark greens a quiet, restful, retiring effect to printed pieces. In the class of inorganic pigments, two types of green pigment usually are utilized, chrome green and hydrated chromium oxide.

Chrome Green, or *Milori Green* is secured by precipitation of lead chromate upon iron blue.[48] Iron blue and lead acetate or nitrate are admixed, and an aqueous solution of sodium bichromate and alum is incorporated, with constant stirring. When precipitation is complete a small proportion of tartaric acid is incorporated in the pigment. The latter step is reported to brighten the shade of the pigment and to reduce the tendency of the green to float to the surface when ground in oil.[49]

Chrome greens are resistant to action of light and do not bleed in lithographic varnish, water, alcohol, or hot paraffin wax. Also, there apparently is only a very slight change in shade of these pigments on baking at 250° F. for 0.5 hour. However, chrome greens are attacked by aqueous alkali, being converted to a brown color by this treatment.

Because of the presence of iron blue in chrome greens, the latter tend to be reduced by lithographic varnish, if the two are kept in contact for a short period. For this reason, chrome greens cannot be used in preparation of standard inks that are to be kept for any length of time. In some instances the iron blue may be reoxidized on printing, returning to its original shade. However, if loss of color of chrome green is caused by utilization of alkali extenders, no reversion of color can be secured by printing.[50]

Dispersion of pigments such as chrome green in inks was said to be aided by materials that are miscible in water and oil.[51] The precipitated pigment, after being washed and filter-pressed, was wetted with a small proportion of acetone or pyridine. Subsequent incorporation in an oil vehicle was stated to be facilitated in this manner. Also, the use of sulphite waste liquor[52] as dispersion agent for pigments has been suggested. The pigment and sulphite liquor are ground together and then run into a colloid mill that has oppositely rotating surfaces. Reduction

[48] E. R. Allen, *Official Digest, Federation Paint & Varnish Production Clubs,* 1931, No. **104**, 409; 1934, No. **138**, 235; *Rev. Paint, Colour, Varnish,* 1931, **4**, 108; *Chem. Abs.,* 1934, **28**, 7558; *Brit. Chem. Abs.* **B**, 1934, 1069. R. M. Reed, *Official Digest, Federation Paint & Varnish Production Clubs,* 1934, No. **138**, 245; *Brit. Chem. Abs.* **B**, 1934, 1069; *Chem. Abs.,* 1934, **28**, 7558.

[49] G. Zerr, *Farbe u. Lack,* 1933, 29; *Rev. Paint, Colour, Varnish,* 1933, **6**, 106. For use of ball mills in preparing pigments, see H. E. Wennström and C. P. Harris, *Amer. Paint J.,* 1928, **12** (25), 16; *Rev. Paint, Colour, Varnish,* 1928, **1**, 87.

[50] S. L. Karpeles, A. B. Portman and P. Thomasset, *Am. Ink Maker,* 1936, **14** (5), 39; *Chem. Abs.,* 1937, **31**, 4141; *Brit. Chem. Abs.* **B**, 1936, 702; *Rev. Paint, Colour, Varnish,* 1936, **9**, 242.

[51] E. C. DeStubner, British P. 277,949, 1926; *Brit. Chem. Abs.* **B**, 1929, 365; *Chem. Abs.,* 1928, **22**, 2672.

[52] Sulphite waste liquor is the aqueous residue from treatment of wood chips with aqueous solutions of sulphurous acid and calcium acid sulphite to prepare paper pulp. See E. R. Riegel, "Industrial Chemistry," New York, Reinhold Publishing Corp., 1937.

of particle size of the pigments from 5-10 microns to 0.5 micron was said to be secured in this way.

Hydrated Chromium Oxide, or emerald green, is made by fusion of potassium dichromate and boric acid at relatively high temperatures.[53] The product, hydrated chromium oxide, usually contains some oxides of boron. Removal of the latter is said to increase the brightness and freshness of the pigment. In place of boric acid, arsenious acid and phosphoric acid have been proposed. Utilization of the arsenic compound is stated to lead to a dull pigment, and phosphoric acid gives a green which is water-soluble.

Greens prepared with boric acid are resistant to light and do not bleed in aqueous alkali, varnish, water, alcohol, or hot paraffin wax.[54] However, they are affected by baking at 250° F. for 0.5 hour, and also are somewhat difficult to grind.

White, symbol of purity and cleanliness, is admirably suited for printing on colored surfaces. Employed in conjunction with colored backgrounds, it gives a sharpness to the printed page that scarcely can be matched by other pigment combinations. In printing inks the white pigments commonly employed are titanium dioxide, lithopone, white lead and zinc white.

Titanium Dioxide. One of the most abundant of the titanium-containing ores is stated to be ilmenite, which is found in the United States, Russia, Norway, Canada and India.[55] This ore, which contains large proportions of $TiO_2 . FeO$, generally is utilized in preparing titanium dioxide, the base of all titanium pigments. The ore first is treated with concentrated sulphuric acid to convert iron and titanium to sulphates. The acid is withdrawn and the solid portion which remains is leached with water to dissolve the water-soluble titanium and iron sulphates. Since some of the iron usually is present as ferric sulphate, the latter is reduced to ferrous sulphate by addition of metallic iron or zinc. The solution subsequently is concentrated by warming, then cooled to 5° C. to effect precipitation of ferrous sulphate. The iron salt is removed by filtration or centrifuging and the remaining solution boiled to bring about hydrolysis of titanium sulphate to hydrated titanium oxide ($TiO_2 \cdot 2H_2O$). The latter is calcined to remove water, leaving the anhydrous oxide (TiO_2) which is the form employed in pigments.

The popularity of titanium dioxide as a pigment has been stated to result principally from the high opacity and chemical inertness of this substance.[56] Also, resistance to change at elevated temperatures, perma-

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[53] V. N. Shul'tz, Yu. P. Nikol'skaya and L. F. Pen'kova, *J. Chem. Ind. (U.S.S.R.)*, 1929, **6**, 1412; *Chem. Abs.*, 1931, **25**, 830; *Brit. Chem. Abs.* **B**, 1931, 403; *Rev. Paint, Colour, Varnish*, 1931, **4**, 113.

[54] *Am. Ink Maker*, 1934, **12** (5), 23; *Rev. Paint, Colour, Varnish*, 1934, **7**, 194.

[55] G. Lovati, *Oil Colour Trades J.*, 1932, **81**, 401; *Rev. Paint, Colour, Varnish*, 1932, **5**, 3.

[56] D. W. Robertson, *Am. Ink Maker*, 1936, **14** (11), 18; *Brit. Chem. Abs.* **B**, 1937, 157; *Chem. Abs.*, 1937, **31**, 1232; *Rev. Paint, Colour, Varnish*, 1936, **9**, 377. See also N. Heaton, *Paint Varnish Production Mgr.*, 1930, **36** (1), 28; *Chem. Abs.*, 1930, **24**, 513, 3386; *Rev. Paint, Colour, Varnish*, 1930, **3**, 141. R. M. Bates, *Am. Ink Maker*, 1937, **15** (6), 25; *Chem. Abs.*, 1937, **31**, 5184; *Rev. Paint, Colour, Varnish*, 1937, **10**, 259.

nence of color in light and resistance to acids and alkalies were said to contribute to the value of titanium dioxide in inks.

The refractive index of titanium dioxide lies between 2.5 and 2.9, and this property is reflected in the high tinting strength of the oxide. Comparison of tinting strengths of various white pigments for a specific method of test[57] is indicated in Table 19. The values obtained were stated to furnish an index of the opacity of the pigments in linseed oil, and to be related directly to hiding power. In this manner, rapid evaluation of obscuring power of pigments was reported to be possible without employment of hiding power tests by brushout methods.[58]

Table 19.—Tinting Strength of Pigments.

Pigment	Relative Tinting Strength
Titanium dioxide	1200
Zinc oxide, American process	170
Lithopone	270
Zinc sulphide	630
Titanium barium pigment (30%)	430
Titanated lithopone	445
Double-strength lithopone	425

The chemical inertness of titanium dioxide is indicated by its insolubility in water, varnish oils, alcohol, and hot paraffin, its failure to react with vehicles or other pigments used in preparation of printing inks, and its fastness to light. Because of these properties and since it is a hydrophilic, polar solid, the ease of wetting and degree of dispersion of titanium dioxide were said to be determined by certain specific vehicle characteristics, independent of chemical reaction. Some white pigments, particularly zinc oxide, have been reported to be wetted and dispersed by chemical action as well as by the mechanical forces introduced in mixing and grinding operations. In the case of titanium dioxide, wetting and dispersion must be accomplished through the physical affinity of the oxide for liquids.[59]

Wetting of titanium dioxide was said to be dependent upon the polarity of the liquid wetting agent.[60] In general, wetting and dispersibility are increased by the presence of polar compounds in the dispersing medium. Thus, in an oil or varnish, the acidic compounds developed from heating an oil such as linseed become relatively important to dispersion. As the acid number of the oil increases, wetting and dispersion

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[57] C. E. Reynolds, *Am. Ink Maker*, 1936, 14 (11), 21 has described a constant volume method of tinting strength determination. This method was employed in the above tests.

[58] See, for example, A. E. Jacobsen and C. E. Reynolds, *Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 393; *Chem. Abs.*, 1935, 29, 4954; *Brit. Chem. Abs.* B, 1935, 69; cf. E. A. Becker, *Angew. Chem.*, 1938, 51, 418; *Farbe u. Lack*, 1938, 307; *Farben-Ztg.*, 1938, 43, (27), 726; *Rev. Paint, Colour, Varnish*, 1938, 11, 253.

[59] E. Sauer and W. Gussmann, *Kolloid-Z.*, 1938, 82, 253; *Chem. Abs.*, 1938, 32, 4360. M. Doniger, *Official Digest, Federation Paint & Varnish Production Clubs*, 1931, 107, 548; *Rev. Paint, Colour, Varnish*, 1931, 4, 223.

[60] L. W. Ryan, W. D. Harkins and D. M. Gans, *Ind. Eng. Chem.*, 1932, 24, 1288; *Chem. Abs.*, 1933, 27, 10; *Brit. Chem. Abs.* B, 1933, 29.

of titanium dioxide were said to be improved. However, the proportion of vehicle required to wet the pigment is comparatively small in relation to the entire vehicle, and further, wetting action was said to be selective with reference to the mixed components of the vehicle. For these reasons it was stated that an increase of the acid number of the linseed oil above 5 or 6 produced no further wetting beyond that obtained with oils having an acid number which approached these values.

In some instances, the acid number of the varnish oil is fixed at a low value, and heat-processing does not result in increased acid number. One such substance is tung oil. To secure good wetting and dispersion with the latter, fatty acids or their soaps have been suggested. Among those which have been reported effective were zinc oleate, zinc naphthenate, lead soaps, sulphonated oils, aluminum stearate,[61] tannic or gallotannic acid,[62] polycyclic alcohols (*e.g.*, cholesterol), fatty acid esters or amino-acids.[63] When aliphatic alcohols are employed as vehicle, suggested dispersing agents include halides of aluminum, cerium, iron, thallium, thorium, titanium or zirconium.[64]

The oil absorption of titanium dioxide has been stated to be about 18-28 pounds of oil per 100 pounds of pigment,[65] using the paste method of determining this value.[66] Low oil absorption types of titanium dioxide were stated to be somewhat more difficult to disperse than medium oil absorption grades. Although the difference in dispersion may not be noticeable in comparing two individual samples, it was said generally to be true, since low absorption types contain larger and more compact aggregates than do pigments which show a medium oil absorption. In some instances where it is possible to sacrifice hiding power because of decreased pigment concentration, dispersibility may be increased by utilization of titanium dioxide which shows medium oil absorption.

Composite titanium pigments marketed as "Titanox B," "Titanox C," "Ti-Bar" and "Ti-Cal" are blends of titanium oxide and an inert white extender. In preparing these blended pigments, the hydrated titanium oxide is precipitated as described in preparation of titanium dioxide, except that the oxide is precipitated on a base of barium or calcium sulphate. Subsequent calcination serves to remove water and to cement the pigment and extender. The final product comprises an inner core of extender surrounded by an outer shell of titanium oxide. "Titanox B," or "Ti-Bar," contains 25 per cent titanium oxide and 75 per cent barium

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[61] French P. 823,589, 1938, to British Titan Products Co., Ltd.; *Chem. Zentr.*, 1938, **109** (1), 4115; *Rev. Paint, Colour, Varnish*, 1938, **11**, 294.

[62] British P. 483,694, 1938, to British Titan Products Co., Ltd.; *Chem. Abs.*, 1938, 32, 7753; *Rev. Paint, Colour, Varnish*, 1938, **11**, 259; *Brit. Chem. Abs.* **B**, 1938, 1454. W. W. Plechner and J. M. Jarmus, French P. 828,698, 1938, to Titan Co., Inc.; *Chem. Abs.*, 1939, 33, 417.

[63] British P. 471,827, 1938, to British Titan Products Co., Ltd.; *Chem. Abs.*, 1938, 32, 1364. Polish P. 25,489, 1938; *Chem. Zentr.*, 1938, **109** (1), 4115; *Rev. Paint, Colour, Varnish*, 1938, **11**, 294.

[64] W. K. Nelson, French P. 828,699, 1938, to Titan Co., Inc.; *Chem. Abs.*, 1939, 33, 417.

[65] D. W. Robertson, *Am. Ink Maker*, 1936, **14** (11), 18; *Brit. Chem. Abs.* **B**, 1937, 157; *Chem. Abs.*, 1937, 31, 1232; *Rev. Paint, Colour, Varnish*, 1936, **9**, 377.

[66] A. S. T. M. D. 281-31; A. S. T. M. Standards, American Society for Testing Materials, Philadelphia, 1933.

sulphate, while "Titanox C," or "Ti-Cal," consists of 30 per cent of the oxide and 70 per cent calcium sulphate.

It is interesting to note that titanium oxide has been suggested as a component of black inks. The oxide, on being treated with an azo dye, was said to form a black pigment which was easily obliterated.[67] The latter was proposed for newspaper printing.

Lithopone is formed when aqueous solutions of zinc sulphate and barium sulphide are admixed. A double decomposition takes place, resulting in formation of a precipitate of zinc sulphide and barium sulphate.

$$ZnSO_4 + BaS \longrightarrow ZnS + BaSO_4$$

The coprecipitate thus secured is not applicable as a pigment, but is dried, then heated to a dull red glow and suddenly plunged into water. The sudden change in temperature develops the opacity of the pigment.

Ordinarily, lithopone contains 28-29 per cent zinc sulphide and 71-72 per cent barium sulphate. Since the tinting strength of lithopone is related to the zinc sulphide content, lithopones have been made which contained 50-60 per cent zinc sulphide.

Lithopone has a fairly good opacity and hiding power, and as a result, good tinting strength. It is insoluble in water, varnish oil, alcohol, and hot paraffin, and resistant to alkalies. However, dilute acids destroy the pigment, with evolution of hydrogen sulphide. With most vehicles lithopone is easily wetted, and produces inks of good whiteness and opacity. It dries with a half-luster which makes it peculiarly suited to overprinting.[68] A somewhat higher luster was stated to be imparted to lithopone when it was admixed with a small proportion of glue, gelatin or casein before being ground into the vehicle.[69]

In place of coalesced zinc sulphide-barium sulphate pigments such as lithopone, mechanically prepared mixtures of zinc sulphide and difficultly water-soluble fluorine compounds have been suggested as pigments.[70] These fluorine compounds have refractive indices less than 1.44, while extenders ordinarily used have refractive indices above this figure, as shown in Table 20. When employed in concentrations ranging from 60 to 75 per cent by weight of the zinc sulphide, the fluorine compounds were reported to give to the composite pigment a greater hiding power than was secured with a 30-per cent lithopone. The increased hiding power was said to be related inversely to the refractive index of the extending agent. Extenders with lowest refractive index were said to furnish pigments of greatest hiding power.

[67] E. Wydler, Swiss P. 179,454, 1936; *Chem Zentr.*, 1936, 107 (2), 876; *Chem. Abs.*, 1936, 30, 8663; *Rev. Paint, Colour, Varnish*, 1936, 9, 209.

[68] See, for example, *Farben-Ztg.*, 1936, 41, 588; *Rev. Paint, Colour, Varnish*, 1936, 9, 241. C. Eckmann, *Farben-Chem.*, 1935, 6 (1), 15; *Chem. Abs.*, 1935, 29, 3535; *Rev. Paint, Colour, Varnish*, 1935, 8, 2.

[69] K. S. Mowlds, U. S. P. 2,134,198, Oct. 25, 1938, to Glidden Co.; *Chem. Abs.*, 1939, 33, 886.

[70] J. B. Nichols, U. S. P. 2,113,381, April 5, 1938, to E. I. duPont de Nemours & Co.

Table 20.—Refractive Indices of Extenders.

Compound	Refractive Index
Sellaite (MgF_2)	1.382
Villiaumite (NaF)	1.336
Sodium silicofluoride (Na_2SiF_6)	1.299
Chiolite ($2NaF . AlF_3$)	1.347
Cryolite ($3NaF . AlF_3$)	1.364
Blanc fixe ($BaSO_4$)	1.64
Anhydrite ($CaSO_4$)	1.586
Aluminum hydrate	1.5-1.7
Magnesium hydroxide ($Mg(OH)_2$)	1.5
Magnesium silicofluoride ($MgSiF_6 . 6H_2O$)	1.349
Pachnolite ($NaF . CaF_2 . AlF_3 . H_2O$)	1.413
Calcium fluoride (CaF_2)	1.434
Magnesium carbonate ($MgCO_3$)	1.5-1.7

To increase dispersibility of lithopone, employment of substances insoluble in water but soluble in linseed oil have been proposed.[71] Among such compounds were included metallic soaps and fatty acid esters of ethylene glycol. On the other hand, it was stated that water-soluble compounds such as hexamethylenetetramine may be utilized to aid in wetting lithopone.[72]

The so-called "photogenic property" of lithopone, that is, its tendency to darken on exposure to sunlight and to be rebleached on being placed in the dark, has been almost completely overcome by manufacturers. However, it is interesting to note the explanations offered for this phenomenon. Lithopones which had been exposed to ultraviolet rays and then rebleached were observed to be more susceptible to darkening on exposure than samples that had not been exposed previously.[73] Also, it was found that metals present in driers tended to increase the darkening of lithopone and that, in this case, rebleaching did not occur. From these results the conclusions were drawn that darkening of lithopone in absence of driers occurred through reduction of zinc sulphide to metallic zinc and free sulphur and rebleaching through oxidation of metallic zinc to zinc oxide. Redarkening of a bleached sample on exposure was thought to be caused by interaction of zinc oxide and free sulphur, as well as by decomposition of more zinc sulphide. Darkening of samples containing metal driers was explained on the basis of formation both of metallic zinc and a dark-colored sulphide of the metal. In the latter case, employment of a drier whose metallic constituent would form a light-colored sulphide was suggested, to obviate formation of dark-colored compounds that could not be rebleached.

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[71] W. F. Meister, U. S. P. 2,113,539, April 5, 1938, to United Color and Pigment Co.; *Chem. Abs.*, 1938, **32**, 4363.

[72] H. Vollmann, German P. 568,693. 1927; *Chem. Abs.*, 1933, **27**, 2829.

[73] J. H. Goshorn and C. K. Black, *Ind. Eng. Chem.*, 1929, **21**, 348; *Chem. Abs.*, 1929, **23**, 5334; *Brit. Chem. Abs.* **B**, 1929, 443.

Addition to lithopone of materials which increase color-fastness of the pigment has been suggested.[74] Among proposed agents for this purpose are titanium dioxide, magnesium oxide, tricalcium phosphate, cobalt sulphate or nickel sulphate.

White Lead is the basic carbonate of lead and may be represented as $PbCO_3 . Pb(OH)_2$. A number of processes are employed in manufacture of white lead, including the old Dutch process, the Carter process, the Matheson, or French, process and the Rawley process.

The old Dutch process depends upon the action of acetic acid and carbon dioxide upon lead.[75] Pure lead, cast in the form of perforated buckles, is placed together with dilute acetic acid (28-per cent) in earthenware pots which have a number of small holes in their sides above the level of the acid. The pots then are set upon a layer of tanbark employed to cover the planking. Stacking of alternate layers of tanbark and charged pots is continued until a tier of eight to ten layers of pots is secured.

The spent tanbark liberates carbon dioxide and heat, the latter serving to maintain the temperature at approximately 70° C. (158° F.). At this temperature the lead buckles are reacted upon by acetic acid, forming lead acetate, which is decomposed by carbon dioxide into basic lead carbonate. After a period of three months, the pots are unpacked, and basic lead carbonate separated from unchanged lead by grinding. The latter then may be recast and used again.

In the Carter Process,[76] melted lead is atomized with superheated steam, then rotated in large cylinders with dilute acetic acid and carbon dioxide for periods of about two weeks. In this manner, basic lead carbonate is formed.

Interaction of litharge (lead oxide, PbO) and acetic acid to yield basic lead acetate is the foundation of the Matheson, or French, Process.[77] Carbon dioxide then is employed to convert the acetate to basic lead carbonate, white lead.

The Rawley process consists of exposing a suspension of atomized lead in water to warm air. By this means lead hydroxide is produced, and the latter then is treated with carbon dioxide to form white lead.

White lead is insoluble in water, varnish oils, alcohols and hot paraffin. When employed in a bodied linseed oil, the pigment reacts with a portion of the fatty acids present, yielding lead linoleate and other soaps. The latter act as driers, eliminating the necessity of extraneous addition of these substances, except where extreme speed of drying is desired.[78] White lead inks possess the undesirable property of darkening on exposure to

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[74] A. P. Polozov and R. P. Govorova, *Mem. Inst. Chem. Tech., Acad. Sci. Ukrain. S.S.R.*, 1938, **9**, 151; *Brit. Chem. Abs.* **B**, 1938, 1326; *Chem Abs.*, 1938, **32**, 9526.

[75] See, for example, J. B. Nealey, *Chem. Met. Eng.*, 1928, **35**, 219; *Chem. Abs*., 1928, **22**, 2069.

[76] J. S. Staudt, *Ind. Eng. Chem.*, 1909, **1**, 758; *Chem. Abs.*, 1910, **4**, 253.

[77] E. R. Riegel, "Industrial Chemistry," Reinhold Publishing Corp., New York, 1937.

[78] A. W. Anderson, *Paint, Oil & Chem. Rev.*, 1935, **97** (8), 42; *Chem. Abs.*, 1935, **29**, 4955.

hydrogen sulphide fumes or on mixing with some lithopones, ultramarine blue, cadmium yellows and reds, or vermilion. The lead pigment is heavy, opaque, and has good hiding power and is stated to be applicable for cover whites and glossine whites particularly.[79] Oil absorption values [80] for white lead lie in the range 7.9-15.8, which would place this pigment below zinc oxide, titanium oxide and lithopone in this respect.[81]

Zinc White has been prepared by two processes, the French, or indirect, and the Weatherill, or direct, methods. In the former method the zinc ore first is reduced to zinc metal.[82] Since the temperature of reduction is higher than the boiling point of metallic zinc, the latter vaporizes as soon as it is formed. Effective separation of the latter from impurities is secured in this way. The zinc vapors then are burned to zinc oxide, or zinc white. The direct process comprises separation of the ore, or franklinite from siliceous material with electromagnets, since the ore is magnetic.[83] The latter, which contains iron and manganese oxides in addition to zinc oxide, is burned together with coal. In this way, zinc oxide is reduced to zinc metal, vaporized and burned to zinc oxide by the air over the fire.

Zinc white is a fairly heavy and very opaque pigment.[84] The fine particle size of zinc white, the result of its formation as a vapor, gives to the oxide a relatively high oil absorption, the values ranging between 8.3 and 27.[85] Also, as a consequence of particle size, zinc white has very good working properties. It is insoluble in water, alcohol, hot paraffin and varnish oils, and exhibits little tendency to react with linseed oil vehicles.[86] Zinc oxide is unaffected by dilute aqueous alkali, but is readily dissolved by concentrated aqueous solutions of alkalies or acids.

Employment of substances having a refractive index less than 1.44 as extending agents for zinc oxide has been suggested.[87] Such mixtures were stated to have a greater hiding power than blends containing materials whose refractive index is above this value. Among the proposed extenders were included sellaite, villiaumite, sodium silicofluoride, chiolite, cryolite, magnesium silicofluoride, pachnolite and calcium fluoride.

[79] R. L. Hallett, *Proc. Am. Soc. Testing Materials*, 1926, 26 (2), 538; *Chem. Abs.*, 1927, 21, 1363.

[80] See H. A. Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," Institute of Paint and Varnish Research, 1935.

[81] E. Klumpp, *Farben-Ztg.*, 1928, 33, 1044; *Brit. Chem. Abs.* B, 1928, 164; *Chem. Abs.*, 1928, 22, 3790.

[82] F. O. Case, *Eng. Mining J.*, 1929, 128, 318; *Chem. Abs.*, 1929, 23, 5115. F. Johannsen, *Metall u. Erz.*, 1927, 24, 249; *Chem. Zentr.*, 1927, 98 (2), 734; *Chem. Abs.*, 1928, 22, 4427.

[83] R. G. Daniels, *J. Oil Colour Chem. Assoc.*, 1928, 11, 277; *Chem. Abs.*, 1929, 23, 242; *Brit. Chem. Abs.* B, 1928, 783.

[84] F. Schmid, *Z. angew. Chem.*, 1929, 42, 1101; *Chem. Abs.*, 1930, 24, 1752; *Brit. Chem. Abs.* B, 1930, 248. For a method of determining particle fineness of zinc white see H. J. Mueller, *Rubber Age (N. Y.)*, 1938, 43, 363; *Chem. Abs.*, 1938, 32, 9408. *Gummi-Ztg.*, 1938, 52, 995; *Brit. Chem. Abs.* B, 1938, 1326.

[85] H. A. Gardner, J. R. Stewart and A. W. Van Heuckeroth, *Am. Paint & Varnish Mfrs. Assoc. Circ.*, 1933, No. 444, 274; *Chem. Abs.*, 1933, 27, 5992. E. L. Klumpp and H. Meier, *Farben-Ztg.*, 1931, 36, 2120; *Chem. Abs.*, 1931, 25, 5999. A. Foulon, *Allgem. Oel-u. Fett. Ztg.*, 1938, 35, 433; *Brit. Chem. Abs.* B, 1939, 74.

[86] K. Charisius and E. Kindscher, *Farben-Ztg.*, 1931, 36, 780; *Chem. Abs.*, 1931, 25, 2308; *Brit. Chem. Abs.* B, 1931, 356.

[87] J. B. Nichols, U. S. P. 2,113,380, April 5, 1938, to E. I. duPont de Nemours & Co.; *Chem. Abs.*, 1938, 32, 4363.

Metallic Pigments

The silvery sheen of aluminum and the golden glint of bronze have made these materials particularly useful as pigmenting agents in printing inks employed in advertisements.[88] In the case of aluminum, successful application of the metal in printing inks appears to depend upon the size of particles. It was reported that aluminum powder that would pass through a 1000-mesh screen would produce a fine, silvery surface on printing.

The preparation of aluminum powder usually is effected by hammering aluminum under mechanical stamps until the particles are small enough and thin enough to pass through a screen of 1000-mesh.[89] During the stamping operation a lubricant is added to the metal to prevent welding of the particles. Among materials suggested for this purpose are stearic acid, tallow, olive oil and rape oil. After the stamping and sifting operations, the aluminum powder usually is polished by brushing.

The ability of aluminum powder to cover a surface was called the covering area on water.[90] This value, usually expressed in square centimeters per gram of aluminum, is analogous to the covering power of paint. Covering areas on water secured for aluminum powder were stated to indicate that well-worked powder films are one flake thick.

The hiding power of aluminum, particularly among those grades which pass through a 1000-mesh screen, has been stated to be high enough to permit obtaining clear, distinct prints on almost all types of background. Opacity to light, which is somewhat related to hiding power, also is high especially in the finely divided metallic pigments.[91]

Printing inks containing aluminum pigments usually employ vehicles similar to those for other coloring agents. Thus, bodied linseed oil may be utilized as dispersing agent, though China Wood oil or perilla oil generally are recommended.[92] Manganese or cobalt driers together with gums, resins and rosin oil also are included in the ink. The metallic pigment, which comprises 20-40 per cent by weight of the printing ink, is mixed with the ink with a knife or spatula, and is not ground in like other coloring agents. Apparently the ink has its maximum color strength when the metallic pigment is admixed with the base just before the printing operation.[93]

Handling of aluminum printing inks on presses requires some special precautions. Because of the tendency of aluminum powder to ball up on rolls, it has been suggested that the ink be transferred from fountain to

[88] See, for example, *Witcombings*, 1937, December.

[89] J. D. Edwards, "Aluminum Paint and Powder," New York, Reinhold Publishing Corp., 1936.

[90] J. D. Edwards and R. B. Mason, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 159; *Brit. Chem. Abs.* **B**, 1934, 630; *Chem. Abs.*, 1934, **28**, 3918.

[91] See J. H. Meyer, *Am. Ink Maker*, 1931, 9 (7). 21; *Chem. Abs.*, 1931, 25, 5582.

[92] F. C. Arthur, *Am. Ink Maker*, 1936, **14** (6), 23; *Chem. Abs.*, 1936, **30**, 5818; *Brit. Chem. Abs.* **B**, 1936, 751; *Rev. Paint, Colour, Varnish*, 1936, **9**, 241.

[93] See *Paint, Colour, Varnish, Ink, Lacquer Manufacture*, 1931, **1** (8), 215; *Rev. Paint, Colour, Varnish*, 1931, **4**, 287.

type with a minimum of rolling and transferring. This may be accomplished by utilization of a small number of rollers, in contrast with non-metallic inks, where the largest number of rollers possible is employed to spread the ink out to a very thin film. Also since aluminum inks tend to pile up on rollers and plates, more frequent wash-ups may be necessary with this type of ink than with non-metallic coloring agents.

Alloys of copper with other metals, known as bronze or bronze powders, are atomized in much the same manner as aluminum powder.[94] The alloy first is hammered until particles small enough to be utilized in the printing process are secured. These particles are sifted and polished, the latter operation being effected by brushing or by heating.

EXTENDERS

Extenders are solid substances that are employed in printing inks to reduce the price of the finished ink. The extending agent has no coloring or hiding power, but if employed in small proportions together with a pigment will serve to increase the area covered per unit weight of pigment. Among natural materials, barytes, whiting and china clay are used as extenders, while the manufactured extending agents include alumina hydrate, blanc fixe, gloss white and magnesium carbonate.

Baryte, or natural barium sulphate, is found in many parts of the world as the mineral, barite or heavyspar. The preparation of the mineral for employment as extending agent is effected by grinding the hard, brittle raw material to a coarse powder. The latter then is ground to a paste with water, and the paste diluted with a further quantity of water. The wetted or levigated extender is placed in a settling tank where the coarse particles settle out. The finer particles, which are held in suspension in the water, are conducted to a second tank where they are allowed to settle from the water. The latter is withdrawn, and the finely divided baryte removed and dried.

Baryte extenders contain 98.7-99.45 per cent barium sulphate, and traces of silica, iron oxide, aluminum and calcium oxides. The specific gravity is high, usually in the range 4.37-4.46, but oil absorption is relatively low, between 7.4 and 8.0. Barytes have been utilized as extenders in plate and stamping inks. Usually this material is employed in relatively small proportions because of its tendency to cause wearing or abrasion on the inking plates and dies.

Prolonged grinding of baryte has been stated to yield an extender whose particle size is approximately equal to that of precipitated blanc fixe.[95] However, the structure of individual particles of the two substances is quite different. Blanc fixe is composed of clumps of very fine

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[94] D. A. Both, *Am. Ink Maker*, 1935, 13 (8), 15; *Ind. Finishing*, 1935, 11 (9), 9, 46; *Chem. Abs.*, 1935, 29, 6442; *Rev. Paint, Colour, Varnish*, 1935, 8, 373. E. Keller, *Papier-Ztg.*, 1937, 62, 1632; *Rev. Paint, Colour, Varnish*, 1938, 11, 109. W. Lange, *Kartonnagen-u, Papierwaren-Ztg.*, 1936, 40, 461; *Farben-Chem.*, 1936, 7, 420; *Rev. Paint, Colour, Varnish*, 1936, 9, 377. E. J. Rhodes, *Brit. Print.*, 1936, 49, (291), 109; *Rev. Paint, Colour, Varnish*, 1936, 9, 377.

[95] H. Wagner, *Farben-Ztg.*, 1938, 43, 361; *Chem. Abs.*, 1938, 32, 8802.

crystallites with a large internal surface. On the other hand, particles of finely-divided baryte are small compact objects. The latter were said to exhibit low oil absorption and to have good covering power.

Whiting or Paris White usually is prepared from naturally occurring limestone or calcium carbonate deposits such as those on the southern shores of England. The raw material is worked up in the same manner as are barytes. The most finely divided particles are used for printing inks. The specific gravity of whiting extenders is in the range 2.63-2.83, and the oil absorption value lies between 12.1 and 19.0.

Utilization of natural whiting generally has been restricted to plate and stamping inks, since it has a tendency to cake and pile up on the forms employed in typographic printing.[96] However, calcium carbonate in colloidal form has been reported, and it was stated that this material could be utilized in printing inks and screen process inks.[97]

China clay or kaolin is a fine white amorphous material that consists of hydrated aluminum silicate together with smaller proportions of quartz, mica, and feldspar.[98] The crude clay, which is found principally in England and the United States, is washed (with a stream of water) through a number of connected wooden troughs in which the coarser particles are separated from the finer material. The latter, which remains in suspension in the water during passage through the troughs is conducted to tanks when the fine clay is allowed to settle out.

In a few cases, specially processed china clays with particle size of colloidal dimensions have been utilized as extenders in some types of inks.[99] Kaolin has a fairly high oil absorption, the values being in the range 20.5-46.8. However, inks in which a fairly high proportion of the clay was employed were said to dry with a somewhat poor finish. Also, china clays apparently show some tendency to cake on plates and forms. Because of this property and its abrasive action, utilization of this extending agent in printing inks has been limited to some extent.

Alumina hydrate, or aluminum hydrate, has found acceptance as extending agent in almost all grades of printing inks. The hydrate is prepared by slowly adding an aqueous solution of sodium carbonate to a solution of aluminum sulphate in water.[100] Alumina hydrate is formed

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[96] A. B. Searle, *Paint Manuf.*, 1937, 7 (6), 188; *Brit. Chem. Abs.* **B**, 1937, 944; *Chem. Abs.*, 1937, **31**, 6033; *Rev. Paint, Colour, Varnish*, 1937, **10**, 238.

[97] See *Am. Ink Maker*, 1938, **16** (12), 41.

[98] H. F. Collins, *Chem. and Ind.*, 1923, **42**, 88, 114; *Chem. Abs.*, 1923, **17**, 1697. J. E. Aitken, *Proc. Tech. Sect. Paper Makers' Assoc., Gt. Brit. Ireland*, 1929, **10**, 213; *Chem. Abs.*, 1930, **24**, 4908; *Brit. Chem. Abs.* **B**, 1930, 558.

[99] For preparation and properties of colloidal kaolin, see E. Soyez and M. Chérouvrier, German P. 634,345, 1936; *Chem. Abs.*, 1936, **30**, 8544. French P. 736,198, 1931; *Chem. Abs.*, 1933, **27**, 1462; French P. 42,823, 1933; *Chem. Abs.*, 1934, **28**, 1483. R. Dubrisay, *Bull. soc. encour. ind. nat.*, 1931, **130**, 176; *Chem. Abs.*, 1931, **25**, 4373. I. I. Zhukoff and M. N. Sokolova, *Kolloid-Z.*, 1929, **48**, 71; *Chem. Abs.*, 1929, **23**, 5383.

[100] G. Reyes, *Bol. minero soc. nacl. mineria (Chile)*, 1934, **46**, 567; *Chem. Abs.*, 1935, **29**, 3265. See also A. W. Whitaker, Jr., *Can. Chem. Met.*, 1936, **20**, 8; *Chem. Abs.*, 1936, **30**, 2327. I. Ya. Klinov and D. I. Suichev, *J. Applied Chem. (U.S.S.R.)*, 1935, **8**, 389; *Chem. Abs.*, 1936, **30**, 3597. J. C. Séailles, *15me Congr. chim. ind. (Bruxelles, Sept., 1935)*, 1936, 894; *Chem. Abs.*, 1936, **30**, 5781. V. A. Plotnikov, O. K. Kudra, D. P. Zosimovich and I. M. Podorvan, *J. Chem. Ind. (Moscow)*, 1934 (10), 50; *Chem. Abs.*, 1935, **29**, 1016.

as a flocculent precipitate which settles slowly. Apparently the optimum precipitation temperature is approximately 60° C. (140° F.). Also, the precipitated alumina hydrate is said to settle out much more quickly if some sodium chloride is present in the aluminum sulphate solution. When the latter step has been completed, the spent solution is withdrawn and the alumina hydrate washed several times with water and then dried.

Alumina hydrate is reported to have excellent working qualities and to impart this property, at least to some degree, to any pigment with which it is employed. The hydrated extending agent is said to have a low specific gravity and high oil absorption. Also, as was mentioned before, alumina hydrate has a fluffy, flocculent form and texture.[101] When an ink vehicle which is somewhat acidic is employed with alumina hydrate, the latter shows a tendency to liver. Because of this property, the use of alumina hydrate in heavy varnishes which are somewhat acidic has been limited. Also aluminum hydrate reacts slowly with driers in the ink. It replaces the metallic portion of the drier, forming aluminum resinate, borate, linoleate, and like compounds. The aluminum salts thus formed are non-driers, so that the effect is to destroy the driers. Thus, utilization of the hydrated extending agent in inks which are to be stored for some time has been precluded to some extent.

Blanc fixe, or manufactured barium sulphate, may be prepared from either natural barium carbonate (witherite) or sulphate (barytes). When witherite is utilized as raw material, it is dissolved in hydrochloric acid to form barium chloride.[102] The solution then is filtered, and the filtrate treated with sulphuric acid. In this manner, barium sulphate is precipitated. The spent solution subsequently is withdrawn from the precipitate, and the latter washed with water and dried. In instances where barytes are employed to furnish blanc fixe, the natural mineral first is roasted with coal. Thus the barium sulphate is converted to barium sulphide. The latter is dissolved in hydrochloric acid, the solution filtered and the sulphate precipitated in a manner similar to that described for witherite.[103]

Blanc fixe has a relatively high specific gravity (3.72-4.36), and the oil absorption of this extending agent lies between 11.7 and 20.6. It grinds fairly easily, but is said to have somewhat poor working qualities. Blanc fixe has been reported to be fairly brilliant in color, as indicated in Table 21. The values were estimated, using a photometer, and the brilliancy of magnesium oxide was set at 100.[104] Also, the stability and inertness of barium sulphate extenders make them useful in almost all types of vehicle, without danger of reaction. The latter property,

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[101] C. Eckmann, *Farben-Chem.*, 1935, 6, 15; *Chem. Abs.*, 1935, 29, 3535.

[102] V. Charrin, *Peintures, pigments, vernis*, 1931, 8, 1560; *Chem. Abs.*, 1931, 25, 5778. I. I. Iskoldskii, *Mineralnoe Suir'e*, 1930, 5, 389; *Chem. Abs.*, 1931, 25, 4772. G. Erdmann, *Farbe u. Lack*, 1930, 381, 391; *Chem. Abs.*, 1930, 24, 5170.

[103] See also H. Wagner and A. Jorzig, *Farben-Ztg.*, 1934, 39, 715; *Brit. Chem. Abs.* B, 1934, 803; *Chem. Abs.*, 1934, 28, 6325; *Rev. Paint, Colour, Varnish*, 1934, 7, 357.

[104] F. Schmid, *Z. angew Chem.*, 1929, 42, 1101; *Chem. Abs.*, 1930, 24, 1752.

Table 21.—Brilliancy of Some Pigments and Extenders.

Substance	Brilliancy	Substance	Brilliancy
Magnesium oxide	100	Lithopone	94-97
Blanc fixe	97-99	Zinc sulphide	94-97
Titanium dioxide	94-97	White lead	94-97
Zinc white	94-97	Heavyspar	92-94

together with the brilliance of blanc fixe, has been reported to render this material very efficient as a cheapening agent. Thus, it has been used in "Titanox B" as a cheapening agent for titanium dioxide.

Gloss White is the product secured by coprecipitation of alumina hydrate and blanc fixe. Usually the two substances are present in the ratio of 3 parts of blanc fixe to 1 part of aluminum hydrate. As might be expected, the specific gravity, oil absorption, brilliancy and stability lie somewhat between that of either of its constituents. Thus, while strong acids dissolve out the alumina hydrate portion of gloss white, the blanc fixe is unaffected. Inks prepared with acidic vehicles and gloss white extenders do not tend to liver as easily as do those made with alumina hydrate. On the other hand the brilliance of gloss white is somewhat less than that of blanc fixe. The working qualities of the coprecipitated extender are very good and it has been utilized as inert base in almost all types of printing inks.

Also it has been been suggested that magnesium carbonate[105] or coprecipitated magnesium and calcium carbonates[106] be utilized as extending agents for printing inks. The coprecipitated mixture may be prepared by treating calcined dolomite (MgO and CaO) with water to form a slurry of the hydroxides of magnesium and calcium. Subsequently the slurry is treated with aqueous sodium carbonate solution to effect precipitation of the mixed carbonates.

Urea-formaldehyde condensation products have been proposed as extenders for all types of pigments.[107] In preparing one such extender 600 parts of urea are dissolved in 1620 parts of a 37-per cent solution of formaldehyde. About 80 parts of active filter carbon are added and the mixture filtered. The water-clear filtrate (which has a pH of about 7) is heated at 100° C. for 8 hours. This increases the viscosity but does not impair the clearness of the solution. 7.5 Parts of finely pulverized thiourea are incorporated in 100 parts of this solution. To obtain the extended pigment, the latter is milled with the above varnish and the water removed. For example, 15 parts of indanthrene blue GGSL are ground overnight in a ball mill with 300 parts of the varnish. The fine suspension thus obtained is heated for 4 hours at 130° C. and the product reduced to a fine powder. Another method is to obtain the dry resin, pulverize it and then grind it in with the pigment.

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[105] W. W. Plowman and W. Feldenheimer, British P. 405,391, 1934; *Brit. Chem. Abs.* **B, 1934**, 450; *Chem. Abs.*, 1934, **28**, 4845.

[106] H. R. Rafsky, British P. 178,806, 1921; *Chem. Abs.*, 1922, **16**, 3405; *J. S. C. I.*, 1922, **41**, 474A.

[107] G. Widmer, British P. 431,168, 1935, to Society of Chemical Industry in Basle; *Brit. Chem. Abs.* **B, 1935**, 815; *Chem. Abs.*, 1936, **30**, 309; French P. 771,966, 1934; *Chem. Abs.*, 1935, **29**, 1647; *Rev. Paint, Colour, Varnish*, 1935, **8**, 180; *Chem. Zentr.*, 1935, **106** (1), 2608.

ORGANIC COLORS

The organic color industry began its important and highly successful career in 1856. In that year Perkins made his now famous discovery that a dye, mauve, could be produced from coal-tar. Within a short period a number of other coloring agents were produced from the same source, and an infant industry began to grow. Because of the cost of preparing early dyes and also because of the great demand, manufacture of coloring agents for textiles, rather than for printing inks, was emphasized for some time after the first preparation of a synthetic organic dye.[108] About 1895 some organic dyestuffs which had been developed primarily as textile coloring agents, such as Para Red, Hansa Yellow, Lithol Red, Lake Red C and Toluidine Red, were employed as printing-ink pigments. From this relatively recent beginning has grown the tremendous printing-ink organic pigment industry.

The factor which, more than any other, gave impetus to the development of a dyeing industry in the United States was the World War of 1914-1918. Prior to this, American color users generally had depended upon German manufacturers for pigments. When this source of supply failed, color users in the United States were forced to make their own pigments.

A classification of organic printing ink pigments may be made on the basis of physical properties of dyes and method of treatment.[109] In this way five classes of coloring agents are obtained:

(1) Water-soluble basic dyes.
(2) Water-soluble acid dyes, including xanthene derivatives.
(3) Mordant dyes.
(4) Insoluble or partially soluble dyes with lake-forming properties.
(5) Insoluble dyes without lake-forming properties, or the so-called pigment dyestuffs.

Any detailed explanation of the reactions or methods of manufacture which lead to the formation of the dyestuffs in the above classes is beyond the scope of this book.[110] However, the preparation of each of the above classes of dyestuffs will be outlined, and some of the properties which make these materials applicable in the printing-ink industry will be mentioned.

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[108] L. E. May, *Am. Ink Maker*, 1937, 15 (11), 16; *Chem. Abs.*, 1938, 32, 1493; *Rev. Paint, Colour, Varnish*, 1938, 11, 3.

[109] R. A. Shive, *Am. Ink Maker*, 1938, 16 (3), 23; *Chem. Abs.*, 1938, 32, 3988; *Brit. Chem. Abs.* B, 1938, 942. See also R. N. Shreve, "Dyes Classified by Intermediates," The Chemical Catalog Company, Inc., New York, 1922. Toxicity of a number of pigments has been reported by A. Beythien, *Farben-Chem.*, 1938, 9, 77; *Chem. Abs.*, 1938, 32, 8801.

[110] For details regarding manufacture, intermediates and properties of dyes, see for example, J. C. Cain and J. F. Thorpe, "The Synthetic Dyestuffs and Intermediate Products," London. Charles Griffin and Co., Lt., 1913. A. G. Green, "Organic Coloring Matters," London, Macmillan and Co., Ltd., 1908. A. Wahl and F. W. Atack, "Organic Dyestuffs," G. Bell and Sons. Ltd., London, 1914. I. W. Fay, "The Chemistry of the Coal-Tar Dyes," New York, D. Van Nostrand Company, 1911. T. Beacall, F. Challenger, G. Martin and H. J. S. Sand, "Dyestuffs and Coal-Tar Products," 4th Edition, London, Crosby Lockwood and Son, 1926.

Water-soluble Basic Dyes. Basic dyes are coloring agents in which a dye-base takes the place of the basic constituent of a salt. Generally they are marketed as colorless hydrochlorides or zinc chloride double salts of the dyestuffs. Production of pigment lakes from these materials is effected by dissolving the dyestuff in water and adding an inert material such as alumina hydrate or bentonite to act as substrate.[111] Subsequently an aqueous solution of an acid such as tannic, phosphotungstic or phosphomolybdic is added to the mixed dye and substrate.[112] In this manner an insoluble colored lake is precipitated on the substrate.[113]

After formation of the lake has been completed, the latter may be suspended in an aqueous solution of aluminum sulphate. Phosphoric acid is incorporated in the mixture to bring about precipitation of a film of aluminum phosphate on the pigment particles.[114] The coating of aluminum salt on the laked pigment was stated to render the latter insoluble in oil vehicles and to prevent agglomeration and thickening of color during formulation of the ink composition.

Also, it has been reported that the amount of coloring matter that must be distributed over a given area base to secure complete coverage can be decreased considerably if the lake is precipitated on a foundation substance such as ground wood pulp or cellulose.[115]

Among the water-soluble basic dyes used for making printing ink pigments are included the triphenylmethane dyes, such as Methyl Violet, Victoria Blue, Malachite Green, Brilliant Green, Victoria Green, Magenta and Setoglaucine.[116] Also, Rhodamine, Thioflavine and Auramine may be classed as basic dyes. To illustrate the general procedure followed in the synthesis of these coloring agents, the steps involved in the preparation of Methyl Violet, one of the more important members of this series, will be outlined.

Benzene secured from the light oil fraction of coal-tar is nitrated to form nitrobenzene. Reduction of the latter with iron in acetic acid furnishes aniline. Alkylation of aniline with methyl alcohol and sulphuric acid results in the formation of dimethylaniline. The dialkylamine then is admixed with copper nitrate, sodium chloride, sand and an acid, and heated at 40-60° C. In this way the amine is oxidized to yield Methyl Violet.

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[111] H. T. Neumann, U. S. P. 2,007,980, July 16, 1935, to Henry T. Neumann Research Inc.; *Chem. Abs.*, 1935, 29, 6081; *Brit. Chem. Abs.* B, 1936, 652; *Rev. Paint, Colour, Varnish*, 1935, 8, 490. French P. 791,708, 1935; *Chem. Abs.*, 1936, 30, 4343.

[112] H. Hadert, *Farben-Chem.*, 1931, 2, 562; *Rev. Paint, Colour, Varnish*, 1932, 5, 25. *Farbe u. Lack*, 1929, 34, 250; *Rev. Paint, Colour, Varnish*, 1929, 2, 116, H. Hadert, "Handbuch über die Herstellung and Verwendung der Druckfarben," Otto Elsner, Verlagsgesellschaft m. b. H., Berlin, 1931. C. A. Curtis, "Kunstliche organische Pigmentfarben," Julius Springer, Berlin, 1929.

[113] W. D. Bancroft and J. W. Ackerman, *J. Phys. Chem.*, 1930, 34, 1767; *Brit. Chem. Abs.* B, 1930, 1247; *Chem. Abs.*, 1930, 24, 5500; *Rev. Paint, Colour, Varnish*, 1930, 3, 176.

[114] A. Chwala, British P. 458,761, 1936; *Chem. Abs.*, 1937, 31, 3716; *Brit. Chem. Abs.* B, 1937, 264; *Rev. Paint, Colour, Varnish*, 1937, 10, 77, French P. 788,001, 1935; *Chem. Abs.*, 1936, 30, 1594; *Rev. Paint, Colour, Varnish*, 1936, 9, 149.

[115] E. O. S. Gentele and H. R. Gentele, British P. 7399, 1897; *J. S. C. I.*, 1897, 16, 546.

[116] A. McNeil, *Am. Ink Maker*, 1936, 14 (8), 17; *Rev. Paint, Colour, Varnish*, 1937, 10, 24; *Chem. Abs.*, 1936, 30, 6967. Kümmel, *Farben-Ztg.*, 1937, 42, (2), 40; *Rev. Paint, Colour, Varnish*, 1937, 10, 24.

As precipitants for preparing lakes from water-soluble basic dyes, acids such as arsenic, phosphoric and resinic have been employed.[117] When tannic acid is utilized to effect formation of lakes, a small proportion of tartar emetic (antimony potassium tartrate) is generally incorporated in the reaction mixture to aid in securing complete precipitation of the laked dyestuff. Also, potassium carbonate has been advocated for the same purpose as the tartaric acid salt.[118] In some instances addition of oxides of antimony either to the finished lake or during preparation of the latter has been proposed.[119]

Lakes produced from basic dyestuffs with precipitants such as those described usually have great clearness and purity of color. However, these pigments generally are apt to bleed in alkali, soap, water, or alcohol. The most objectionable property of such coloring agents is their tendency to fade very quickly on exposure to light. These are the so-called light-fugitive dyes.

The tendency to fading of lakes produced from water-soluble basic dyestuffs has been overcome, to a considerable extent, by utilization of certain complex acids, particularly phosphomolybdic and phosphotungstic as precipitating agents.[120] The tungstated or molybdated lakes are reported to be brilliant, to have good light resistance, to be relatively non-bleeding in lithographic varnish, water and paraffin. However, bleeding is somewhat pronounced in alkali, soap, or alcohol.

The qualities and characteristics of lakes prepared with phosphotungstic acid have been compared with those made with phosphomolybdic acid.[121] It was stated that lakes produced under comparable conditions indicated that tungsten lakes required more precipitating agent than those prepared with molybdenum. Further, lakes containing the latter metal were reported to be much bulkier than the corresponding tungsten lakes. It was said that the acidity of a solution containing a water-soluble basic dyestuff could be controlled more easily when the precipitant was an acid containing molybdenum. Lakes prepared from complex molybdenum acids were stated to have a lower specific gravity, higher oil absorption, greater strength, and to be easier to grind than tungsten lakes. However, the latter were slightly brighter in top tone.[122]

[117] See, for example, T. Beacall, F. Challenger, G. Martin and H. J. S. Sand, "Dyestuffs and Coal-Tar Products," Crosby Lockwood and Son, London, 1926. S. L. Karpeles, A. B. Portman and P. Thomasset, *Am. Ink Maker*, 1936, 14 (5), 39; *Chem. Abs.*, 1937, 31, 4141; *Brit. Chem. Abs.* **B**, 1936, 702; *Rev. Paint, Colour, Varnish*, 1936, 9, 242. G. J. Baker, *Verfkroniek*, 1936, 9, 256; *Chem. Abs.*, 1936, 30, 7851. G. Zerr, *Farbe u. Lack*, 1933, 223; *Chem. Abs.*, 1933, 27, 3336; *Rev. Paint, Colour, Varnish*, 1933, 6, 106.

[118] E. C. Philippe-Lavallée, French P. 791,135, 1935; *Chem. Abs.*, 1936, 30, 3261; *Rev. Paint, Colour, Varnish*, 1936, 9, 242.

[119] *Am. Ink Maker*, 1938, 16 (4), 39; *Rev. Paint, Colour, Varnish*, 1938, 11, 192. *Farben-Ztg.*, 1936, 41, 306; *Rev. Paint, Colour, Varnish*, 1936, 9, 169.

[120] A. B. Portman, *Am. Ink Maker*, 1935, 13 (6), 37; *Brit. Chem. Abs.* **B**, 1935, 684; *Chem. Abs.*, 1935, 29, 4955; *Rev. Paint, Colour, Varnish*, 1935, 8, 284. A. Linz, *Am. Ink Maker*, 1938, 16 (5), 18; *Chem. Abs.*, 1938, 32, 5645. E. R. Allen, *Official Printing Ink Maker*, 1933, 3 (8), 14; *Chem. Abs.*, 1933, 27, 4105. L. M. Larson and F. A. Weymouth, *Paint, Oil & Chem. Rev.*, 1937, 99 (17), 20; *Chem. Abs.*, 1937, 31, 7673.

[121] A. Linz, *Am. Ink Maker*, 1938, 16 (5), 18; *Chem. Abs.*, 1938, 32, 5645.

[122] See G. E. Jones, *Oil Colour Trades J.*, 1932, 81, 906; *Rev. Paint, Colour, Varnish*, 1932, 5, 90.

The resistance of molybdated lakes or toners as compared with tungstate lakes has been discussed. Tungsten lakes, as well as lakes containing maximum tungsten and minimum molybdenum, were reported to fade on exposure to light. On the other hand molybdenum lakes or those containing a maximum of molybdenum and a minimum of tungsten, darken on exposure. It was concluded, therefore, that the question of comparative light fastness was not as important as the question as to whether a consumer prefers a change in color in the direction of fading or in the direction of darkening.

Basic dyes can be converted into oil-soluble coloring agents by dissolving the dyestuff in a fatty acid, such as oleic or stearic. In this manner, the dye is rendered soluble in oleo-resinous vehicles. One of the more important members of this class of pigments is the base toner formed by dissolving Methyl Violet base in oleic acid. This color often is utilized in toning less expensive blacks such as news ink.

Water-soluble Acid Dyes. The acid dyes are sulphonic or carboxylic acid derivatives of color bases. They are laked by precipitation with metallic precipitants onto an inert substrate. The most common precipitating agent is barium chloride although lead, sodium and calcium salts find application.[123] Aluminum hydroxide serves most frequently as a substrate or carrier for this type of dye.[124] Lakes made from acid dyes are fairly fast to light. These lakes are particularly valuable because of their good working properties and brilliance.[125]

The following procedure is an illustration of the way in which an acid lake may be prepared.[126] One hundred parts of aluminum sulphate are dissolved in 1000 parts of water and the solution heated to 170° F. Fifty parts of soda ash in 500 parts of water are admixed in the solution with constant stirring. Aluminum hydroxide thus precipitated is washed by decantation until no trace of sodium sulphate remains. Next are added 30 parts of the acid dyestuff dissolved in boiling water, and the mixture brought to the desired temperature. Forty parts of barium chloride in 400 parts of water then are incorporated in mixture, the latter being agitated thoroughly. The lake thus obtained is washed by decantation, filtered, dried and ground. A poster lake (for lithographic printing inks) can be produced by omitting the washing after addition of the soda ash, *i.e.*, leaving the sodium sulphate in the solution. By employing an excess of barium chloride the halide and sulphate will react to produce blanc fixe which acts as a carrier. In general, the higher the tempera-

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[123] E. Thorpe, "Dictionary of Applied Chemistry, Vol. III," New York, Longmans, Green, and Co., 1912; R. A. Shive, *Am. Ink Maker*, 1938, 16 (3), 23; *Rev. Paint, Colour, Varnish*, 1938, 11, 173. *Farbe u. Lack*, 1929, 34, 250; *Rev. Paint, Colour, Varnish*, 1929, 2, 116. For discussion of the theory of lake formation see F. A. Mason, *J. Oil Colour Chem. Assoc.*, 1931, 14, 252; *Chem. Abs.*, 1931, 25, 5778; *Rev. Paint, Colour, Varnish*, 1931, 4, 226.

[124] S. L. Karpeles, A. B. Portman and P. Thomasset, *Am. Ink Maker*, 1936, 14 (5), 39; *Chem. Abs.*, 1937, 31, 4141; *Brit. Chem. Abs.* B, 1936, 702; *Rev. Paint, Colour, Varnish*, 1936, 9, 242.

[125] R. A. Shive, *Am. Ink Maker*, 1938, 16 (3), 23; *Chem. Abs.*, 1938, 32, 3988; *Brit. Chem. Abs.* B, 1938, 942.

[126] H. Clayton, *J. Soc. Dyers Colourists*, 1930, 46, 154; *Rev. Paint, Colour, Varnish*, 1930, 3, 91.

ture of the solution from which the lake is deposited the greater its brilliance.

A slightly different procedure, described by Morris[127] for obtaining neutral lakes, comprises absorbing acid dyes under acid conditions on aluminum hydroxide. The colored mass then is treated with a neutral solution of a salt of the same or another dyestuff to remove the acidity. The shade of the pigment may be varied by treatment with barium chloride. Scarlet 3R, Ponceaus and naphthol yellows may be laked in this manner.

Pigments with shades between yellow and bluish red are obtained by precipitating the barium or calcium salts of dyestuffs obtained by coupling halogen-substituted amino-benzene, -toluene, or -naphthalene, with 2-naphthol-6 (or 7) -sulphonic acid.[128] The barium salt of the dyestuff 2-chloroanilineazo-2-naphthol-6-sulphonic acid, for example, is a reddish-orange powder said to be resistant to water and oil and to be fast to light.

The barium and aluminum salts of sulphonated nigrosine may be employed as pigments in bleachable inks.[129] Such a pigment is precipitated, for example, when 1250 parts of a 20-per cent barium chloride solution and 500 parts of a 20-per cent aluminum sulphate solution are added to a solution of 250 parts of sulphonated nigrosine in 2500 parts of water.

The preparation of various sulphonated triphenylmethane dyes for use in printing inks is described by Larjushkina.[130]

Among the water-soluble acid dyestuffs utilized in preparation of lakes are included azo dyes such as Orange II, Lake Scarlet 2R, Bordeaux BS, Crimson BS. Also quinone-imide dyes, for example, nigrosine and induline have been employed. Other classes of dyestuffs used for preparing printing pigments are the hydrazones, *e.g.*, tartrazine; nitro-dyes such as Naphthol Yellow S and xanthenes, for example, eosine.

Mordant Dyes. *Alizarin Lakes.* 1,2-Hydroxyanthraquinone and its derivatives comprise a group of mordant dyes known as the alizarin dyestuffs. The latter react with various metal oxides[131] (the mordant) to form insoluble pigments. The dyestuffs formerly were obtained from the madder, a root of Indian origin which was cultivated in France and Holland until the synthesis of alizarin by Graebe and Lieberman in 1868. Alizarin now is prepared by sulphonation of anthraquinone to the monosulphonate. The latter then is hydrolyzed to produce the dihydroxy-

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[127] E. F. Morris, British P. 122,540, 1918; *J. S. C. I.*, 1919, **38**, 187A; *Chem. Abs.*, 1919, **13**, 1771.

[128] W. Hentrich and M. Hartmann, U. S. P. 1,878,698, Sept. 20, 1932, to General Aniline Works; *Chem. Abs.*, 1933, **27**, 433; *Rev. Paint, Colour, Varnish*, 1933, **6**, 43.

[129] Italian P. 340,540, 1936, to Soc. An. Fabrica Italiana di colori ed inchiostri da stampa; *Chem. Zentr.*, 1937, **108** (1), 4562; *Rev. Paint, Colour, Varnish*, 1937, **10**, 242. Italian P. 340,553, 1936; *Chem. Zentr.*, 1937, **108** (2), 3967; *Rev. Paint, Colour, Varnish*, 1938, **11**, 25. See also Chapter 15, the section on bleachable inks.

[130] V. K. Larjushkina, *Anilinokrasochnaya Prom.*, 1934, **4**, 573; *Brit. Chem. Abs.* **B**, 1935, 143; *Chem. Zentr.*, 1935, **106** (2), 763; *Rev. Paint, Colour, Varnish*, 1935, **8**, 401.

[131] See F. A. Mason, *J. Oil Colour Chem. Assoc.*, 1931, **14**, 252, and F. H. Burstall, *ibid.*, 1937, **20**, 176; *Chem. Abs.*, 1937, **31**, 7267, for discussion of the compounds formed.

derivative. The color of the product is varied by nitrating and sulphonating. The lake color is determined by the color base and mordant which go into its make-up and various shades are produced by the relative amounts of color base and mordant and the method of preparation of the base.

The alizarin lakes exhibit good fastness to light and are insoluble in water, oils, greases, alcohols and the usual organic solvents. Their use in the past has been somewhat limited because of their high price and comparative lack of tinctorial strength.[132] However, recent improvements, including lighter top tones, increased strength, as well as lower oil absorption may make these lakes more popular in the printing-ink industry.[133]

In addition to alizarin and aluminum hydroxide the lakes generally contain calcium salts, turkey red oil and sodium phosphate. The calcium salt is necessary in most cases for the formation of a satisfactory lake, the function of the turkey red oil and sodium phosphate being to increase the brightness of the lake.[134] The general procedure followed in preparing an alizarin lake comprises dissolving the dyestuff in a cold sodium carbonate solution and adding successively the sodium phosphate and turkey red oil. Subsequently a solution of aluminum sulphate is incorporated slowly in the mixture until evolution of carbon dioxide ceases. Lime water next is added and the mixture, with constant stirring, slowly brought to the boiling point. After several hours of boiling the solution is allowed to cool and the lake washed by decantation, filtered and dried at room temperature.

The presence of ferric salts has a marked dulling effect on aluminum lakes due to the formation of purple iron alizarate. Viktorov [135] found that the presence of reducing agents such as formates, lactates and sulphites (preferably as the anion of the mordant) successfully prevented such discoloration. These compounds reduce the ferric salts in the laking solution and thus preclude the formation of ferric alizarate. On the other hand any ferrous lakes formed are unstable and decompose in favor of the aluminum lake. It is also pointed out that brighter shades are obtained if the laking proceeds slowly. To effect this an aluminum salt (rather than the hydroxide) which slowly hydrolyzes on boiling may be used.

Although the aluminum lakes are the most common, chromium and iron lakes are also prepared. The latter of these two is purple, whereas the chromium salts produce maroon lakes.

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[132] H. J. Wolfe, "The Manufacture of Printing and Lithographic Inks," 2nd Ed., New York, MacNair-Dorland Co., 1933.

[133] R. A. Shive, *Am. Ink Maker*, 1938, 16 (3), 23; *Rev. Paint, Colour, Varnish*, 1938, 11, 173; *Chem. Abs.*, 1938, 32, 3988.

[134] E. Thorpe, "Dictionary of Applied Chemistry," Vol. III, New York, Longmans, Green, and Co., 1912.

[135] P. P. Viktorov, *J. Soc. Dyers Colourists*, 1928, 44, 336; *Brit. Chem. Abs. B*, 1929, 92; *Chem. Abs.*, 1929, 23, 518; *Rev. gén. Mat. Col.*, 1928, 32, 253; *Rev. Paint, Colour, Varnish*, 1928, 1, 155.

Printing inks may be colored by converting a mordant dyestuff of the triarylmethane group into a complex chromium compound of the dye by treatment with chromic acid or a chromate salt directly in the varnish itself.[136] For example 1 g. of Eriochrome Azurol B is dissolved in 100 g. of a nitrocellulose composition and this gently warmed with 0.5 g. of sodium dichromate. The product is a clear blue lacquer, said to be fast to light.

Insoluble or Partially Soluble Dyes with Lake-forming Properties. Most of the important dyes of this class are red monoazo compounds containing a sulphonic acid radical or, in a few cases, a carboxyl group in the molecule. Lithol Red, Red Lake C and Lithol Rubine are members of this class. These dyestuffs are obtained by coupling a diazotized amino- compound and a naphthol derivative, and are marketed as the sodium and, more frequently, as the barium or calcium salts. The strontium salts of the Lithols are also prepared and are said to exhibit greater light fastness than is generally associated with this group of dyes.[137] As an example of the method used in preparing these compounds, the operations involved in the production of Lithol Red dyestuff will be described. The procedure is given in some detail since it serves to illustrate the general method of coupling followed in the preparation of a large number of azo dyes.

Lithol Red R is produced by diazotizing 2-naphthylamine-1-sulphonic acid and coupling the diazonium salt with β-naphthol. To prepare the β-naphthol solution, 16.4 parts of β-naphthol are dissolved in 16.4 parts of 40° Bé. (35 per cent) sodium hydroxide solution diluted with 50 parts of water, and 8 parts of calcined sodium carbonate in 40 parts of water incorporated in the solution. After complete dissolution is secured the mixture is diluted with 100 parts of water, filtered through cloth into a large vat and further diluted with 800 parts of water. The preparation of the diazo solution from 2,1-naphthylaminesulphonic acid (Tobias acid) is effected in the following manner. Twenty-three parts of the Tobias acid are added to a hot solution of 9.6 parts of calcined sodium carbonate in 60 parts of water and the whole diluted to 200 parts with water. Subsequently, 46 parts of 20° Bé. (31.5 per cent) hydrochloric acid are incorporated in the mixture. The solution is cooled to 0° C. and the amine diazotized with 7.6 parts of sodium nitrite. The reaction requires a few minutes. The solution then is run into alkaline β-naphthol solution in which coupling takes place. As soon as all the diazo solution has been incorporated, 15.5 parts of sodium carbonate in 200 parts of water are added to bring about formation of the insoluble sodium salt of the dye. The supernatant liquor is drawn off and the residue washed.[138]

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[136] J. R. Geigy, British P. 423,892. 1935; *Brit. Chem. Abs.* B, 1935, 367; *Chem. Abs.*, 1935, 29, 4610; *Rev. Paint, Colour, Varnish*, 1935, 8, 178.

[137] R. A. Shive, *Am. Ink Maker*, 1938, 16 (3), 23; *Rev. Paint, Colour, Varnish*, 1938, 11, 173; *Chem. Abs.*, 1938, 32, 3988.

[138] *Farben-Ztg.*, 1931, 37, 379; *Rev. Paint, Colour, Varnish*, 1932, 5, 24. See also G. Zerr, *Farbe u. Lack*, 1933, 196; *Chem. Abs.*, 1933, 27, 3336; *Rev. Paint, Colour, Varnish*, 1933, 6, 106.

The barium salt is obtained by cooking the sodium salt paste in a solution of barium chloride (36 parts $BaCl_2 . 2H_2O$ in 500 parts of water) for 15 to 20 minutes. The dye is allowed to settle and the supernatant liquid removed. The substrate or extender then is added to the paste and the two thoroughly mixed.

Red Lake C is made similarly by diazotizing 2-amino-5-chloro-*p*-toluenesulphonic acid and coupling with β-naphthol.[139] Bronze Orange (the sodium lake) is very sensitive to heat. The heat of the mill on grinding tends to darken this pigment, making it difficult for the ink maker to check the shade of his dry color or ink. This difficulty can in part be overcome by starting to grind the color on a cool mill and adding a little water from time to time as the grinding proceeds.[140] The admixture of solid carbon dioxide in certain cases of dry grinding is also recommended.[141]

Alkali Blue. Although not an azo dye, alkali blue nevertheless belongs in this group because of its insolubility and lake-forming properties. The dyestuff is obtained by phenylating rosaniline to spirit blue (alcohol-soluble dye) and sulphonating. The free sulphonic acid is insoluble in water but dissolves in alkali, giving colorless solutions. The paste of the pure dye, in which form it is generally marketed, is obtained by "drowning" (dissolving) the dye in concentrated sulfuric acid and pouring the solution thus obtained into a tank containing water at about 15° C. Precipitation results, leaving the dye in a pulp form known as "worms." The pulp is filtered and the pigment flushed into linseed oil.[142]

Insoluble Dyes without Lake-forming Properties or Pigment Dyestuffs. The so-called pigment dyestuffs may be divided into three subgroups: (1) Azo dyestuffs; (2) Vat dyes; (3) Phthalocyanine compounds.

Azo dyes. Among the more common members of this group are Para Red, Toluidine Red, Permanent Red R, Permanent Orange (Lithol Fast Orange), Hansa Yellow, and Fire Red Toner. These dyes possess a high degree of light-fastness and permanence. The general procedure in preparing these dyes is the same as that described for Lithol Red, with the exception that the extender or substrate generally is present in the coupling solution so that an intimate mixture of the dye and base is obtained.[143]

Vat Dyes. The term "vat dyes," includes those dyes which are insoluble in water, dilute acids and alkalies but which, on being reduced, form

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[139] See H. Bossel, (*Farben-Chem.*, 1936, 7, 245; *Chem. Abs.*, 1936, 30, 8653; *Brit. Chem. Abs.* B, 1936, 804; *Rev. Paint, Colour, Varnish*, 1936, 9, 291) and A. W. C. Harrison (*Paint, Varnish, Prod. Man.*, 1930, 36, 5, 34; *Rev. Paint, Colour, Varnish*, 1930, 3, 176) for description of the preparation of this and other acid azo dyes.

[140] A. B. Portman, *Am. Ink Maker*, 1930, 8, 21; *Chem. Abs.*, 1930, 24, 4637.

[141] I. T. Thornton, U. S. P. 2,098,798, Nov. 9, 1937, to National Aniline & Chemical Co.; *Chem. Abs.*, 1938, 32, 366; *Rev. Paint, Colour, Varnish*, 1938, 11, 148.

[142] See G. B. Palmer, U. S. P. 1,339,219, May 4, 1920; *Chem. Abs.*, 1920, 14, 1903; *J. S. C. I.*, 1920, 39, 460A.

[143] E. Thorpe, "Dictionary of Applied Chemistry," Vol. III, New York, Longmans, Green and Co., 1912.

a "color base" soluble in alkaline solutions. In applying these dyes to cloth, the latter is dipped into a solution of the color base, subsequent exposure to air producing the original colored compound by oxidation. These dyestuffs, although extremely fast to light, are not generally used in printing inks because of their high price and, from the standpoint of the ink maker, lack of brilliance.[144]

The pigmenting of these dyes may be effected by mixing the dyestuff and a paste of extender. Thus a yellow pigment for lithographic ink is obtained by mixing together 5 parts of naphthanthraquinone and 50 parts of a 4.5-per cent aluminum hydroxide paste. The product is filtered and dried.[145] A reddish blue pigment is obtained from 1,4,5-trianisoylamino-8-hydroxyanthraquinone.[146]

Relatively brilliant pigments are said to be obtained from vat dyes employing regenerated cellulose as an extender.[147] The dyestuff may be added to the finely divided regenerated cellulose, or the cellulose may be formed from its derivative in the presence of the color. The procedure in preparing a Ponsol Blue GD pigment by the latter method consists of dissolving 5 parts of chloro-N-dihydro-1,2,2',1'-anthraquinoneazine (Ponsol Blue GD) in a solution of 6.4 parts of sodium hydroxide and 5 parts of sodium hydrosulphite ($Na_2S_2O_4$) in 1000 parts of water at 50° C. To this is added a solution of 21 parts of sodium cellulose phthalate in 1000 parts of water and the whole heated at once to 90° C. with a further addition of 10 parts of sodium hydroxide to complete hydrolysis of the ester. When hydrolysis is complete, the product is cooled, filtered and washed free from inorganic material. If the dye is not completely oxidized by this procedure the product may be suspended in water and air passed through it until the color has been fully formed.

Phthalocyanine Dyes. The most celebrated member of this group of dyes is copper phthalocyanine known as Syan Blue B or Monastral Blue. It is reported to be extremely fast to light, insoluble in water and most organic solvents, and resistant to alkali, acids and to heat.[148] However, its working properties could be better and it could be stronger to be classified as an ideal pigment.[149] The other dyes of this group are all green, blue or purplish-blue in color, depending on the metal used and modifications introduced such as chlorination or sulphonation.

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[144] R. A. Shive, *Am. Ink Maker*, 1938, **16** (3), 23; *Rev. Paint, Colour, Varnish*, 1938, **11**, 173; *Chem. Abs.*, 1938, **32**, 3988.

[145] A. Lüttringhaus, U. S. P. 968,376, Aug. 23, 1910, to Badische Anilin und Soda Fabrik; *Chem. Abs.*, 1910, **4**, 3015.

[146] French P. 809,993, 1937, to Soc. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1938, **32**, 800; *Rev. Paint, Colour, Varnish*, 1938, **11**, 89.

[147] F. W. Johnson, U. S. P. 2,046,267, June 30, 1936, to E. I. duPont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 5821. British P. 427,248, 1935; *Chem. Abs.*, 1935, **29**, 6081; *Brit. Chem. Abs.* **B**, 1935, 562.

[148] See for example, H. Samuels, *Dec. Paint Mag.*, 1937, **36**, 516; *Rev. Paint, Colour, Varnish*, 1937, **10**, 150. *Am. Ink Maker*, 1937, 15 (8), 17; *Brit. Chem. Abs.* **B**, 1937, 1237; *Rev. Paint, Colour, Varnish*, 1937, **10**, 318; J. D. Cohen, *Paint Manuf.*, 1937, **7**, 346; *Chem. Abs.*, 1938, **32**, 810; *Rev. Paint, Colour, Varnish*, 1937, **10**, 412.

[149] L. E. May, *Am. Ink Maker*, 1937, **15** (11), 16; *Rev. Paint, Colour, Varnish*, 1938, **11**, 3; *Chem. Abs.*, 1938, **32**, 1493.

The first phthalocyanine was observed in 1928 as an impurity during the manufacture of phthalimide on an industrial scale.[150] The process, which consists of passing ammonia into molten phthalic anhydride in iron vessels, was found to yield traces of a blue substance. This was isolated and was found to be insoluble in the usual organic media and in water, dilute alkali and acid. The value of these phthalocyanine compounds as pigments for printing inks was soon recognized.[151]

The preparation of the metal phthalocyanines may be effected in various ways such as reacting phthalic anhydride or phthalimide and ammonia in the presence of a metal (iron, copper, nickel, magnesium),[152] or heating an *o*-cyanoarylcarboxylic amide, *e.g.*, cyanobenzamide with a metal or metal compound[153] to yield blue, purple or blue-green pigments. Copper phthalocyanine may also be prepared by heating the metal-free phthalocyanine with copper in a solvent, *e.g.*, quinoline.[154] (The metals may be removed from these compounds by treatment with concentrated sulphuric acid.) A green pigment is obtained by condensing phthalonitrile with lead, litharge or lead carbonate.[155] The pigment does not, however, possess the same outstanding permanence to light as the copper compound.[156] Green pigments with similar properties are also prepared by chlorinating or brominating phthalocyanines.[157] The metal-free compound is also a green pigment.

The molecular structure of phthalocyanine has been determined by Linstead and his co-workers.[158] It was shown that the molecule consists of four isoindole units joined together by means of extracyclical nitrogen atoms. In the metal derivatives the two hydrogen atoms attached to nitrogens are replaced by the metal which probably is also attached to the other nitrogen atoms by coördinate covalent linkages. This structure has received confirmation by x-ray studies of several of the metal compounds.[159]

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[150] H. Samuels, *J. Oil Colour Chem. Assoc.*, 1938, **21**, 171. Precursors of the phthalocyanines were prepared (See *Am. Ink Maker*, 1937, **15**, (8), 17) by H. deDiesbach and E. von der Weid (*Helv. Chim. Acta*, 1927, **10**, 886; *Chem. Abs.*, 1928, **22**, 1149; *Brit. Chem. Abs.* **A**, 1928, 62), who obtained complex copper salts such as $Cu[C_6H_4(CN)_2 + C_5H_5N]_2$ by heating copper cyanide, pyridine and a dibromo compound in sealed tubes. These complexes were reported to exhibit "astonishing" stability to heat, alkali and acids.

[151] H. Samuels, *loc. cit.*

[152] A. G. Dandridge, H. A. E. Drescher, and J. Thomas, British P. 322,169, 1928, to Scottish Dyes, Ltd.; *Chem. Abs.*, 1930, **24**, 2890; *Brit. Chem. Abs.*, **B**, 1930, 316.

[153] J. F. Thorpe, R. P. Linstead and J. Thomas, British P. 389,842, 1932, to Scottish Dyes, Ltd.; *Brit. Chem. Abs.* **B**, 1933, 639; *Chem. Abs.*, 1933, **27**, 4941. J. F. Thorpe and J. Thomas, U. S. P. 2,000,051, May 7, 1935; *Chem. Abs.*, 1935, **29**, 4194.

[154] R. P. Linstead and C. E. Dent, U. S. P. 2,124,742, July 26, 1938, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1938, **32**, 7057.

[155] R. P. Linstead and C. E. Dent, British P. 441,332, 1936, to Imperial Chemical Industries, Ltd.; French P. 791,086, 1935; *Chem. Abs.*, 1936, **30**, 4678; *Brit. Chem. Abs.* **B**, 1936, 463.

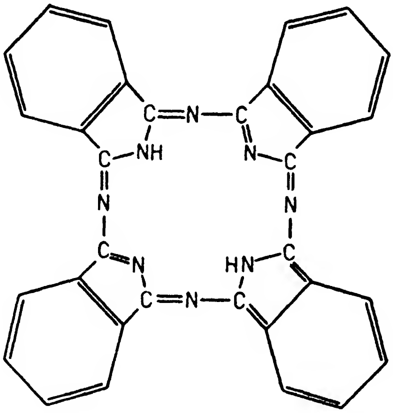
[156] H. Samuels, *loc. cit.*

[157] R. P. Linstead and C. E. Dent, British P. 461,268, 1937, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1937, **31**, 4830; *Brit. Chem. Abs.* **B**, 1937, 471.

[158] R. P. Linstead, C. E. Dent and A. R. Lowe, *J. Chem. Soc.*, 1934, 1016; *Brit. Chem. Abs.* **A**, 1934, 1114; *Chem. Abs.*, 1934, **28**, 6142.

[159] J. M. Robertson, *J. Chem. Soc.*, 1934, 615; *Chem. Abs.*, 1935, **29**, 4989; *Brit. Chem. Abs.* **A**, 1935, 813.

The phthalocyanines are sulphonated to yield lake-forming dyes. The lake is deposited from aqueous solution of the sodium sulphonate onto substrates such as aluminum hydroxide, blanc fixe, or cellulose derivatives. The usual inorganic precipitating agents, *e.g.*, barium, calcium or zinc chloride,[160] or organic bases, such as aliphatic and aromatic amines or basic dyes [161] may be used.



Phthalocyanine

Naphthalocyanines have been investigated by Linstead and Bradbrook [162] who showed that only the 1,2 and 2,3 of the ten possible dicyanonaphthalenes form naphthalocyanines. This is to be expected inasmuch as only adjacent nitrile groups (ortho to one another) are involved in the formation of the phthalocyanines.[163] The copper, magnesium, zinc and lead naphthalocyanines were prepared.

PROPERTIES OF PIGMENTS

The properties of a number of pigments which are utilized in the printing industry have been compiled by Doty.[164] The data are given in Tables 22, 23, 24, 25, 26, 27. The colors tested were dry, and only organic toners, organic lakes and inorganic C. P. colors were considered.

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[160] See, for example, British P. 457,796, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, 31, 3299; *Brit. Chem. Abs.* **B**, 1937, 264. K. Holzach and G. Niemann, U. S. P. 2,099,689 and U. S. P. 2,099,690, Nov. 23, 1937, to General Aniline Works; *Chem. Abs.*, 1938, 32, 366. J. F. Thorpe and R. P. Linstead, British P. 390,149, 1932, to Imperial Chemical Industries, Ltd.; *Rev. Paint, Colour, Varnish*, 1933, **6**, 160; *Brit. Chem. Abs.* **B**, 1933, 639; *Chem. Abs.*, 1933, **27**, 4680.

[161] British P. 460,147, 1937, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, 31, 4825; *Brit. Chem. Abs.* **B**, 1937, 264.

[162] R. P. Linstead and E. F. Bradbrook, *J. Chem. Soc.*, 1936, 1744.

[163] C. E. Dent, R. P. Linstead and A. R. Lowe, *J. Chem. Soc.*, 1934, 1016.

[164] M. B. Doty, *Paint, Oil & Chem. Rev.*, 1937, **99** (8), 10; *Chem. Abs.*, 1937, 31, 7268.

Table 22.—Reds.

Red Toners

	Para Reds		Toluidine Red	Lithol Reds		Chlorinated Nitraniline Reds	
	Light	Dark		Barium	Calcium	Ortho-Chlor	Para-Chlor
Resistance to Light							
Full Shade	Good	Good	Excellent	Fair	Fair	Excellent	Excellent
Tints	Poor	Poor	Good	Poor	Poor	Fair	Fair
Resistance to Heat	230° F.	230° F.	320° F.	165° F.	230° F.	165° F.	165° F.
Resistance to Acid	Good	Good	Good	Good	Good	Good	Good
Resistance to Alkali	Good	Good	Good	Good	Good	Good	Good
Bleeding in Water	Slight	Slight	No	No	No	No	No
Bleeding in Oil	Yes	Yes	No	No	No	No	No
Bleeding in Lacquer	Yes	Yes	Yes	No	No	No	No
Bleeding in Synthetic	Yes	Yes	Yes	Slight	Slight	Yes	Yes
Specific Gravity	1.49	1.49	1.40	1.74	1.65	1.56	1.60
Bulking Value	.08058	.08058	.08576	.06901	.07278	.07698	.07550
Oil Absorption	36 1-53.9	32.0-50.2	34.6-37.2	40.0	34.0	27.9	32.7
Fineness (Res. on 325-mesh)(%)	.15-.75	.08-.30	.04-.12	.30	.24	.10	.10

Red Toners (Continued)

	Beta-Oxy Reds						
	Lithol Rubine	Solfast Reds		Solfast Pinks		Tungstated Rhodamine Reds	
		Y	B	3Y	3B	Y	B
Resistance to Light							
Full Shade	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Tints	Good	Very Good	Very Good	Excellent	Excellent	Very Good	Good
Resistance to Heat	320° F.	230° F.	230° F.	230° F.	230° F.	320° F.	320° F.
Resistance to Acid	Good	Good	Poor	Fair	Fair	Good	Good
Resistance to Alkali	Good	Good	Poor	Fair	Fair	Poor	Poor
Bleeding in Water	No	No	No	No	No	No	No
Bleeding in Oil	No	No	No	No	No	No	No
Bleeding in Lacquer	No	No	No	No	No	Yes	Yes
Bleeding in Synthetic	Slight	Slight	Slight	Slight	Slight	Slight	Slight
Specific Gravity	1.61	1.92	1.73	1.93	1.77	2.63	2.52
Bulking Value	.07457	.06254	.06940	.06219	.06784	.04583	.04763
Oil Absorption	43.0	33.5	37.2	41.9	41.0	40.9	44.0
Fineness (Res. on 325-mesh)(%)	0.68	0 30	0.12	0.04	0.05	0.10	0.40

Table 22.—*Continued.*

	Red Lakes		*Inorganic Reds*			
	Scarlet 2R Lake	Pigment Scarlet Lake	Synthetic Iron-Oxides	Cadmium Reds	**English Vermilion**	**American Vermilion**
Resistance to Light						
Full Shade	Fair	Good	Excellent	Excellent	Excellent	Good
Tints	Poor	Fair	Excellent	Excellent	Excellent	Fair
Resistance to Heat	230° F.	230° F.	320° F.	320° F.	320° F.	230° F.
Resistance to Acid	Poor	Poor	Good	Poor	Good	Poor
Resistance to Alkali	Poor	Poor	Good	Good	Good	Excellent
Bleeding in Water	No	No	No	No	No	No
Bleeding in Oil	No	No	No	No	No	No
Bleeding in Lacquer	No	No	No	No	No	No
Bleeding in Synthetic	No	No	No	No	No	No
Specific Gravity	2.82	2.54	4.65-5.13	3.9-4.3	7.9-8.1	8.0
Bulking Value	.04257	.04726	.02580-.02340	.03078-.02792	.01516-.01478	.01501
Oil Absorption	36.0	60.0	39.0-22.5	9.0-10.0	10.0-6.0	5.5
Fineness (Res. on 325-mesh)(%)	60	.30	.30-1.0	.2-.3	.03-.15	.9

Table 23.—Maroons.

	Maroon Toners				*Maroon Lakes*					*Inorganic Maroons*	
	Lithol Maroon	Beta-Oxy Tobias	Napthol AS-BS Toluidine	Helio Bordeaux BL	Alizarin	Alizarin Cyclamine	Helio Fast Rubine 4BL	Amaranth	Bordeaux	Synthetic Iron Oxide Maroons	Cadmium Lithopone Maroon
Resistance to Light											
Full Shade	Good	Good	Excellent	Good	Ex.	Ex.	Ex.	Fair	Fair	Ex.	Ex.
Tints	Fair	Fair	Good	Fair	Good	Fair	Good	Poor	Poor	Ex.	Ex.
Resistance to Heat	230° F.	320° F.	320° F.	230° F.	230° F.	230° F.	230° F.	230° F.	230° F.	320° F.	320° F.
Resistance to Acid	Good	Good	Good	Fair	Good	Good	Good	Poor	Fair	Good	Poor
Resistance to Alkali	Good	Good	Good	Good	Ex.	Ex.	Ex.	Poor	Fair	Good	Good
Bleeding in Water	No	No	No	No	No	No	No	No	No	No	No
Bleeding in Oil	No	No	No	No	No	No	No	No	No	No	No
Bleeding in Lacquer	No	No	Slight	No	No	No	No	No	No	No	No
Bleeding in Synthetic	Slight	Slight	Slight	Slight	No	No	No	No	No	No	No
Specific Gravity	1.20	1.62-1.81	1.58	1.58	1.76	1.67	1.91	2.95	2.88	4.9-4.95	4.27
Bulking Value	.1000	.07413-.06631	.07599	.07599	.06821	.07189	.06285	.04070	.04168	.02450-.02425	.02811
Oil Absorption	37.0	42.0-32.0	37.8	41.1	33.6	37.2	54.0	31.7	32.5	15.0-16.0	17.88
Fineness (Res. on 325-mesh)(%)	.07	.65-.31	2.48	.42	7.4	.10	.50	6.9	0.4	1.0	.07

Table 24.—Yellows.

Inorganic Yellows

	Chrome Yellows			Zinc Yellow
	Primrose	Lemon	Medium	
Resistance to Light				
Full Shade	Fair	Fair	Good	Excellent
Tints	Poor	Poor	Fair	Good
Resistance to Heat	230° F.	230° F.	320° F.	165° F.
Resistance to Acid	Good	Good	Good	Poor
Resistance to Alkali	Poor	Poor	Poor	Poor
Bleeding in Water	No	No	No	Yes
Bleeding in Oil	No	No	No	No
Bleeding in Lacquer	No	No	No	No
Bleeding in Synthetic	No	No	No	No
Specific Gravity	5.86-6.00	5.84-5.95	5.84-6.00	3.41-3.54
Bulking Value	.02049-.02001	.02056-.02018	.02056-.02001	.03520-.03391
Oil Absorption	15.9-13.0	20.1-17.0	12.1-13.0	24.1-18.6
Fineness (Res. on 325-mesh)(%)	.47	.19	.04	.39

	Synthetic Iron Oxides Lemon	Cadmium Lithopone Yellows		
		Primrose	Lemon	Golden
Resistance to Light				
Full Shade	Excellent	Excellent	Excellent	Excellent
Tints	Excellent	Excellent	Excellent	Excellent
Resistance to Heat	230° F.	320° F.	320° F.	320° F.
Resistance to Acid	Excellent	Poor	Poor	Poor
Resistance to Alkali	Good	Good	Good	Good
Bleeding in Water	No	No	No	No
Bleeding in Oil	No	No	No	No
Bleeding in Lacquer	No	No	No	No
Bleeding in Synthetic	No	No	No	No
Specific Gravity	4.03	4.02	4.26	4.25
Bulking Value	.02979	.02986	.02818	.02825
Oil Absorption	23.5	17.88	16.51	17.42
Fineness (Res. on 325-mesh)(%)	0.20	.04	.05	.02

	Yellow Lakes			*Yellow Toners*	
				Hansa Yellows	
	Quinoline	Naphthol	Tartrazine	10G-Primrose	G-Lemon
Resistance to Light					
Full Shade	Fair	Fair	Fair	Excellent	Excellent
Tints	Poor	Poor	Poor	Good	Good
Resistance to Heat	230° F.	230° F.	230° F.	230° F.	320° F.
Resistance to Acid	Poor	Poor	Good	Good	Good
Resistance to Alkali	Poor	Poor	Poor	Good	Good
Bleeding in Water	Slight	Slight	Slight	No	No
Bleeding in Oil	No	No	No	No	No
Bleeding in Lacquer	No	No	No	Slight	Slight
Bleeding in Synthetic	No	No	No	Yes	Yes
Specific Gravity	1.63	1.94	2.60	1.58	1.46
Bulking Value	.07364	.06188	.04617	.07599	.08224
Oil Absorption	50.0	40.0	53.9	45.0	33.5
Fineness (Res. on 325-mesh)(%)	.12	.10	.10	.11	.10

Table 25.—Oranges.

Inorganic Oranges

	Chrome Oranges						
	Light	Medium	Deep	DD	Molybdate Oranges	Synthetic Iron Oxide Orange	Cadmium Lithopone Orange
Resistance to Light							
Full Shade	Ex.	Ex.	Ex.	Ex.	Good	Ex.	Ex.
Tints	Good	Good	Good	Good	Fair	Ex.	Ex.
Resistance to Heat	320° F.	320° F.	320° F.	320° F.	230° F.	320° F.	320° F.
Resistance to Acid	Poor	Poor	Poor	Poor	Good	Fair	Poor
Resistance to Alkali	Good	Good	Good	Good	Poor	Good	Good
Bleeding in Water	No	No	No	No	No	No	No
Bleeding in Oil	No	No	No	No	No	No	No
Bleeding in Lacquer	No	No	No	No	No	No	No
Bleeding in Synthetic	No	No	No	No	No	No	No
Specific Gravity	6.98	6.75	6.92	6.71	5.75-6.95	4.03	4.18
Bulking Value	.01720	.01779	.01735	.07189	.02088-.01727	.02979	.02872
Oil Absorption	8.3	7.4	7.5	6.5	14.9	25.5	23.16
Fineness (Res. on 325-mesh)(%)	.08	.09	.18	.06	.10	.02	0.02

	Orange Lake	*Orange Toners*	
	Persian Orange	Ortho Nitraniline	2:4 Di-Nitraniline
Resistance to Light			
Full Shade	Fair	Excellent	Very Good
Tints	Poor	Poor	Excellent
Resistance to Heat	230° F.	230° F.	230° F.
Resistance to Acid	Poor	Good	Good
Resistance to Alkali	Poor	Good	Good
Bleeding in Water	Slight	Slight	No
Bleeding in Oil	No	Yes	No
Bleeding in Lacquer	No	Yes	No
Bleeding in Synthetic	No	Yes	No
Specific Gravity	1.80	1.46	1.45
Bulking Value	.06671	.08224	.08278
Oil Absorption	45.0	39.1	32.0
Fineness (Res. on 325-mesh)(%)	.10	.08	.11

Table 26.—Greens.

Inorganic Greens

	C.P. Chrome Greens				Chromium		Paris
	Light	Medium	Deep	DD	Oxide	Hydroxide	Green
Resistance to Light							
Full Shade	Good	Good	Good	Good	Ex.	Ex.	Ex.
Tints	Fair	Fair	Fair	Fair	Ex.	Ex.	Ex.
Resistance to Heat	230° F.	320° F.	320° F.	320° F.	230° F.	230° F.	165° F.
Resistance to Acid	Good	Good	Good	Good	Ex.	Ex.	Poor
Resistance to Alkali	Poor	Poor	Poor	Poor	Ex.	Ex.	Poor
Bleeding in Water	No	No	No	No	No	No	No
Bleeding in Oil	No	No	No	No	No	No	No
Bleeding in Lacquer	No	No	No	No	No	No	No
Bleeding in Synthetic	No	No	No	No	No	No	No
Specific Gravity	5.01	4.31	3.41	2.84	5.20	3.2	3.21
Bulking Value	.02396	.02786	.03520	.04155	.02308	.03751	.03740
Oil Absorption	13.0	20.5	22.3	23.3	10.0	63.0	10.2
Fineness (Res. on 325-mesh)(%)	0.28	.10	.10	.60	.10	.10	.06

Green Toners

	Phospho-Tungstic			
	Brilliant Green Thioflavine	Brilliant Green	Malachite Green	Pigment Green B
Resistance to Light				
Full Shade	Very Good	Very Good	Very Good	Excellent
Tints	Fair	Fair	Fair	Good
Resistance to Heat	320° F.	320° F.	320° F.	230° F.
Resistance to Acid	Good	Good	Good	Good
Resistance to Alkali	Fair	Fair	Good	Very Good
Bleeding in Water	No	No	No	No
Bleeding in Oil	No	No	No	No
Bleeding in Lacquer	Yes	Yes	No	No
Bleeding in Synthetic	Slight	Slight	Slight	Slight
Specific Gravity	2.63	2.41	2.63	1.47
Bulking Value	.04564	.04980	.04564	.08163
Oil Absorption	40.9	58.6	38.2	37.2
Fineness (Res. on 325-mesh)(%)	.10	.10	.08	.02

Table 27.—Blues.

Inorganic Blues

	Iron Blues			Ultramarine Blues	Cobalt Blue
	Chinese	Prussian	Non-Bronze		
Resistance to Light					
Full Shade	Excellent	Excellent	Excellent	Excellent	Excellent
Tints	Good	Good	Good	Good	Excellent
Resistance to Heat	320° F.	320° F.	320° F.	320° F.	320° F.
Resistance to Acid	Excellent	Excellent	Excellent	Poor	Good
Resistance to Alkali	Poor	Poor	Poor	Good	Good
Bleeding in Water	No	No	No	No	No
Bleeding in Oil	No	No	No	No	No
Bleeding in Lacquer	No	No	No	No	No
Bleeding in Synthetic	No	No	No	No	No
Specific Gravity	1.85	1.85	1.84	2.33	4.2-4.4
Bulking Value	.06489	.06489	.06523	.05131	.02858-.02729
Oil Absorption	40.2	57.2	58.0	28.8	36.8-30.5
Fineness (Res. on 325-mesh)(%)	.10	.40	.30	.10	.14

	Blue Lakes	*Blue Toners*		
	Patent Blue Peacock	Phospho-Tungstic		Monastral Blue
		Victoria	Peacock	
Resistance to Light				
Full Shade	Poor	Good	Good	Excellent
Tints	Poor	Fair	Fair	Excellent
Resistance to Heat	230° F.	230° F.	320° F.	320° F.
Resistance to Acid	Poor	Good	Good	Excellent
Resistance to Alkali	Poor	Good	Fair	Excellent
Bleeding in Water	Slight	No	No	No
Bleeding in Oil	No	No	No	No
Bleeding in Lacquer	Slight	Slight	Slight	No
Bleeding in Synthetic	Slight	Slight	No	No
Specific Gravity	2.02	1.99	2.66	1.64
Bulking Value	.05942	.06031	.04513	.07321
Oil Absorption	57.2	41.0	44.0	25.0
Fineness (Res. on 325-mesh)(%)	.10	.03	.10	.10

Violets.

	Violet Toners	*Violet Lakes*		*Inorganic Violets*	
	Phospho-Tungstic Methyl Violet	Tannic Acid Methyl Violet	Helio Fast Violet AL	Cobalt Violet	Mineral Violet
Resistance to Light					
Full Shade	Fair	Poor	Good	Excellent	Excellent
Tints	Poor	Poor	Fair	Good	Good
Resistance to Heat	230° F.	230° F.	230° F.	320° F.	320° F.
Resistance to Acid	Good	Poor	Poor	Good	Good
Resistance to Alkali	Good	Poor	Poor	Excellent	Poor
Bleeding in Water	No	No	No	No	No
Bleeding in Oil	No	No	No	No	No
Bleeding in Lacquer	Slight	No	Yes	No	No
Bleeding in Synthetic	Slight	No	No	No	No
Specific Gravity	2.24	1.37	1.97	3.77	2.62
Bulking Value	.05359	.08764	.06094	.03185	.04583
Oil Absorption	37.0	94.6	68.5	16.0	25.6
Fineness (Res. on 325-mesh)(%)	.04	.10	.10	.10	.10

CARBON BLACK

Manufacture of Carbonaceous Blacks. The methods of producing blacks have been divided into five groups by Chamberlin and Rose.[165]

(1) A hydrocarbon gas, burning in a limited supply of air, is allowed to impinge on a cool surface. The channel, disc and roll processes are examples of this type. Carbon black is manufactured by these methods.

(2) A liquid or solid hydrocarbon is burned in a limited supply of air. The products of combustion are conducted to a collecting chamber where the soot is deposited by reducing the velocity of the gas. Lampblack is the carbon obtained by this method.

(3) A hydrocarbon gas or atomized oil is subjected to high temperature in the absence of air and decomposition into carbon and hydrogen thus effected,[166] *e.g.*, Thermatomic process.

(4) A hydrocarbon gas such as acetylene is exploded in a limited supply of air. The carbon is collected by settling or scrubbing.[167]

(5) Organic materials are subjected to destructive distillation and the charcoals and cokes obtained pulverized. Bone black (animal black, hard black) is made by the destructive distillation of bones and animal refuse. Vegetable black (soft black) is obtained similarly from plant matter such as wood or grape husks. These pigments are used in plate inks. They are absolutely fast to light, heat, acids, and alkalies.[168]

Coal, carbonaceous shale or slate are sometimes pulverized for use as pigment (mineral black). For example, powder produced by grinding brown coal to pass through a sieve of at least 3,500 meshes per sq. cm. has been proposed as a pigment for black printing inks.[169] Mineral black, like all carbonaceous blacks, is stable toward light, heat, acids, alkalies and solvents. It is, however, weak tinctorially and very abrasive.[170]

Blacks obtained by other means have been recommended as pigment for inks. Carbon obtained by catalytic decomposition of carbon mon-

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[165] D. S. Chamberlin and A. Rose, *Trans. Am. Inst. Chem. Eng.*, 1929, 22, 155. See also, Carleton Ellis, in "The Science of Petroleum." Oxford University Press, London, 1938, Volume 4. H. Wagner and G. Hoffman, *Fachaussch. Anstrichtechn. Ver. Deut. Ingen.*, 1934, 9 (9), 1; *Chimie & Industrie*, 1934, 32, 405; *Brit. Chem. Abs.* B, 1934, 636; *Chem. Abs.*, 1934, 28, 7039; *Rev. Paint, Colour, Varnish*, 1934, 7, 76; *Farben-Ztg.*, 1934, 39 (21), 549; *Rev. Paint, Colour, Varnish*, 1934, 7, 264. I. Drogin, *Am. Ink Maker*, 1936, 14, (7), 17; *Chem. Abs.*, 1936, 30, 6218; *Brit. Chem. Abs.* B, 1936, 964; *Rev. Paint, Colour, Varnish*, 1936, 9, 292. H. M. Langton, *Oil Colour Trades J.*, 1930. 77, 1400; *Rev. Paint Colour, Varnish*, 1930, 3, 95. *Paint Manuf.*, 1935, 5, 348; *Chem. Abs.*, 1936, 30, 629 W. Esch, *Farben-Chem.*, 1937, 8, 150; *Chem. Abs.* 1937, 31, 8958; *Rev. Paint, Colour, Varnish*, 1937, 10, 174. G. L. Roberts, *Paint, Oil & Chem. Rev.*, 1935, 97 (11), 22; *Chem. Abs.*, 1935, 29, 4956; *Rev. Paint, Colour, Varnish*, 1935, 8, 284. *Farbe u. Lack*. 1930, 35, 42; *Rev. Paint, Colour, Varnish*, 1930, 3, 1. R. Benerle, *Deutscher Drucker*, 1935, No. 484, 119; *Farben-Chem.*, 1935. 6 (3), 102; *Rev. Paint, Colour, Varnish*, 1935, 8, 109. *Farben-Ztg.*, 1919, 25, 449; *Chem. Abs.*, 1920, 14, 637. L. V. Venuto, *Official Digest Federation Paint Varnish Production Clubs*, 1936, No. 158, 256; *Rev. Paint, Colour, Varnish*, 1936, 9, 358.

[166] The use of dehydrogenating catalysts comprising mixtures of iron, cobalt, or nickel oxides with other oxides is said to reduce the temperature required for decomposition to about 450° C. (British P. 325,207, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 4127; *Brit. Chem. Abs.*, B, 1930, 405.

[167] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," New York, Reinhold Publishing Corp., Vol. 1, 1934, Vol. 2, 1937, for description of this and the Thermatomic processes.

[168] K. R. Werner, *Farbe u. Lack*, 1930, 35, 2; *Rev. Paint, Colour, Varnish*, 1930, 3, 6.

[169] G. Callmann, British P. 20,830, 1889.

[170] A process calculated to reduce abrasiveness in mineral blacks has been proposed (German P. 196,292, 1906, to Rudolph Koepp & Co.; *Chem. Abs.*, 1908, 2, 2162).

oxide under pressure and at a temperature of about 400° C. is said to be a satisfactory pigment.[171]

A pigment for black inks is prepared by treating starch, corn flour or other carbohydrate with tannic acid and a ferric salt, *e.g.*, ferric chloride.[172] For example, a solution consisting of 200 parts of carbohydrate in 800 parts of water is mixed with 5 parts of tannic acid and 2 volumes of 5.0-per cent aqueous ferric chloride solution. The black obtained by the reaction precipitates out and may be collected and dried.

The blacks obtained as by-products in the production of hydrogen by pyrolysis of organic compounds sometimes are employed in printing inks.[173] Also, pyrolysis of soybean oil, pitch from sulphite waste liquor or coumarone resin has been proposed for securing black pigments.[174]

Manufacture of Carbon Black. The first factory to make carbon black from natural gas on an industrial scale was erected at New Cumberland, W. Va., in 1872. In this plant the gas from the gas holder passed through pipes to gas jets arranged in a horizontal plane. Directly above the jet openings was placed a slab of soapstone pierced with orifices to permit escape of waste gases. The slab was covered by a dome or roof that was provided with a damper for controlling the ventilation. The transverse horizontal scrapers below the slabs traveled in horizontal grooves in the lower and opposite side of the dome. At regular intervals the scraper removed the deposited carbon black which fell into sheet-iron aprons or troughs. From the latter, the black fell through pipes to a container. The depositing surface was kept cold by circulating water through pans set on the upper surface of the soapstone.[175]

It was soon shown that no beneficial effect was obtained by artificial cooling. Also it was found that cast-iron was superior to soapstone as a depositing surface. Metal surfaces are now almost exclusively employed. The function of the depositing surface is twofold. In the first place the liberated carbon is cooled so that no oxidation changes or agglomeration of the particles from too prolonged heating takes place. Secondly, the uncooled metal surface maintains the carbon at a temperature high enough to free the latter from empyreumatic substances. The temperature of the depositing surface should not exceed 500° C.[176]

In modern carbon black production, the channel process is by far the most important, accounting for about 90 per cent of the carbon black made in America.[177] This process first was employed by McNutt in

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[171] British P. 310,977, 1928, to General Carbon-Alpha Co.; *Chem. Abs.*, 1930, **24**, 697.

[172] J. F. Duke, British P. 131,769, Sept. 24, 1918; *Chem. Abs.*, 1920, **14**, 358; *J. S. C. I.*, 1919, **38**, 834A.

[173] See, for instance, R. Pictet, *Oesterr. Chem. Ztg.*, **16**, 9; *Chem. Zentr.*, 1913, **84**, 662; *Chem. Abs.*, 1913, **7**, 2667.

[174] Waldmann, *Farbe u. Lack*, 1937, 258; *Chem. Abs.*, 1937, **31**, 6034.

[175] R. O. Neal and G. St. J. Perrott, *U. S. Bur. Mines Bull.*, 1922, 192; *Chem. Abs.*, 1922, **16**, 3174; *J. S. C. I.*, 1922, **41**, 770 A.

[176] W. B. Plummer and T. P. Keller (*Ind. Eng. Chem.*, 1930, **22**, 1209), found the optimum temperature in the manufacture of carbon black from propane to be 516° C.

[177] G. Ewald, *Brennstoff-Chem.*, 1936, **17**, 41; *Brit. Chem. Abs.* B, 1936, 354; *Chem. Abs.*, 1936, **30**, 6142.

1892.[178] Natural gas is burned with a controlled deficiency of air in burners provided with lava tips of various kinds. The flame is directed against the underside of steel channels 7 or 8 inches wide, on which the black collects. A number, usually 8, of these channels hang side by side from trucks which run on overhead rails parallel to the channels. The channels are bolted together in lengths as great as 100 feet. The channels are moved continuously in a longitudinal direction with a reciprocating motion over the stationary gas flame. The deposited black is removed by scrapers and falls into a hopper from which it is continuously removed, generally by spiral conveyors, and transported to the bolting and packing houses. The arrangement of channels is enclosed in so-called hot houses. The latter are placed in rows about 15 feet apart. The space between houses is reserved for the conveyors which transport the product to the packing house. Factories with as many as 60 hot houses per packing house are in operation. Grit, scale and hard particles in the carbon black are removed by bolting machines. In the latter the black is forced through a 45- to 60-gauge steel screen by means of fiber brushes. The material which does not pass through the screen is discarded.[179]

The source of grit has been ascribed to the formation of graphitized carbon by black which has not been removed during the first scraping and which therefore is exposed further to the heat of the flame.[180] The amount of grit formation is greatly reduced by efficient scraping.

Other methods in use for producing carbon black are the rotating-disk and the roller or rotating-cylinder processes. In the former [181] the carbon is deposited on a cast-iron disk. The disk ranges in diameter from 36 inches to 42 inches and has a 50-inch face. Lava tips are set in a circular piece of pipe about 28 inches in diameter and containing from 18 to 24 tips. The black is deposited on the under side of the disk which makes approximately one revolution every 15 minutes. A fixed scraper removes the deposited black which is collected in a hopper radially with the disk. The roller process first was employed by Hallock and Blood. Although the yield of black in this process is much smaller than in the channel or disk process, the black produced has many desirable qualities.[182] It possesses extreme length or flow and, despite its inferior color, finds frequent application in lithographic, offset and half-tone inks. The rollers, with an outside diameter of about 8.5 inches, are from 3 to 8 feet in length. The burner pipe holding the lava tips is

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[178] L. J. McNutt, U. S. P. 481,240, Aug. 23, 1892.

[179] For more details see R. O. Neal and G. St. J. Perrott, *U. S. Bur. Mines Bull.*, 1922, 192; *Chem. Abs.*, 1922, 16, 3174; *J. S. C. I.*, 1922, 41, 770 A. R. G. Allen, H. W. Price and E. B. Reinbold, *Refiner*, 1935, 14, 384; *Chem. Abs.*, 1935, 29, 8249

[180] See H. J. Wolfe, "Manufacture of Printing and Lithographic Inks," 2nd Ed., New York, MacNair-Dorland Co., 1933.

[181] A. R. Blood, U. S. P. 387,487, Aug. 7, 1888.

[182] J. K. Hallock and E. R. Blood, U. S. P. 205,955, July 16, 1878. See also E. R. Blood, U. S. P. 269,378, Dec. 16, 1882.

placed 3 to 5 inches below the cylinder. The lava tips have a round instead of a fishtail or bat-wing opening so that the flame is cylindrical. The scrapers for removing the deposited carbon are placed near the top of the rollers and run longitudinally the entire length. One revolution is made every 15 to 45 minutes. The black which is scraped from the rollers is collected in a hopper.

Manufacture of Lampblack. Lampblack is produced by incomplete combustion of raw materials such as tung oil, rosin, creosote oil, naphthalene or tar oils.[183] The smoky vapors are conducted from the furnace to a settling chamber. The black may be absorbed directly in an ink by causing the cooled gases to impinge against a sheet or film of the vehicle.[184]

Iron Oxide Black. Iron oxide black is composed of magnetic black ferro-ferric oxide. It is made [185] by precipitating ferrous oxide by means of alkali from a cold solution of a ferrous salt. The precipitate is oxidized by a current of air until the proportion of ferrous to ferric iron (as determined by analyses of samples) is within the limits of 1:0.5 and 1:2. The product then is filtered, washed and dried in air or *in vacuo*. If dried in air, further oxidation of some of the ferrous oxide is unavoidable and must be allowed for.

The pigment in which the ratio of ferrous and ferric oxide is between 1:1.3 and 1:1.6 has been reported best adapted for printing inks.[186] Further, it is recommended that the liquid containing the suspended ferrous oxide be heated [187] during the oxidation and that the oxidized precipitate, after filtering, be dried with exclusion of air. The latter step allows closer control of the oxide ratio in the final pigment. When mixed with a varnish the product will print a decided black.

Iron oxide black has been utilized in plate and stamping inks. To these the black imparts characteristics of good flow and easy wiping qualities. Its low oil absorption and high specific gravity also make it valuable in these inks.

Iron or chromium oxides were suggested for use in conjunction with aniline black,[188] and basic iron gallate and tannate have been recommended for book-printing inks.[189]

Manganese Dioxide. Precipitated manganese dioxide is a brownish-black pigment. It is weak tinctorially but finds occasional use in black plate inks in conjunction with bone and vegetable blacks. Manganese

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[183] See also H. Koehler, "The Manufacture of Lampblack and Printers Ink from Refuse and By-Products" (German), Braunschweig, Germany, F. Vieweg & Son, 1912. Y-H Yu, *Chemistry* (*China*), 1935, 2, 779; *Chem. Abs.*, 1936, 30, 2409; *Rev. Paint, Colour, Varnish*, 1936, 9, 169.

[184] A. L. Miller, U. S. P. 1,765,991, June 24, 1930, to Ault & Wiborg Co.; *Chem. Abs.*, 1930, 24, 4176; *Brit. Chem. Abs.* B, 1930, 781; British P. 286,207, 1927; *Brit. Chem. Abs.* B, 1929, 196.

[185] P. Fireman, U. S. P. 802,928, Oct. 24, 1905, to E. G. Portner: *J. S. C. I.*, 1905, 24, 1180. German P. 182,221, 1905; *Chem. Abs.*, 1907, 1, 2333. German P. 189,944, 1905 (Addn. to 182,221); *Chem. Abs.*, 1908, 2, 1211.

[186] P. Fireman, British P. 25,859, 1905; *J. S. C. I.* 1907, 26, 57.

[187] See also French P. 357,912, 1905; *Chem. Abs.*, 1907, 1, 666.

[188] J. Schmidlin, British P. 3161, 1879, *Chem. Zentr.*, 1880, 11, 608.

[189] F. Kircher and E. Ebner, *Polit. Notizbl.* XXV, 176; *Chem. Zentr.*, 1870, 1, 393.

dioxide makes the ink lift well and eliminates gathering trouble. Stephan[190] suggested the use of manganese dioxide with an apparent specific gravity less than one, either alone or with a fat-soluble blue toner. Because it is easily reduced, the manganese pigment also has been proposed for bleachable printing inks.[191]

Silica Black. Silica black is the product obtained when finely divided coal and siliceous material such as diatomite are heated together in the absence of air.[192] Jacobson[193] prepared this pigment by heating a mixture of silicon dioxide and finely ground coal in an iron retort at 650-1100° C. for 4 hours. The powder obtained was air-floated and graded. The finest grade (of three) had an apparent specific gravity of 0.25 and contained approximately 18 per cent carbon, 75.5 per cent silica and 6.5 per cent of oxides, sulphates and silicides. Silica black has a high oil absorption, mixes well and has good spreading quality. Experiments indicate that it might be used successfully as a pigment for black inks.

Grüne[194] obtained a black pigment by effecting decomposition of soot-forming carbon compounds mixed with diatomite (kieselguhr) in the absence of air. The resulting product is worked up with a binding agent.

Resinous Black Pigments. Resinous black printing colors are obtained by oxidizing tar or tar oils with oxygen in the presence of catalysts such as aluminum, iron, vanadium oxide, ferric chloride or sulphur chloride.[195]

PROPERTIES OF CARBON BLACK

Results obtained by various investigators and brought together by Wiegand and Snyder[196] show that the color intensity of carbon black increases with decrease in particle size. The evidence although indirect apparently is convincing. It is impossible to secure reliable data on particle size by direct examination since the particle diameter of carbon black (the average diameter) probably does not exceed 0.1 micron.[197] It was found however that color intensity of blacks of the same chemical composition increased with increase both in oil absorption[198] and spe-

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[190] K. Stephan, U. S. P. 1,689,368, Oct. 30, 1928, to Chemische Fabrik auf Aktien vorm E. Schering; *Chem. Abs.*, 1929, 23, 293.

[191] Italian P. 342,214, 1937, to Fabrica Italiana di Colori ed inchiostri da stampa; *Chem. Zentr.*, 1937, 108 (2), 3676; *Rev. Paint, Colour, Varnish*, 1938, 11, 25.

[192] See *Science News Letters*, 1932, 22, 129; *A. P. V. M. Abs.*, No. 21, 42; *Rev. Paint, Colour, Varnish*, 1933, 6, 96.

[193] C. A. Jacobson, *Ind. Eng. Chem.*, 1934, 26, 798; *Chem. Abs.*, 1934, 28, 5184; *Brit. Chem. Abs.* **B**, 1934, 740. U. S. P. 1,940,352, Dec. 19, 1933; *Chem. Abs.*, 1934, 28, 1555.

[194] C. Grüne, German P. 288,879, 1914; *Chem. Abs.*, 1916, 10, 2533; *J. S. C. I.*, 1916, 35, 429.

[195] German P. 364,830, 1920, and addition 367,495, to Rütgerswerke A.-G.; *J. S. C. I.*, 1923, 42, 614A, 731A.

[196] W. B. Wiegand and J. W. Snyder, *Ind. Eng. Chem.*, 1934, 26, 413; *Chem. Abs.*, 1934, 28, 3531; *Brit. Chem. Abs.* **B**, 1934, 485; *Rev. Paint, Colour, Varnish*, 1934, 7, 171. See also H. Hadert, *Farbe u. Lack*, 1928, 33, 118; *Rev. Paint, Colour, Varnish*, 1928, 1, 20. H. Niemnitz, *Farbe u. Lack*, 1933, No. 10, 115; *Rev. Paint, Colour, Varnish*, 1933, 6, 80. F. Besser, *Farbe u. Lack*, 1933, No. 21, 247; *Rev. Paint, Colour, Varnish*, 1933, 6, 153.

[197] See Carleton Ellis, "Chemistry of Petroleum Derivatives," New York, Reinhold Publishing Corp., Vol. 2, 1937, 249 and Vol. 1, 1934, 245, for a survey of the work done on particle size measurement of carbon black.

[198] N. Goodwin and C. R. Park, *Ind. Eng. Chem.*, 1928, 20, 621; *Brit. Chem. Abs.* **B**, 1928, 579; *Chem. Abs.*, 1928,22, 3802.

cific surface.[199] All other data adduced also point to an inverse variation between color intensity and particle size.[200]

As would be expected from what has been said, high-intensity blacks are produced by arranging the flames and depositing surface so as to obtain minimum particle size. These blacks require for their manufacture a higher ratio of secondary air to hydrocarbon gas, more burning tips and closer channel setting. Each increase in color, however, is attended with increased oil absorption, increased difficulty in grinding and (subsequent to grinding) marked tendencies toward reagglomeration, seeding and flocculation. However, it has been noted that high oil absorption values of carbon black sometimes are misleading.[201] Thus, alkyd types of varnish were stated to be responsible for losses in drying power that often are attributed to the pigment. High-color blacks are sensitive to vibration, compression and other manipulations. Such agitation, which results in marked deterioration of color, should be guarded against. Wetting down of high-intensity blacks, followed by drying out with a view to eliminating entrained air, has been found injurious to color. There is a marked improvement in color upon incorporation of the blacks into vehicles. The intensification of color thus produced depends on the vehicle. The surface tension relationship between the black and the medium is considered by Wiegand and Snyder as most likely to be the controlling factor, lower interfacial tension corresponding to greater intensity. This is substantiated by the fact that an increase in intensity is accompanied by lower oil absorption and greater ease of dispersion. Greater intensity, greater stability, ease of dispersion and lower oil absorption are all concomitant in the case of most carbon blacks. To produce these improvements by pretreatment the specific vehicle in which the pigment is to be incorporated must be considered. In dispersion of carbon black, milling up to a certain point improves the color but if the operation is carried beyond this point, the color falls off. Excessive temperature also operates against the production of full color.[202]

Volatile Matter in Blacks. Whether a black forms a long or short ink depends to a large extent on the amount of volatile matter in the black. The so-called "long" blacks used in making long inks generally contain a relatively high percentage of volatile matter compared to the short blacks.

Freshly prepared mixtures of a long black and a short black in thin lithographic varnish appear quite similar.[203] After a few minutes, however, the particles of the short black begin to agglomerate into masses of

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[199] L. Hock, *Kautschuk*, 1928, 4, 266; *Chem. Abs.*, 1929, 23, 1772; *Brit. Chem. Abs.* **B**, 1929, 180.

[200] F. Hebler (*Kolloid-Z.*, 1927, 41, 365; *Chem. Abs.*, 1927, 21, 2566), showed that light absorption of graphite dispersions asymptotically approached 100 per cent with decreasing particle size.

[201] F. R. Jones and C. R. Watts, *Oil Colour Trades J.*, 1937, 91 (2010), 1290; *Rev. Paint, Colour, Varnish*, 1937, 10, 185.

[202] W. B. Wiegand and J. W. Snyder, *Paint Manuf.*, 1934, 4 (6), 192; *Rev. Paint, Colour, Varnish*, 1934, 7, 265. *Drugs, Oils, Paints*, 1933, 48 (10), 388; *Rev. Paint, Colour, Varnish*, 1933, 6, 291.

[203] Carleton Ellis, "Chemistry of Petroleum Derivatives," Vol. 1, New York, Reinhold Publishing Corp., 1934, 245.

30 to 40 particles loosely held together, and after an hour groups of over a hundred have formed. These agglomerates may be broken down by grinding but once more coalesce upon standing. The long blacks on the contrary do not exhibit this tendency to agglomerate to any marked degree. It has been suggested[204] that adsorbed volatile matter tends to prevent agglomeration. This conclusion is substantiated by the fact that, after treatment with steam at 500° C., long blacks display a decided tendency to agglomerate.

The tinting strength (as contrasted to hiding power or color intensity) of carbon black depends to a large degree on the amount of adsorbed gas, the tinting strength being greater for pigments containing a large proportion of gaseous impurities.[205]

Wiegand[206] has correlated the acidity and the volatile matter content of blacks. The acidity or pH of carbon black is taken as that of the sludge obtained when 1 part of pigment is boiled with 3 to 10 parts of water for 15 minutes and the supernatant liquid decanted.

The effect of heat treatment on the pH of Micronex Mark II (a rubber-grade impingement carbon black) is shown in Figure 34. In Figure 35 are plotted the pH of various carbons against volatile matter content. The results seem to show that the pH change produced by colloidal carbons is an adsorption phenomenon in which the selective adsorption of the particles of the colloid varies as some function of the volatile matter content. The higher the volatile matter content the lower (more acid) is the pH.

In Figure 36 are shown the relation of pH values of the different carbons to the diphenylguanidine (DPG) adsorption values. The DPG values are expressed as per cent of diphenylguanidine removed from a solution of 0.1 gm. diphenylguanidine in 50 cc. alcohol, by 1 gm. of carbon.

The volatile matter from carbon black is chiefly oxygen in the form of carbon oxides.[207] This indicates that oxygen is combined on the surface of the carbon particle in the form of a complex which may be expressed by the formula C_xO_y.[208] According to this view the change of pH which takes place after heating may be regarded as due to the changes in the amount of the C_xO_y complex associated with the pure carbon. Removal of oxygen by heating in the absence of air decreases the adsorption activity of carbon toward alkaline substances and instead induces a selective adsorption toward acidic material. The adsorption characteristics change continuously from alkaline to acidic substances as oxygen is progressively removed. The flattening of the pH curves

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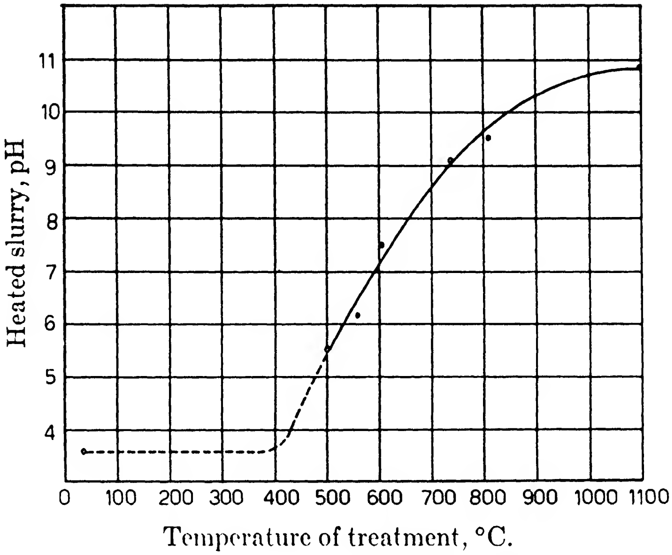
[204] R. O. Neal and G. St. J. Perrott, *U. S. Bur. Mines Bull.*, 1922, 192; *Chem. Abs.*, 1922, 16, 3174; *J. S. C. I.*, 1922, 41, 770A.

[205] P. W. Kearsley and G. L. Roberts, *Ind. Eng. Chem.*, 1931, 23, 835; *Chem. Abs.*, 1931, 25, 4722; *Brit. Chem. Abs.* B, 1931, 817; *Rev. Paint, Colour, Varnish*, 1931, 4, 175. *Farben-Chem.*, 1933, 4 (7), 249; *Rev. Paint, Colour, Varnish*, 1933, 6, 156.

[206] W. B. Wiegand, *Ind. Eng. Chem.*, 1937, 29, 953; *Chem. Abs.*, 1937, 31, 6832. *Paint, Varnish, Prod. Man.*, 1937, 17 (2), 12. *India-Rubber J.*, 1937, 94 (16), 6; *Rev. Paint, Colour, Varnish*, 1937, 10, 319. *Kautschuk*, 1938, 14, 61; *Brit. Chem. Abs.* B, 1938, 611; *Rev. Paint, Colour, Varnish*, 1938, 11, 258.

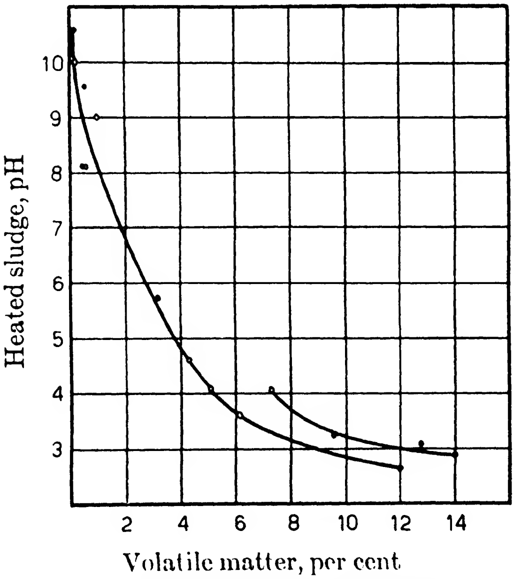
[207] C. R. Johnson, *Ind. Eng. Chem.*, 1929, 21, 1288; *Chem. Abs.*, 1930, 24, 692. W. B. Wiegand and J. W. Snyder, *Rubber Age*, 1931, 29, 311; *Chem. Abs.*, 1932, 26, 1717.

[208] T. F. E. Rhead and R. V. Wheeler, *J. C. S.*, 1913, 103, 461; *Chem. Abs.*, 1913, 7, 2362.



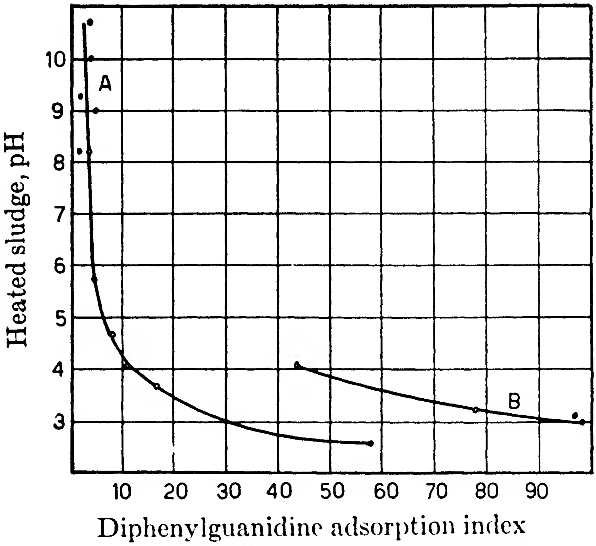
Courtesy Industrial and Engineering Chemistry

FIGURE 34. Effect of Deactive Heat Treatment on pH of Micronex Mark II Carbon (W. B. Wiegand).



Courtesy Industrial and Engineering Chemistry

FIGURE 35. Effect of Volatile Matter Content on pH of Carbon Blacks (W. B. Wiegand).



Courtesy Industrial and Engineering Chemistry

FIGURE 36. Relation of Diphenylguanidine Adsorption Index and pH of Carbon Blacks (W. B. Wiegand).

Curve A. Rubber-grade and nonimpingement carbons
Curve B. High-color carbons

(Figures 34, 35 and 36) at a minimum value of approximately 2.6 suggests complete saturation of the carbon surface with C_xO_y radicals.

The decrease of pH or increase in oxygen content in general increases the stability, ease of dispersion and intensity of the blacks. There is an optimum pH value depending on the vehicle employed and the amount of dispersing agent present. The use of very low pH (2.6-3.0) carbons in inks also involves retardation of drying so that a compromise is sometimes desirable for this reason.

The color intensification of impingement blacks generally is accomplished by heating the carbon in an atmosphere of oxygen. Damon[209] heats the black, with continuous agitation, to a temperature (400 to 425° C.) high enough to increase the oxygen content but below the temperature at which calcining occurs. Wiegand[210] subjects the carbon black to controlled oxidation at temperatures ranging from 300 to 1000° C. The oxygen content of lignite coke is similarly increased to improve the properties of the ground product.[211] Lignite distillation residues are heated to glowing in presence of air. On grinding the heated product, a pure black carbon is said to be obtained. Also, the black is stated to be easily dispersible in water.

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[209] E. H. Damon, U. S. P. 2,005,022, June 18, 1935, to Cabot Carbon Co.; *Chem. Abs.*, 1935, **29**, 5231; *Brit. Chem. Abs.* **B**, 1936, 679; *Rev. Paint, Colour, Varnish*, 1935, **8**, 378.

[210] W. B. Wiegand, U. S. P. 2,013,774, Sept. 10, 1935; *Chem. Abs.*, 1935, **29**, 7020.

[211] K. Bube and E. Kersten, German P. 647,671, 1937, to Werschen-Weissenfelser Braunkohlin-A.-G.; *Chem. Abs.*, 1937, **31**, 8207; *Rev. Paint, Colour, Varnish*, 1937, **10**, 325.

Because of its extremely fine state of division, there is considerable dust formation in the handling of blacks. To prevent this, various methods of forming loosely bound non-dusty aggregates, which are more readily handled, have been proposed.[212] For example, lampblack is sent through rollers so that non-dust forming flakes are secured.[213] The addition to lampblack of up to 10 per cent of tarry material, such as pine tar or natural asphalt, also has been recommended as rendering the black less dusty without impairing its pulverulent condition.[214] Another procedure [215] consists of wetting the black with water and gasoline. The latter preferentially wets the carbon so that the pigment collects in the gasoline phase. After separation of the water from the gasoline, the latter is evaporated to leave the carbon in a granulated form. The properties of pulverulent black are said to be regained on milling. A similar method [216] comprises moistening the black with a liquid such as alcohol, benzene or water and milling to form a stiff paste. The latter then is broken up and the liquid removed by heating to 400-500° F.[217] Such agglomeration as occurs in the above processes, according to Snyder,[218] impairs the color, especially of high-quality blacks.

Testing of Carbon Blacks. The following specifications have been recommended by Neal and Perrott [219] for carbon blacks designed for printing inks.

Chemical Test:

Moisture: less than 5%
Ash: less than 0.1%
Acetone extract: less than 0.1%

Physical Test:

Color: must match standard
Tinting strength: must match standard
Grit: none

Practical Test:

The black, when made into an ink, must have satisfactory working properties as determined by an actual run on the press. The ink must have satisfactory transfer, tack, color, drying properties and must print

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[212] For an example of the apparatus employed in granulating carbon black see E. Billings and H. H. Uffutt, U. S. P. 2,102,054, Dec. 14, 1937, to G. L. Gabot, Inc.; *Chem. Abs.*, 1938, **32**, 1060; *Rev. Paint, Colour, Varnish*, 1938, **11**, 147.

[213] P. Burger, French P. 772,276, 1934; *Chem. Zentr.*, 1935, **106** (1), 2576; *Chem. Abs.*, 1935, **29**, 1596; *Rev. Paint, Colour, Varnish*, 1935, **8**, 178.

[214] British P. 300,610, 1927, French P. 656,765, 1927, to Compagnie Lorraine de Charbons pour l'électricité; *Chem. Abs.*, 1929, **23**, 4029; *Brit. Chem. Abs.* **B**, 1929, 631.

[215] W. B. Wiegand and L. J. Venuto, U. S. P. 1,889,429, Nov. 29, 1933; *Chem. Abs.*, 1933, **27**, 1462; *Brit. Chem. Abs.* **B**, 1933, 774. British P. 327,979, 1929; *Brit. Chem. Abs.* **B**, 1930, 700; *Chem. Abs.*, 1930, **24**, 5118. Canadian P. 301,071, 1930; *Chem. Abs.*, 1930, **24**, 3866.

[216] British P. 437,647, 1935, to United Carbon Co.; *Chem. Abs.*, 1936, **30**, 2717; *Brit. Chem. Abs.* **B**, 1936, 135; *Rev. Paint, Colour, Varnish*, 1936, **9**, 76. French P. 779,681, 1935; *Chem. Zentr.*, 1935, **106** (2), 1932; *Chem. Abs.*, 1935, **29**, 5610; *Rev. Paint, Colour, Varnish*, 1935, **8**, 380 Also, G. C. Lewis, U. S. P. 1,263,082, April 16, 1918; *Chem. Abs.*, 1918, **12**, 1590; *J. S. C. I.*, 1918, **37**, 383A.

[217] See Carleton Ellis, "Chemistry of Petroleum Derivatives." Vol 2, New York, Reinhold Publishing Corp., 1937, for description of other methods of granulating carbon black.

[218] J. W. Snyder, *Off. Digest Fed. Paint and Varnish Prod. Clubs*, 1933, No. 130, 285; *Chem. Abs.*, 1934, **28**, 915.

[219] R. O. Neal and G. St. J. Perrott, *U. S. Bur. Mines* **Bull.**, 1922, **192**, 65.

Courtesy Chemical & Metallurgical Engineering
Courtesy J. M. Huber, Inc.

FIGURE 36A. Carbon Black Being Packed (I. Drogin).

a sufficient number of pages per pound.[220] There must be no separation of oil and pigment and no offset or smutting.

The moisture content is determined by heating a sample of the black for 1 hour at 105° C. in circulating dry air. No bad effects are experienced in general with blacks containing up to 5 per cent water. The moisture regained in a saturated atmosphere varies from 4 per cent for

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[220] One pound of black can print about 4,000 pages of newsprint; Carleton Ellis, *loc cit.*, 250.

news ink blacks[221] to 30 per cent for high-quality blacks[222] and, in the case of Royal Spectra, may be as high as 60 per cent.[223] Warm, dry storage and moisture-proof packing in transit[224] are important for carbon blacks.

The ash content is determined by ignition at 750° C. (a cherry-red heat). An ash content greater than 0.2 per cent indicates that the sample is probably adulterated with mineral black or charcoal.

The method of determining extractable matter suggested by Goodwin and Park[225] is as follows: One to two grams of air-dried black are placed with 3 or 4 gms. of diatomaceous earth in a double-thickness Whatman thimble, folded down and wired shut. The thimble is placed in an Underwriters' apparatus and extracted continuously with xylene for 5 days. The extract in the flask is dried overnight at 56° C. and weighed. In the opinion of these investigators the amount of extractable matter stands in no relation to the quality of the black and it is furthermore practically impossible to determine the total amount of extractable matter. The test, for these reasons, is regarded as of little importance.

The physical tests are described in Chapter 17. The presence of grit may be determined by rubbing a portion of the black under the finger or by placing a small portion on the tongue and rubbing it between the tongue and the palate.

Dispersion of Carbon Black. The ease of dispersion and stability in polar liquids of carbon blacks may be increased by treatment of the black with an alkali sulphite.[226] The black is mixed and heated with a 1- to 10-per cent solution of sodium sulphite in a polar liquid medium, *e.g.*, water or alcohol. The carbon is separated by filtration and dried. Stable dispersions in water also are obtained by addition of 2 to 6 per cent (based on dry carbon) of a soluble salt of the condensation product of 1 mole of formaldehyde and 2 moles of β-naphthalenesulphonic acid[227] or an alkylated product of the latter.[228] The color, luster and gloss as well as stability of blacks in non-aqueous printing ink media are enhanced by treatment of the black with alkaline-earth naphthenates.[229]

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[221] F. D. Cranor and L. J. Venuto, *Am. Ink Maker*, 1932, **10** (11), 9 and **10** (12), 17; *Chem. Abs.*, 1933, **27**, 2589; *Rev. Paint, Colour, Varnish*, 1932, **5**, 292.

[222] W. B. Wiegand and J. W. Snyder, *Can. Chem. Met.*, 1931, **15**, 265; *Chem. Abs.*, 1932, **26**, 564.

[223] J. W. Snyder, *Off. Digest Fed. Paint and Varnish Prod. Clubs*, 1933, No. 130, 285; *Chem. Abs.*, 1934, **28**, 915.

[224] It has been recommended that carbon black for transport by sea be mixed with a suitable oil to obtain a paste which does not absorb moisture, M. W. Haenke and W. L. Haenke, Australian P. 19,485, 1934; *Chem. Zentr.*, 1935, **106** (2), 134; *Rev. Paint, Colour, Varnish*, 1935, **8**, 287.

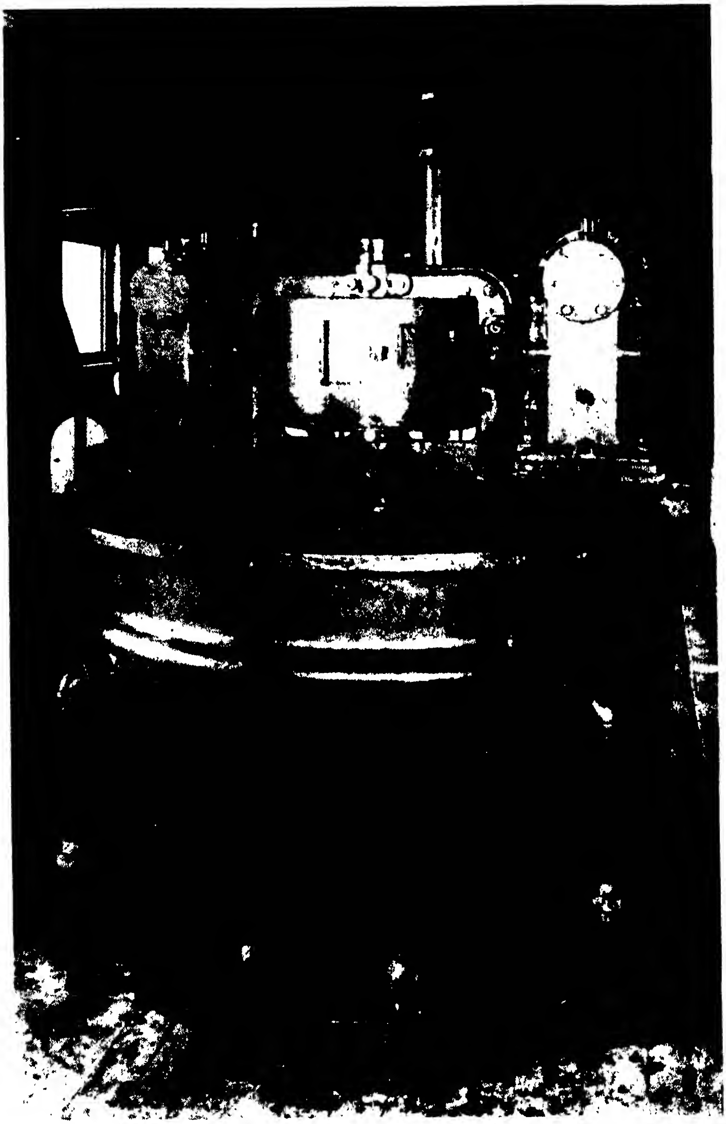
[225] N. Goodwin and C. R. Park, *Ind. Eng. Chem.*, 1928, **20**, 621.

[226] W. F. Tuley, U. S. P. 1,818,770, Aug. 11, 1931, to Naugatuck Chemical Co.; *Chem. Abs.*, 1931, **25**, 5584; *Brit. Chem. Abs.* **B**, 1932, 490.

[227] G. R. Tucker, U. S. P. 2,046,757, July 7, 1936, to Dewey and Almy Chemical Co.; *Chem. Abs.*, 1936, **30**, 5740; Canadian P. 354,103, 1935; *Chem. Abs.*, 1936, **30**, 1469; *Rev. Paint, Colour, Varnish*, 1936, **9**, 181.

[228] G. R. Tucker, U. S. P. 2,046,758, July 7, 1936, to Dewey and Almy Chemical Co.; *Chem. Abs.*, 1936, **30**, 5740.

[229] A. A. Brizzolara, E. L. Duhring and A. M. Erskine, U. S. P. 2,062,159, Nov. 24, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1937, **31**, 824; *Brit. Chem. Abs.* **B**, 1938, 693; *Rev. Paint, Colour, Varnish*, 1938, **11**, 294. British P. 443,470, 1936, to Krebs Pigment and Color Corp.; *Rev. Paint, Colour, Varnish*, 1936, **9**, 182; *Chem. Abs.*, 1936, **30**, 5376; *Brit. Chem. Abs.* **B**, 1936, 485.



Courtesy Sowers Manufacturing Co.

FIGURE 37. Dopp Seamless Jacketed Kettle with Motor Driven Double-motion Positive-scraping Agitator for Mixing Printing Inks. Capacity 350 Gallons.

The carbon black is suspended in a 1- to 10-per cent aqueous solution of a soluble naphthenate. An insoluble alkaline-earth naphthenate is precipitated onto the carbon by addition of the corresponding alkaline-earth salt. After filtering, washing and drying, the carbon is ready for dispersion in the ink medium. However, it has been stated that utilization of excessive quantities of naphthenates results in a poor film on drying.[230] The naphthenic acid salts were said to have a plasticizing effect upon the carbon film.

DISPERSION

The mixing and grinding of pigment and vehicle to secure a stable dispersion of the former in the latter constitutes the last step, and one of the most important, in the production of a printing ink. The main factor governing the stability of a dispersion is the degree of wetting of the solid by the medium or the affinity between the two phases. The degree of wetting is determined by the energy relationships at the liquid-solid interfaces. The energy associated with an interface is known as the surface energy.

The isothermal, reversible formation of an interface between two phases is attended with an increase in energy equal to the sum of the heat absorbed and the work done in creating the interface. The work done equals the free energy increase and is proportional to the area of interface formed. The term "free surface energy" (E), will be restricted in this discussion to the free energy per unit area.

If the phases are designated by the subscripts x and y, the free surface energy may be expressed as E_{xy}. It is numerically equal to the interfacial tension. Free surface energy is potential energy and exists as a strain arising from the unbalancing of the cohesive forces at the interface. Thus a molecule in the interior of a phase has, over a period of time, a resultant of zero acting on it. A molecule near the bounding surface, on the other hand, has resultant force acting normal to the interface.[231] The free surface energy of a material in contact with a vacuum is equal to one-half the cohesive energy of a substance; for if the substance is divided at a plane to form two new surfaces of unit area each, the work done against cohesion equals the increase in free energy of the body, namely $2E$.

If the equal surfaces of a liquid and a solid in contact with air are brought together to form a liquid-solid interface, the decrease in free surface energy will be $E_{sa}+E_{la}-E_{sl}$ where the subscripts s, l, a, stand for solid, liquid, and air phases respectively. This quantity is defined as the

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[230] F. R. Jones and C. R. Watts, *Oil Colour Trades J.*, 1937, 91 (2010), 1290; *Rev. Paint, Colour, Varnish*, 1937, 10, 185.

[231] See R. S. Willows and E. Hatschek, "Surface Tension and Surface Energy," 3rd Ed., London, J. and A. Churchill, 1923, and H. L. Sulman, *Trans. Inst. Mining and Metallurgy*, 1919-20, 29, 44, for complete discussion.

Courtesy Sowers Manufacturing Co.

FIGURE 38. View of Dopp Seamless Jacketed Kettle after Discharging Mixing Batch.

"work of adhesion." In incorporating solid particles in the bulk of a medium however, the "work of immersion" is a measure of the energy change. This quantity (A) which is popularly referred to as the "adhesion tension," the name given it by Freundlich,[232] is defined by the equation:

$$A = E_{sa} - E_{sl}$$

and is equal to the loss in free energy per unit area of particle surface, when the solid is incorporated in the vehicle. The adhesion tension may alternately be defined as the difference between the surface tension of the solid and the interfacial tension between liquid and solid. A method of determining adhesion tension has been described by Bartell and Osterhof.[233]

The greater the free energy decrease when a solid is dispersed the greater will be the stability of the suspension. The adhesion tension,

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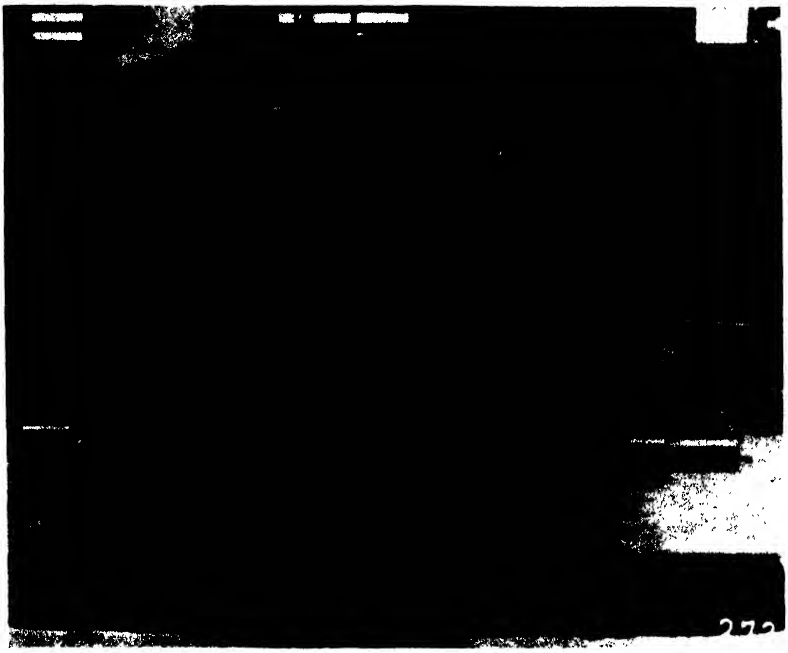
[232] H. Freundlich, "Colloid and Capillary Chemistry," New York, E. P. Dutton & Co., 1926, 157.

[233] F. E. Bartell and H. J. Osterhof, *Ind. Eng. Chem.*, 1927, 19, 1277; *Chem. Abs.*, 1928, 22, 523.



Courtesy National Engineering Company

FIGURE 39. Simpson Intensive Mixer for Preparing Inks.

equal to the loss in free energy, is therefore a direct measure of the degree of wetting of the solid by the liquid.

A suspension will be most stable in that liquid which shows the highest adhesion tension for the solid. From the above equation it is seen also that a high interfacial free energy for a given solid indicates a low adhesion tension. The addition of a wetting agent to the liquid results in a lowering of the interfacial tension, an equal increase in the adhesion tension, and consequently in greater stability of the suspension. The interfacial free energy is lowered by adsorption of the wetting agent on the solid particles, forming particles whose effective surface consists of molecules of the wetting agent. The latter therefore must show affinity for both the solid and the liquid medium.

WETTING

The function of a wetting agent is twofold: to hasten initial dispersion and to render the resulting system more stable. The wetting agents generally used in printing inks are soluble in the vehicle.[234] They are the so-called polar-non-polar molecules containing a strongly polar group, such as the carboxylic or sulphonic acid radical, attached to a non-polar

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[234] See Chapter 8 for detailed description of wetting agents.

organic residue of high molecular weight, *e.g.*, the fatty and unsaturated acids, naphthenates, lecithin and tung oil (glycerides). The polar groups are attracted to the surface of the solid, leaving the organic end directed away from the solid into the medium in which it is soluble. The orientation of a fatty acid is traditionally compared to match sticks with their heads, corresponding to the carboxyl group, attached to a sphere (the particle), and with the stem (hydrocarbon chain) extending radially outward. The disposition of the more complicated molecules is not definitely known in most cases. After more or less complete formation of a monomolecular film, the wetting agent in most cases is adsorbed further [235] but presumably in a more random manner, since the monomolecular layers have been found to correspond to the greatest degree of dispersion.[236] The amount of acid necessary to procure a monomolecular layer may be calculated, provided the mean size of the particles and the effective cross-sectional area of the molecule are known. The weight of palmitic acid required for blanc fixe may be roughly calculated as illustration. Assume a mean particle size of 0.75 micron (7.5×10^{-5} cm.); then the minimum surface area, corresponding to spheres, is 1.77×10^{4} cm.^{2}/g. (density of blanc fixe = 4.5 g./cm.^{3}). The area occupied by an oriented molecule of a fatty acid is 21×10^{-16} cm.^{2},[237] so that 1.39×10^{-5} gm. mols of fatty acid or 0.0036 gm. of palmitic acid are required. This figure agrees closely with experimental results.[238]

Dispersion in Oil Media

In a dispersion of pigment in a drying oil, a layer of adsorbed molecules of the medium is oriented on the pigment particles. If a wetting agent is added to the medium before or while incorporating the pigment, however, the agent will be adsorbed more or less preferentially to form a more stable system than would be obtained with pigment and vehicle alone. Another method of securing a layer of adsorbed wetting agent is to treat the pigment with the latter before incorporation in the medium (pretreatment). Apparently no hard or fast rule can be made regarding the relative merits of pretreatment and incorporating the wetting agents in the medium. Campbell [239] says that in practice it is generally more effective to dissolve or disperse the wetting agent in the oil medium rather than attempt pretreatment of the powder. Price,[240] on the other hand, states that the addition of wetting agents to the medium (oil) has little effect on the ease of dispersion.

[235] See C. W. Price, *J. Oil Colour Chem. Assoc.*, 1938, **21**, 63; *Chem. Abs.*, 1938, **32**, 9525.

[236] C. W. Price, *loc. cit.* and K. N. Kathju, *Paint, Oil, Chem. Rev.*, 1937, **99** (8), 30; *Chem. Abs.*, 1937, **31**, 7268.

[237] N. K. Adam "The Physics and Chemistry of Surfaces," 2nd Ed., Oxford, Clarendon Press, New York, 1938. See I. Langmuir, *Proc. Nat. Acad. Sci.*, 1917, **3**, 251; *Chem. Abs.*, 1917, **11**, 2422; *J. A. C. S.*, 1917, **39**, 1848 for a report of the first determinations of these quantities.

[238] See C. W. Price, *loc. cit.*

[239] G. A. Campbell, symposium, "Wetting and Detergency," London, A. Harvey, 1937.

[240] C. W. Price, *loc. cit.*

Wetting agents suggested for aiding dispersion of pigment in vehicle include alkali, ammonium or organic-base salts of high-molecular weight unsaturated acids.[241] For example, the triethanolamine salt of eleostearic acid was utilized to effect dispersion of pigment in stand oil.

Many methods of pretreatment have been proposed. Thus, the pigment may be milled with a benzene or gasoline solution of the wetting agent. Monomolecular films are obtained by using the calculated amount of dispersing agent.[242] Pigments such as lithopone and zinc sulphide may be coated with fatty acids and esters by adding the water-insoluble agent in the form of an emulsion during wet milling of the pigment or by spraying the pigment during the dry disintegration.[243] Another method comprises passing hot oxidized fatty acid vapors over the pigment[244] or treating the latter with unoxidized fatty acid in an (inert) atmosphere of carbon dioxide.[245] Zinc oxide is coated with an acid such as lauric acid by vaporizing the pigment and the acid and condensing them together.[246]

In carrying out the pretreatment processes, polar compounds of lower molecular weight must be excluded since they are more strongly attracted to the pigment surface and will be adsorbed selectively in contrast to the more useful long-chain compound.[247]

GRINDING

The grinding or milling of vehicle and pigment has two purposes, namely, separation or breaking down of aggregates or agglomerates of pigment particles and establishment of intimate contact between the pigment particles and the medium. For realization of these objects both shearing and crushing action must be exerted. The most common mills producing this action and used in the grinding of inks are the ball, roller, buhrstone and edge runner mills.

Dispersion of dry pigments in a liquid may be accomplished without the usual milling by passing mixtures of pigments and vehicles through tubes at speeds above their critical velocity.[248] Another method comprises dispersing the pigment in a gaseous medium, displacing the latter with the vapor of the vehicle and condensing the vapor.[249]

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[241] A. Chwala, French P. 780,799, 1935; *Chem. Abs.*, 1935, 29, 6081.

[242] K. N. Kathju, *loc. cit.*; British P. 406,513, 1934, to Week and Co., Ltd.; *Rev. Paint, Colour, Varnish*, 1934, 7, 269; *Brit. Chem. Abs.* B, 1934, 371.

[243] See, for example, W. F. Meister, U. S. P. 2,113,539, April 5, 1938, to United Color and Pigment Co.; *Chem. Abs.*, 1938. 32, 4363. G. F. A. Stutz, British P. 429,553, 1935, to New Jersey Zinc Co.; *Chem. Abs.*, 1935, 29, 7101. Canadian P. 351,382, 1935; *Chem. Abs.*, 1935, 29, 6445.

[244] J. T. Baldwin, U. S. P. 1,946,052, Feb. 6, 1934, to Sandura Co.; *Chem. Abs.*, 1934, 28, 2552.

[245] H. R. Minor, U. S. P. 2,067,060, Jan. 5, 1937, to Industrial Process Corp.; *Chem. Abs.*, 1937, 31, 1528.

[246] A. C. Eide, U. S. P. 1,997,925, April 16, 1935, to American Zinc, Lead and Smelting Co.; *Chem. Abs.*, 1935, 29, 3863.

[247] H. Samuels, *Official Digest Federation Paint and Varnish Production Clubs*, 1937, No. 164, 91; *Chem. Abs.*, 1938, 32, 8801.

[248] W. S. Calcott and I. Williams, U. S. P. 2,021.143. Nov. 19. 1935, to E. I. duPont de Nemours & Co.; *Chem. Abs.*, 1936, 30, 548; *Brit. Chem. Abs.* B, 1936, 816.

[249] E. C. de Stubner, U. S. P. 2,086,997, July 13, 1937; *Chem. Abs.*, 1937, 31, 6490; *N. P. V. L. Abs.*, 1937, No. 50, 134.

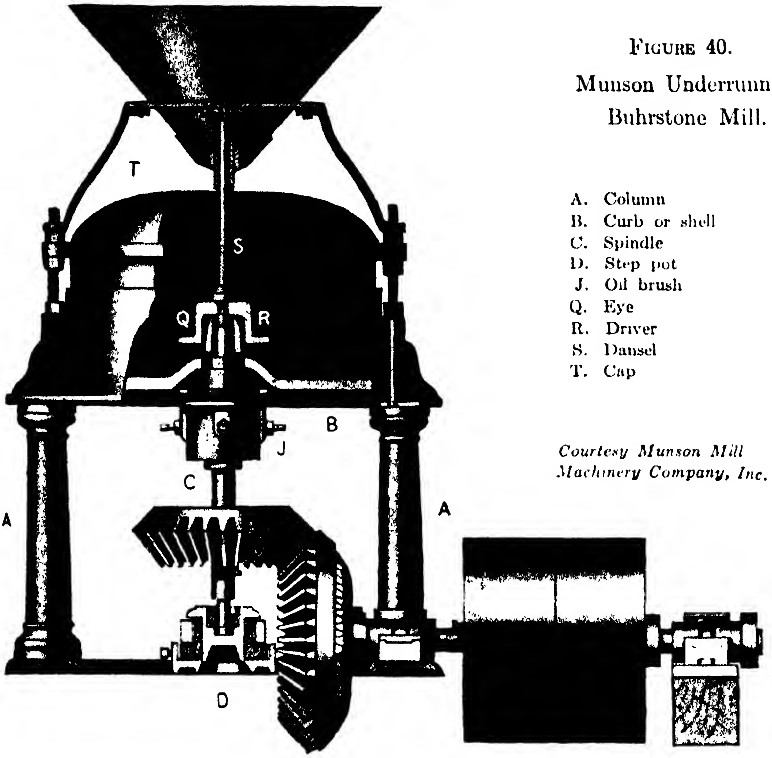

FIGURE 40.

Munson Underrunner Buhrstone Mill.

A.	Column
B.	Curb or shell
C.	Spindle
D.	Step pot
J.	Oil brush
Q.	Eye
R.	Driver
S.	Dansel
T.	Cap

Courtesy Munson Mill Machinery Company, Inc.

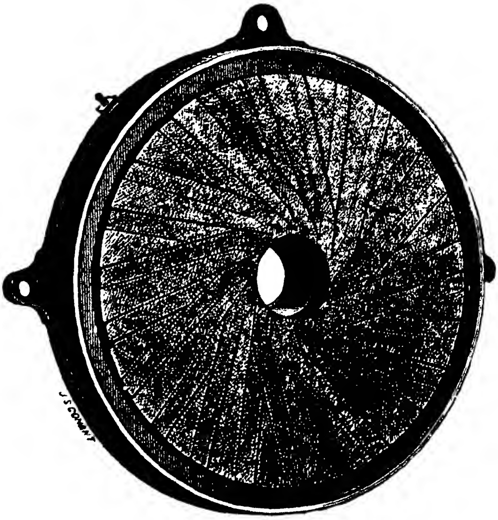

FIGURE 41.

Munson Buhrstone set in Iron Cap.

Courtesy Munson Mill Machinery Company, Inc.

FLUSHING

The flushing (fleshing) process, in which a water-wet pigment is transferred directly to an oil-wet condition, provides a method of obtaining dispersions which avoids both drying and pretreatment of pigments. In the production of wet colors, the water-wet cakes are put in a mixing machine and a definite amount of vehicle[250] is added and, if necessary, a wetting agent. Hydroxyalkylamines[251] such as triethanolamine[252] and alkylamines containing at least one alkyl group having more than 3 carbon atoms[253] have been proposed for facilitating water-to-oil transfer. The mass is mixed at optimum temperature, the pigment and vehicle forming a paste from which the water is displaced; stirring is continued until the water is clear, after which it is poured off. The paste is heated to a safe temperature and vacuum-dried[254] to remove last traces of moisture. The paste obtained is reduced with additional vehicle and thinners to the desired composition.[255]

Flushed colors, since they are made with pigments which have not been dried or ground, are relatively freer from agglomerates and in general show better dispersion than dry colors.[256] Comparison of dry and flushed colors[257] has shown the latter on the whole to be superior in gloss and tinting strength. Dry colors on the other hand exhibit, as a rule, better covering power. Dry ground light and medium chrome yellow and chrome green also are superior in light-fastness to the corresponding flushed colors.

In vacuum-drying the residual moisture content of the oil paste may be closely controlled. This is an important virtue of the flushing process since a small amount of moisture improves the flow and stability of dispersions in bodied linseed oil.[258] The saving in time and power costs is another virtue of the flushing process of not inconsiderable importance to the ink-maker.[259]

[250] The use of a pigment-oil paste rather than the pure vehicle has been recommended; J. D. Todd and M. Silverman, U. S. P. 1,986,029, Jan. 1, 1935, to Sherwin-Williams Co.; *Chem. Abs.*, 1935, 29, 1269; *Brit. Chem. Abs.* **B**, 1935, 1103.

[251] F. Guenther, F. Teller, C. Immerheiser and B. Zschimmer, U. S. P. 1,802,174, April 21, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3497.

[252] E. C. Holton Canadian P. 321,477, 1932, to Sherwin-Williams Co.; *Chem. Abs.*, 1932, 26, 3391.

[253] L. W. Ryan and E. K. Fischer, U. S. P. 2,126,925, Aug. 16, 1938, to Interchemical Corp.; *Chem. Abs.*, 1938, 32, 8174. British P. 469,559, 1937, to United Color and Pigment Co., Inc.; *Chem. Abs.*, 1938, 32, 814.

[254] *Cf.* H. Samuels, *J. Oil Colour Chem. Assoc.*, 1938, 21, 171; *Chem. Abs.*, 1938, 32, 7291.

[255] See K. M. Sprinkel, *Paint, Oil Chem. Rev.* 1937, 99 (8), 40; *Chem. Abs.*, 1937, 31, 7268; *Brit. Chem. Abs.* **B**, 1937, 809, and H. Cajar, British P. 219,562, 1923; *Brit. Chem. Abs.* **B**, 1924, 797; *Chem. Abs.*, 1925, 19, 739. See also G. B. Palmer, U. S. P. 1,339,219, May 4, 1920; *Chem. Abs.*, 1920, 14, 1903; *J. S. C. I.*, 1920, 39, 460A, for one of the first reports of the flushing process used in the production of reflex blue.

[256] K. M. Sprinkel, *loc. cit.*

[257] St. Louis Paint and Varnish Prod. Club; *Paint, Oil Chem. Rev.*, 1938, 100 (22), 82; *Am. Paint. J.*, 1938, 23, 8, 25 (Oct. 26); *Chem. Abs.*, 1939, 33, 414. J. J. Flannery and J. J. McCormick (Detroit Club); *Am. Paint. J.*, 1938, 23, Convention Daily 6, 24 (Oct. 25); *Chem. Abs.*, 1939, 33, 413.

[258] J. Mattiello, Dissertation "A Study of the Flow, Dispersion and Livering Characteristics of Pigments and Pastes Made With Linseed Oils," Columbia Univ., New York, 1936.

[259] H. Samuels, *loc. cit.*

Various modifications of the process outlined above have been proposed. Grinding of the water paste and vehicle instead of simple mixing has been recommended.[260] In another process[261] the aqueous paste is frozen and the frozen pulp shaved to produce a snow-like mass. The latter is agitated with oil or varnish while raising the temperature of the mixture to the melting point of ice, and the liberated water eliminated. Another process[262] comprises passing the vapors of the displacing liquid into the aqueous paste. Water and displacing fluid are distilled off together, the latter collected from the condensate and the cycle repeated until all the water has been displaced.

Transfer of pigment from water to oil may be accomplished by adding an emulsion of oil in water to an aqueous suspension of the pigment. Upon coagulating the protective colloid (*e.g.*, casein) the oil separates carrying the pigment with it.[263] In another process[264] the oil is emulsified with an aqueous pigment paste by means of water-soluble, fatty acid soaps such as sodium oleate. The emulsion is destroyed by adding a salt such as barium chloride which precipitates the emulsifier, and the oil containing the pigment settles out. Lithographic pigment may also be made into a water-soluble form,[265] the water solution of it emulsified in oil, and the insoluble form then regenerated. The latter step may be accomplished, for example, by adding a water solution of a precipitating agent to the emulsion.

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[260] H. Dreyfus, Canadian P. 330,812; *Chem. Zentr.*, 1935, **106** (1), 3206; *Rev. Paint, Colour, Varnish*, 1935, **8**, 178. R. R. Denslow, A. M. Erskine and S. C. Horning, U. S. P. 2,153,515, April 5, 1939, to E. I. duPont de Nemours & Co.

[261] H. Dourif, U. S. P. 2,067,906, Jan. 19, 1937; *Chem. Abs.*, 1937, **31**, 1642; *Rev. Paint, Colour, Varnish*, 1937, **10**, 152.

[262] E. C. de Stubner, U. S. P. 1,955,738, April 24, 1934; *Chem. Abs.*, 1934, **28**, 4255; *Rev. Paint, Colour, Varnish*, 1934, **7**, 266; *Brit. Chem. Abs.* **B**, 1935, 161; *N. P. V. L. Abs.*, 1934 (28), 195.

[263] H. Grossman, U. S. P. 1,696,034, Dec. 18, 1928, to W. S. Pritchard; *Brit. Chem. Abs.* **B**, 1929, 566; *Rev. Paint, Colour, Varnish*, 1929, **2**, 179.

[264] A. J. Shroeder, U. S. P. 2,112,222, March 22, 1938, to Interchemical Corp.; *Chem. Abs.*, 1938, **32**, 3991; *Rev. Paint, Colour, Varnish*, 1938, **11**, 275; *Nat. Paint Bull.*, 1938, **2** (5), 17. British P. 452,556, 1936, to International Printing Ink Corp.; *Chem. Abs.*, 1937, **31**, 1234.

[265] A. J. Hailwood, A. Sheperdson and A. Stewart, British P. 326,516, 1928, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1930, **24**, 4944. French P. 680,695, 1929; *Chem. Abs.*, 1930, **24**, 4103.

Chapter 7

Typographic Inks—Drying-oil Types

Although typographic printing was invented in the fifteenth century, inks similar to those used in printing from type were made considerably earlier. Samples of prints from engraved stone blocks, found in China and originating in the 10th century, show that the ink consisted of a carbonaceous black pigment mixed with an oil.[1] In the 15th and 16th centuries, when the art of printing was spreading throughout Europe, the printer usually mixed his own inks. These were often very lightfast, since various prints well preserved up to the present show very little signs of fading. Towards the middle of the 17th century, it became the usual practice for printing inks to be made by inkmakers, and not by printers. Particularly the Dutch and English were engaged in the industry of ink manufacture.

PRESSES

Of the three general methods of printing—typography, lithography and intaglio—the most extensively used is typography.[2] This type of printing is applied to publications having a large circulation, which comprise newspapers, magazines, books, as well as cards, folders, cartons, covers and wrappers. Printing is done with hand-driven or automatic machines from a metal type-plate, which bears in relief the character or design to be printed. Instead of metal type plates, printing may be done from plastics types. The material used is a thermoplastic resin which is cast by a linotype machine in the same way as with metal type.[3] Presses are of widely varying design with regard to construction and speed. As a consequence, inks must be compounded to fit properly the conditions furnished by the character of work.

Typographic presses are classified according to their construction in three types: platen, cylinder and rotary presses. A characteristic of each variety is, as already mentioned, that the paper is pressed against a "printing form" which consists of the assembled types (*i.e.*, letters,

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[1] F. L. Burt, "Printing Inks, Their History, Composition and Manufacture"; *The Inland Printer*, 1919, 64 (2), 190. See also Thaddeus Davids, "The History of Ink," New York, Th. Davids & Co., 1860.

[2] *Typography* is the process of printing with types.

Lithography is a printing method involving the employment of stone or metal plates on which the figures are very slightly raised or not raised at all. Distribution of ink depends upon repulsion of the "greasy" ink employed from the water-wetted non-printing areas and attraction of ink by the "greasy" printing areas. "Greasy" is defined as water-repellent. (See: Chapter 9.)

Intaglio is a printing process in which engraved plates are used. (See: Chapter 10.)

[3] See H. R. Simonds, "Industrial Plastics," New York, Pitman Publishing Corp., 1939.

punctuation marks and spaces) cast in relief and fastened together by a frame. The paper to be printed is supplied either in single sheets or as a continuous web which runs off a roll. The platen press prints a single sheet by pressing the entire form against the sheet at the same moment. Single sheets of paper are printed on a form of cylinder press also,[4] but the paper is pressed to the form by means of a cylinder which rolls along the sheet while the latter is laying on the type-frame. These two types of presses are so-called flat-bed machines, *i.e.*, the paper is pressed against a flat form. The rotary press has a plate cylinder, around which the curved printing form is fastened. A second cylinder, called the impression cylinder, presses the paper, which is supplied either in single sheets or in the form of a continuously running web, against the plate cylinder.

PAPER

The paper used in typographic printing varies from hard-sized, supercalendered papers, such as cardboard, to highly absorbent, unsized newspaper material. Since the finished print is the result of a combination of paper, press and ink, any one of these factors cannot be chosen independently of the remaining two. For example, a certain kind of ink may be satisfactory on one type of press with a particular paper, but if these two are replaced by other presses or papers, various troubles may arise which make the use of that kind of ink difficult or even impossible. The fluidity of inks should increase with the speed of the press, since the time in which the paper picks up ink is less at increased speed of printing. When printing on stiff, hard and non-absorbent papers, the printing plate or impression cylinder should be applied with greater pressure than normal or usual, in order to secure proper adherence of ink to the surface of the paper. Also, in printing on such papers, inks should not be very fluid, since the increased pressure would squeeze it out under the edges of the printing form. As a consequence, such papers are usually printed on a platen press [5] on account of its lower speed.[6]

Cylinder presses are those most frequently used, and with them a wide variety of papers is printed. Cheaper grades of paper, such as employed in newspaper printing (less sized, very absorbent stock) are used with rotary presses.

PROPERTIES REQUIRED IN INKS

A good ink must possess several properties in order to satisfy printing conditions set by press and paper. Factors which are relevant to these requirements are viscosity, tack, drying time and the tendency of the ink

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[4] A *cylinder press* is a printing machine in which the impressions are made from plates or type laid upon a flat surface (or bed) which usually moves backward and forward, under a rotating impression cylinder.

[5] A *platen press* (bed-and-platen press) is one in which the paper and form are both on flat surfaces.

[6] See Chapter 18 which discusses paper.

to smear or offset. Drying time is defined as the time required for the composition either to penetrate the surface of the paper or to dry to a hard permanent film. The printing compositions should be adaptable, in some instances, to overprinting with colors or varnish. The inks must not penetrate to the opposite side of the printed page ("strike through") or cause transparency of the paper as a result of oily materials present in the ink ("show through").

To secure an ink possessing the requisite properties, proper selection of the ingredients is necessary. An important ingredient of printing inks is the coloring matter (or pigment) dispersed in a vehicle, which carries the pigment from the type to the paper. In typographic inks the coloring matter usually consists of solid particles of a pigment, or mixtures of pigments, incorporated in the vehicle, in which it is insoluble.

DRYING-OIL VEHICLES

The preparation of the vehicle is one of the most important of the various stages of printing ink manufacture.[7] Inks with drying-oil vehicles have been made for a very long time. During the earlier stages of the development of typographic printing, the English and Dutch inkmakers were especially noted for the vehicles mentioned above. Both used linseed oil as the basic ingredient, but there were of course differences in the method of preparation and in the selection and quantities of substances which were employed to adjust the properties of their inks.[8]

Moxon,[9] who probably wrote the first extensive treatment on the art of printing, considered the Dutch method as the better one. He states that the Dutch in making printers' varnish used old linseed oil only, which eventually was admixed with a small proportion of rosin. The English used a relatively large amount of rosin. Also British linseed oil was often not sufficiently aged, which circumstance, it is held, sometimes caused yellowing of the inks. Furthermore, the English practice, in order to save on the cost of inks, was to admix train (whale) oil with the varnish, thereby causing clogging of type and slower drying. Also, due to its "fatness," train oil is reported to cause offsetting and to render prints "dull and unpleasant to the eye." Other differences between the English and Dutch methods of this period were that the English did not boil and burn linseed oil as long as the Dutch did, so the oil remained greasy and dried more slowly. The Dutch clarified their varnish more thoroughly than the English, by boiling the oil with litharge and straining it before the admixture of pigment. However, the Dutch inkmakers usually left the addition of pigment to the printer. The English method included the admixture of a pigment, which was mostly lampblack, with the hot or

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[7] The various types of vehicles are discussed in Chapter 3.

[8] F. L. Burt, *The Inland Printer*, 1919, 64 (2), 190.

[9] J. Moxon, "Mechanick Exercises on the Doctrine of Handy-works Applied to the Art of Printing," a literal reprint of the first edition, published in the year 1683; "The Typothetae of the City of New York," 1896.

boiling varnish, but the amount of the former was, according to Moxon,[10] often insufficient, so that the ink when printed was too pale, and hence more pigment had to be added by the printer.

The procedure followed by Dutch inkmakers in preparing printers' varnish consisted, as described by Moxon,[11] in boiling "old" linseed oil in a kettle (filled half full only to avoid danger of fire by scumming) until a scum began to rise and then adding (in small portions) about half a pound of rosin for every gallon of oil. When all the rosin dissolved, the oil was ignited and burned until it was sufficiently heavy. The consistency of the oil was judged by testing the stickiness of a drop between two fingers. To clarify the product, about an ounce of litharge per four gallons of oil was added; then the varnish was cooled and strained. It was stored for a considerable period of time before use, since the longer a varnish was stored, the less likely was the ink to turn yellow when printed.[12]

During the 18th century, linseed oil and nut oil were regarded as the most appropriate for printing purposes. According to Fertel[13] and Breton,[14] rape oil and hemp oil were used for low-priced books. Breton says: "The ink that is used for printing books is a mixture of oil and black. The oil is converted into varnish by boiling, and the black is extracted from pitch resin."

In more recent times the treatment of linseed oil was improved. Also, other drying oils were introduced, for example vegetable drying oils such as tung (China Wood), soybean and perilla oils. Rosin oils are now widely used for the purpose of lowering the cost of production of inks.[15] In addition to these, animal drying oils, such as menhaden oil (a fish oil) are being employed as printing ink vehicles.

The drying oil is now boiled, usually in a closed metal kettle, until it becomes thick and sticky, and in this state it is used as lithographic varnish. Its consistency is regulated by varying the temperature and duration of heating. According to viscosity tests made with the Gardner-Holdt viscosimeter, lithographic varnishes are classed in various grades as shown in Table 28. The grades more frequently employed in printing inks are those from No. 00 to No. 3. However, thinner or thicker grades, than those just mentioned, may be employed, depending on special requirements. The selection of the right grade of varnish depends largely on the press and paper used. For example, in printing on a hard, non-absorbent paper such as bond paper and using a platen press, lithographic varnish No. 2 or 3 will be satisfactory, but for printing on a smoother

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[10] J. Moxon, *loc. cit.*

[11] J. Moxon, *loc. cit.*

[12] See Chapter 2 for further historical information.

[13] W. Savage, "On the Preparation of Printing Ink," London, Longman, Rees, Orme, Brown, Green and Longman, 1832. Fertel's Method of Preparing Printing Ink and Lampblack, 1723.

[14] M. Breton's article in the *Encyclopédie Méthodique*, 1751; W. Savage, *loc. cit.*

[15] F. L. Burt, *The Inland Printer*, 1919, 64 (2), 190.

Table 28.—**Classification of Lithographic Varnish.**[16]

No.	Viscosity (poises)	No.	Viscosity (poises)
000	1.8	4	62.1
00	4.8	5	120.0
0	8.0	6	200.0
1	14.4	7	.....
2	23.5	8	1250.0
3	34.0		

paper, such as enamel stock with the same press, the appropriate varnish is No. 00 or No. 0.[17]

The proportion of pigment and varnish determines the consistency of an ink. Short ink is one in which the percentage of pigment is relatively high, whereas an ink with low pigment concentration is termed long ink. However, the same consistency may be secured by varying either the pigment content, or the viscosity of the varnish. Also, the amount of oil absorbed by the pigment is of importance. For example, an ink composed of four parts of English vermilion and one part lithographic varnish No. 2 has a consistency similar to a composition made with one part of carbon black and three parts of No. 1 lithographic varnish.[18] When employing platen presses, a short thick ink will work well on pressure-resistant, non-absorbent surfaces. However, if this printing composition were replaced by one composed of less pigment and more varnish, mottled impressions would be produced. The excess varnish causes spreading which results in uneven pigment distribution. Again, the working conditions, *e.g.*, paper and speed of press, decide what pigment concentration and kind of varnish will be desirable.[19]

On non-absorbent surfaces, where the ink should dry to a hard film, a rather short and thick composition will be required, but in absorption-drying inks, such as are employed with cheaper grades of paper, the pigment concentration may be held relatively low. Stiff inks, but still of sufficient length for proper distribution on the type plate,[20] are used for carton covers and also for bond paper printing. Inks of thinner body and lower strength of color are usually employed with high-speed presses for news and poster printing.

It has been suggested[21] that train oil (whale oil)[22] together with anthracene oil and asphalt be used as a vehicle for printers' ink. An example of such an ink is one containing 40 parts of pitch or asphalt, 45 parts of anthracene oil, 3 to 15 parts of an aniline color (soluble in aniline), 10 parts of a lubricating soap, and 8 parts of Greenland train oil, mixed at a temperature of 140 to 176° C.

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[16] H. A. Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," 8th Edition, Institute of Paint and Varnish Research, Washington, D. C., 1937, p. 564.

[17] H. E. Rice, *Paint, Oil Chem. Rev.*, 1935, **97** (13), 15; *Chem. Abs.*, 1935, **29**, 5680; *Rev. Paint, Colour, Varnish*, 1935, **8**, 306.

[18] H. E. Rice, *loc. cit.*

[19] See: Chapter 18.

[20] E. F. Nurse, *Paper & Print*, 1937, **10**, 166; *Rev. Paint, Colour, Varnish*, 1937, **10**, 413; *Chem. Zentr.*, 1937, **108** (2). 2268.

[21] H. Gunther, British P. 2868, 1882; *J. S. C. I.*, 1882, **1**, 182.

[22] The odors of these inks are objectionable.

VEHICLES FROM RUBBER

Inks containing vehicles derived from rubber have been employed for some time. It is reported that as early as 1872 an ink of this sort was in common use in Germany.[23] This product is said to have been prepared by first making a rubber varnish, by grinding together 5 parts of linseed oil and 1 part of rubber, and then incorporating pigment.[24] Advantages mentioned for this product were a better covering power and greater economy (lower cost of production) than was afforded by the usual linseed oil and pigment mixtures. Also, the rubber may be passed through a colloid mill until the particles have reached colloidal dimensions.[25] The ground material then may be incorporated in a linseed or tung oil vehicle.

Millar [26] has prepared ink vehicles by distilling and simultaneously agitating waste vulcanized rubber, such as disintegrated rubber tires. In Figure 42 is shown an apparatus for distilling rubber for utilization in printing inks. The rubber is distilled at a temperature of 525° F. until a condensate free from water is secured. This procedure destroys any fabric present and decomposes the rubber. Steam, at a temperature of 475° F., is blown through the liquid residue to remove objectionable pungent matter. The cooled carbonaceous still residue contains from 25 to 35 per cent carbon and may be ground to form a printing ink. Drying oils or toning materials [27] may be added as necessary. It has been stated [28] that compositions of this type have the disadvantage of causing rubber printing plates to swell.

Another procedure involves finely grinding scrap rubber and then treating it with sulphuric acid to destroy any fabric which may be present.[29] The acid is neutralized with sodium hydroxide, and the liquor is extracted with heated crude oil. Treatment with sulphuric acid may be omitted, however, and extraction with heated crude oil may be applied directly to the disintegrated rubber. To the filtered extract (in crude oil), pigment, rosin-wood oil varnish, China Wood oil,[30] and magnesium oxide are added. The mixture is ground to the proper consistency.

It has been suggested [31] that a vehicle be manufactured by heating together, to the vulcanizing temperature, a mixture of linseed or other drying oil, and a solution of rubber in gasoline. In some instances, the

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[23] *Deutscher Farber-Consum-Vereine, Muster-Zeitung*, 21, 6; *Chem. Zentr.*, 1872, 3, 58.

[24] Rubber inks are usually slow drying.

[25] A. Davies, British P. 421,820, 1934; *Rev. Paint, Colour, Varnish*, 1935, 8, 246.

[26] C. F. P. Millar, U. S. P. 2,125,683, Aug. 2, 1938; *Am. Ink Maker*, 1938, 16 (10), 43. French P. 810,299, 1937; *Chem. Abs.*, 1937, 31, 8964; *Rev. Paint, Colour, Varnish*, 1938, 11, 54. British P. 444,683, 1936; *Chem. Abs.*, 1936, 30, 6586.

[27] *Toners* are organic pigments containing no inorganic pigments or inorganic carrying bases. (Webster's New International Dictionary of the English Language, G. and C. Merriam Co., Springfield, Mass., 1939.)

[28] R. A. Crawford, U. S. P. 2,120,393, June 14, 1938, to B. F. Goodrich Co.; *Chem. Abs.*, 1938, 32, 6083; *Rev. Paint, Colour, Varnish*, 1938, 11, 365. Canadian P. 374,102, 1938, to B. F. Goodrich Co.; *Chem. Abs.*, 1938, 32, 6484.

[29] L. C. Neale, French P. 664,554, 1928; *Chem. Abs.*, 1930, 24, 979. German P. 555,174, 1928; *Chem. Abs.*, 1932, 26, 5220. British P. 321,558, 1928; *Chem. Abs.*, 1930, 24, 2903. U. S. P. 1,856,035, June 28, 1932; *Chem. Abs.*, 1932, 26, 4486.

[30] The drying rate will increase as the per cent of tung oil increases.

[31] H. Plauson, British P. 393,575, 1933; *Chem. Abs.*, 1933, 27, 6021.

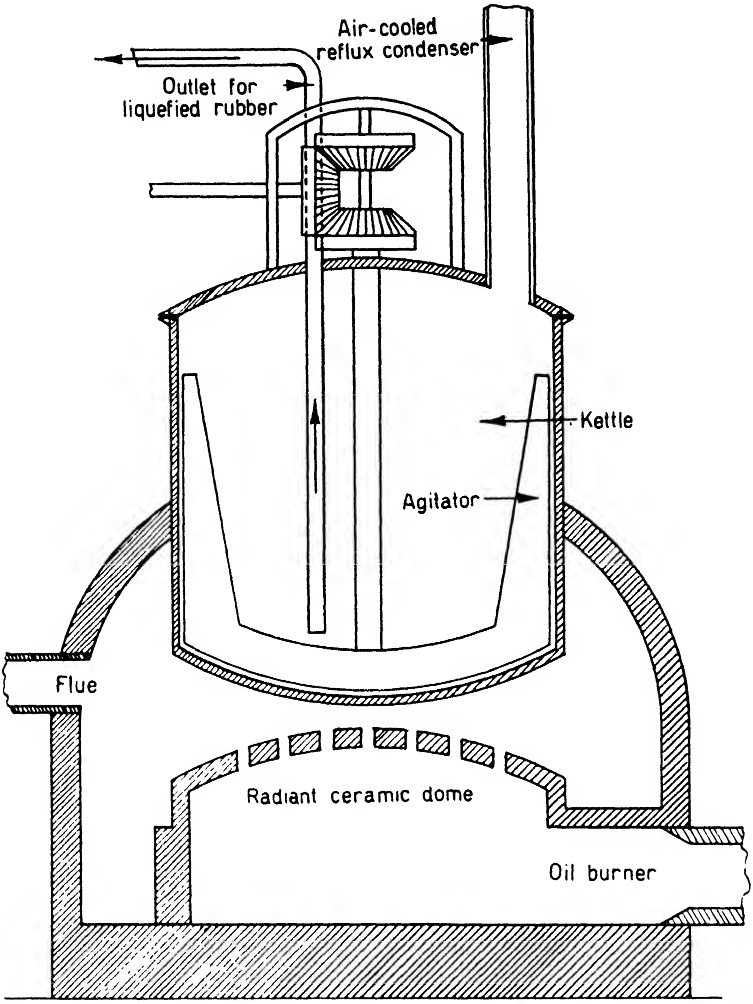

Figure 42. Diagrammatic Sketch of Apparatus for Preparing Liquefied Rubber.

rubber may be vulcanized before admixture with the drying oil, and oxidized tar oil may be used instead of linseed oil. Albertol resins, sulphur, anti-agers and other modifying agents may be introduced.

Vehicles for drying-oil inks have been prepared[32] by heating caoutchouc, latex, balata, or scrap vulcanized rubber at atmospheric pressure or higher and at a temperature of at least 250° C. Thus, crude plantation rubber or crepe rubber (in an oil-fired kettle equipped with an agi-

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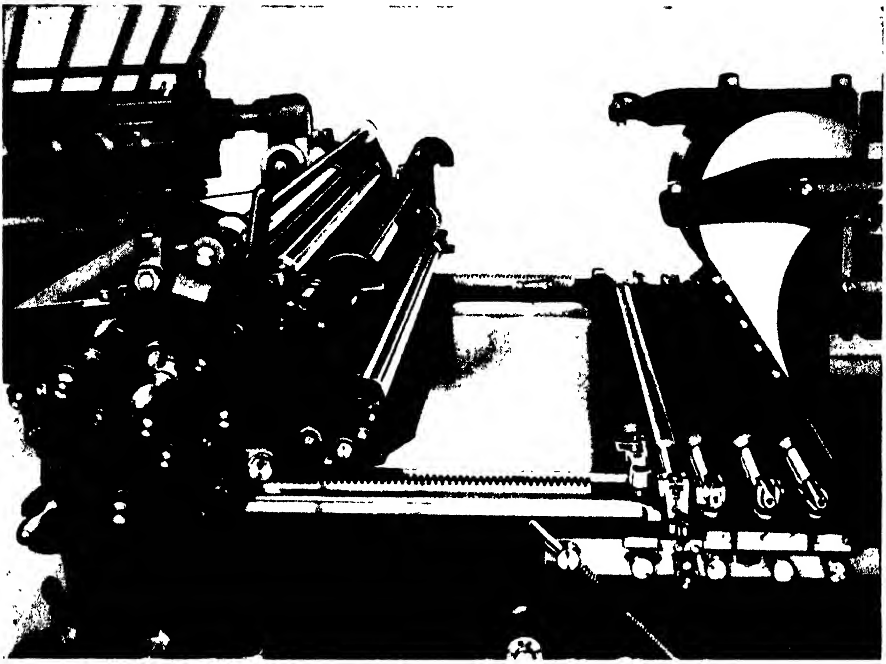
[32] R. A. Crawford, U. S. P. 2,120,393, June 14, 1938, to B. F. Goodrich Co. R. A. Crawford and D. B. Forman, *Am. Ink Maker*, 1939, 17 (3), 21; *Rubber Age*, 1938, 43, 281; *Chem. Abs.*, 1938, 32, 8206.

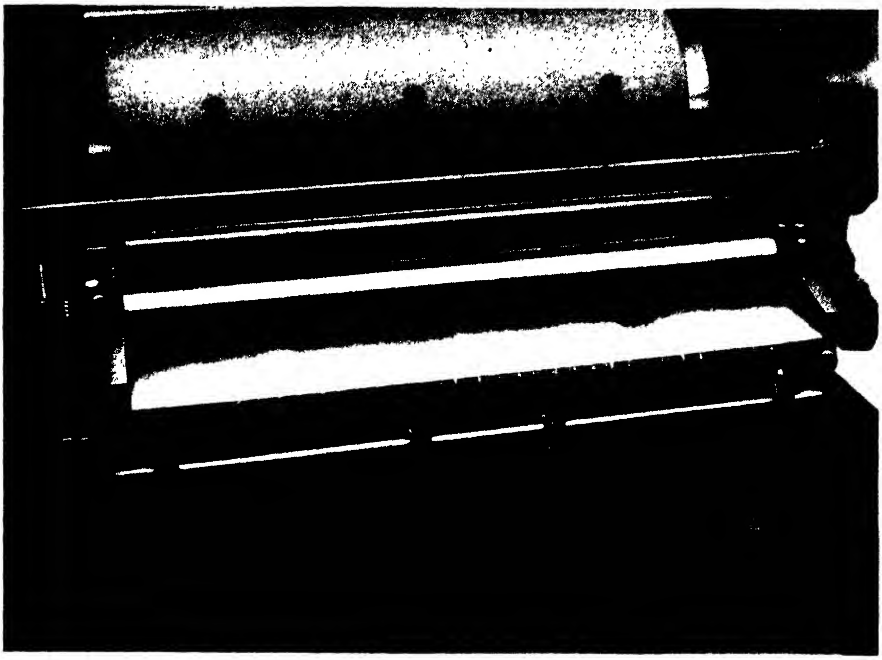


Courtesy Miller Printing Machinery Company

FIGURE 43. Side View of Miller Automatic Cylinder Press, with Inker Rolled Back to Expose Form Rollers.

tator and an air-cooled reflux condenser) is decomposed thermally at 250 to 260° C. and atmospheric pressure, whereby the rubber is converted into a liquid which is removed as quickly as it is formed. Upon cooling, the composition, which is designated as "liquefied rubber," has the consistency of molasses. The product is mixed in the following proportions to give an ink: "liquefied rubber," 100 parts; ink black, 50 parts; petrolatum, 10 parts; montan wax, 4 parts; castor oil, 15 parts.

The latter process may be modified in that superatmospheric pressures and hydrogenating or reducing catalysts are employed. To illustrate, 100 parts by weight of crude plantation rubber are placed in an autoclave with 264 parts of normal hexane and 10 to 15 parts of an active nickel catalyst. Air in the autoclave is swept out with the aid of hydrogen, and a pressure (of hydrogen) of 1000 pounds per square inch is maintained throughout the heating operation. A temperature of 300° C. is used, and hydrogenation is carried out for two hours, which results not only in the liquefaction of rubber but also in a considerable reduction of its degree of unsaturation. The hexane is evaporated and the residue compounded as follows: "liquefied rubber," 100 parts (by weight); aluminum powder, 50 parts; wool grease, 7 parts.



Courtesy Miller Printing Machinery Company

FIGURE 44. End View of Miller Automatic Cylinder Press with Fountain Blade Dropped.

The advantages mentioned for these inks are that they are stable, produce good detail, and will not skin. Crawford calls the compositions "liquefied rubber inks" and the vehicle "liquefied rubber." These inks, however, are slow-drying in some instances.

Other solvents such as naphtha may be used, or the ink may be applied to rubber goods and then vulcanized.[33]

MODIFYING AGENTS

Besides changing the proportion of coloring matter and body of the varnish, consistency and working qualities of inks may be adjusted by addition of various substances. These are binding agents, thickeners and thinners and are often designated as modifying agents.[34] Incorporation of such materials promotes a change in density or in tackiness and smoothness of the ink film. Substances such as beeswax, which decrease the tendency to offset, as well as driers which accelerate setting and drying of the ink film, may be incorporated into the composition.

The substances employed as binding agents may form homogeneous

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[33] For vulcanized inks, see Chapter 15. Rubber compositions with volatile solvents are discussed in Chapter 8.

[34] For a more detailed discussion of modifying agents, see Chapter 5.

molecular mixtures with the bodied oil. The vehicles thus prepared are approximately a solution of the admixed substance in the oil. However, the admixed material may be insoluble in the oil, in which case the binding agent is more or less colloidally dispersed in the latter. Binders are used to produce a change in the viscosity of the varnish, to attain a certain fluidity on the press, and to promote penetration of the paper, where such properties are required. For example, stearin pitch, a residue from the distillation of fatty acids, was used with drying-oil varnish, but has not proved entirely satisfactory in improving distribution qualities and eliminating stickiness of ink. A frequent addition to lithographic varnishes is gilsonite, an asphaltite, the use of which is stated to allow the incorporation of an increased proportion of pigment (carbon black) without otherwise changing the character of ink.[35]

Petroleum oil or pitch,[36] shale oil[37] (the crude tar from bituminous shale), pitch from peat tar,[38] Vaseline or grease, paraffin or other mineral waxes[39] are employed as modifying agents for lithographic varnish. Some waxes are used to diminish offsetting and impart scratch-proofness to the printed ink film, the latter being required for inks printed on extremely hard papers, *e.g.*, flint paper, or cartons, such as tea cartridges.[40]

A too heavy or too soft varnish may be thinned or thickened, respectively, by raw oil or thin varnish, or by heavier varnish. Raw linseed oil, turpentine oil, menhaden oil, or vegetable tar oil[41] may be used for this purpose. As plasticizing agents and to prevent excessive fluidity of ink on the paper, salts of unsaturated fatty acids with two or more double bonds may be used. Fatty acids occurring in vegetable or animal drying oils are suitable. For example, triethanolamine salts of linoleic or eleostearic acid (obtained from linseed oil) or of clupanodonic acid (from fish oil) may be incorporated into drying-oil varnish.[42] Solid powdered minerals and inorganic materials are employed as thickening agents. These also may eliminate the use of driers, since some of them are reported to possess drying properties, *e.g.*, finely powdered oyster shells.[43] Other substances for similar purposes are: colloidal graphite,[44] which may be mixed (before adding to the varnish) with gelatin, glue, or similar hydrophilic substances; charcoal from cocoanut shells or peat;[45] or finely divided carbon.[46]

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[35] H. E. Rice, *Paint, Oil, Chem. Rev.*, 1935, **97** (13), 15; *Chem. Abs.*, 1935, **29**, 5680; *Rev. Paint, Colour, Varnish*, 1935, **8**, 306.

[36] *Farben-Ztg.*, 1938, **43**, 302; *Brit. Chem. Abs.* **B**, 1938, 552.

[37] D. T. Ogilvy, British P. 18,533, 1897; *J. S. C. I.*, 1897, **16**, 1012.

[38] J. W. Leadbeater and W. A. Towler, British P. 228,996, 1923; *Chem. Abs.*, 1925, **19**, 3027.

[39] S. Horii, Japanese P. 90,585, 1931; *Chem. Abs.*, 1931, **25**, 4724; *Rev. Paint, Colour, Varnish*, 1931, **4**, 250.

[40] E. F. Nurse, *Paper and Print*, 1937, **10**, 166; *Chem. Zentr.*, 1937, 108 (2), 2268; *Rev. Paint, Colour, Varnish*, 1937, **10**, 413.

[41] G. Motegi and K. Asakura, Japanese P. 31,189, 1917; *Chem. Abs.*, 1918, **12**, 231.

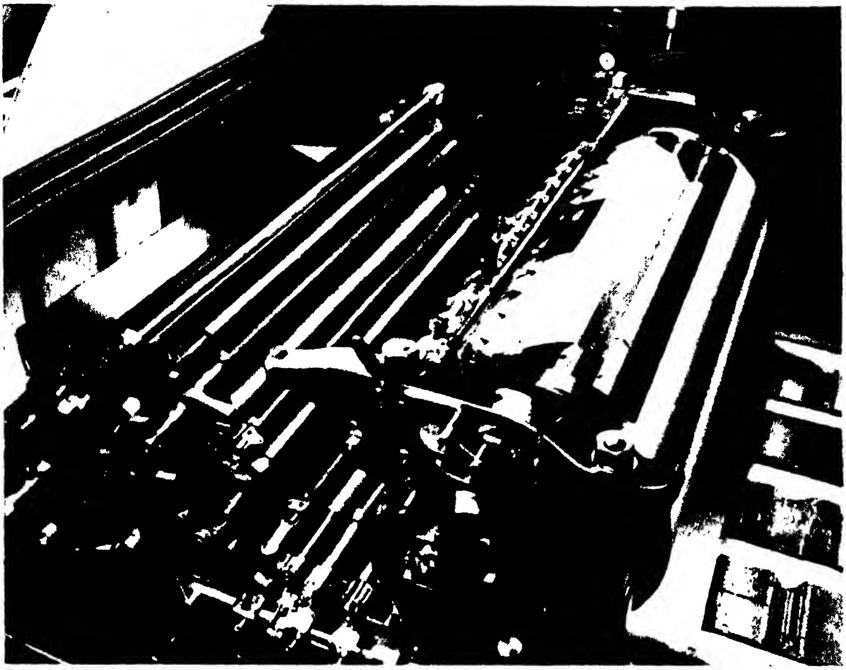
[42] A. Chwala, French P. 780,799, 1935; *Chem. Abs.*, 1935, **29**, 6081.

[43] F. J. Baumgardner, U. S. P. 1,234,264, July 24, 1917; *Chem. Abs.*, 1917, **11**, 2619.

[44] W. G. Dewsbury and A. Davies, U. S. P. 2,014,760, Sept. 17, 1935; *Chem. Abs.*, 1935, **29**, 7678.

[45] J. W. Leadbeater and W. A. Towler, *loc. cit.*

[46] M. Wolff, Dutch P. 1424, 1917; *Chem. Abs.*, 1917, **11**, 1758.



Courtesy Miller Printing Machinery Company

FIGURE 45. Top Side View of Miller Automatic Cylinder Press with Inker Half Rolled Back.

Modifying agents of vegetable origin have been used almost since the beginning of typographic printing. Rosin was commonly added to linseed oil in making printing varnish.[47] A composition made by Baskerville, which is described by Hansard,[48] includes boiled linseed oil admixed with a small quantity of black or amber rosin and lampblack. Savage also used rosin as a regular addition to printing inks. The same authority recommended natural balsams such as balsam of Capivi (copaiba) or Canada balsam as substitutes for linseed oil.[49] Rosin, as well as other natural and synthetic resins, is employed to increase tackiness of inks to a sufficient degree and to secure a hard ink film. These properties are especially required of inks to be used in printing on smooth-surfaced, hard and non-absorbent papers.[50]

As early as 1845, Clark suggested that rosin be mixed with either asphalt, pitch, turpentine, balsam, linseed oil, caoutchouc or bitumens,

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[47] See Noxon's description of the preparation of printers' varnish by Dutch inkmakers in the 17th century.

[48] T. C. Hansard, "Typographia," London, 1825. W. Savage, "On the Preparation of Printing Ink," London, Longman, Rees, Orme, Brown, Green and Longman, 1832.

[49] W. Savage, *loc. cit.*

[50] H. E. Rice, *Paint, Oil, Chem. Rev.*, 1935, 97 (13), 15; *Chem. Abs.*, 1935, 29, 5680; *Rev. Paint, Colour, Varnish*, 1935, 8, 306.

or with any combination of these materials.[51] Pigment was admixed with the vehicle, produced from the above-mentioned ingredients, in sufficient quantity to yield an ink possessing the requisite color. Such compositions indicate an early use of rosin as a binding agent and protective colloid in American inks.

A special composition containing treated linseed oil is employed for work with roller presses. "Aqueous matter" is said to be removed from the drying oil by heating vigorously a mixture of 40 gallons of linseed oil, 7 pounds of zinc sulphate, 7 pounds of litharge, 7 pounds of red lead, and 7 pounds of manganese dioxide.[52] The warm product is mixed with pigment and an equal quantity of Vaseline. When the product has cooled to 110° F., a jelly is formed by the addition of 1 per cent of fir balsam and 10 per cent of linseed oil. At room temperature benzine is admixed with the cold composition to give the desired consistency. This is an example of the use of so-called "prepared" linseed oil.

Soap is sometimes used in printing inks in order to produce clean, sharp impressions and to prevent clogging of the type. Its use was introduced early in the 19th century. Savage cites the first instance in which soap was incorporated in a printing ink. This composition was prepared by admixing a pint of boiled linseed oil (also burned for a short time) with 2 pounds of black rosin and 1 pound of hard soap.[53] Curd soap or metallic soaps, such as soaps of magnesium or aluminum, have been employed as swelling agents.[54] An ink, said to be relatively resistant to water but not to alkali, may be prepared by adding coloring matter to a fused mixture of a drying oil, wax, resin and soap.

Other modifying agents of vegetable origin are the distillation products of rosin, such as rosin oil,[55] or turpentine (also known as turpentine oil).[56] Also polymerized pinene or other polymerized terpenes of the empirical formula $C_{20}H_{32}$ are employed. These, when used with a stand oil from tung oil, are reported to yield an ink film free from offsetting.[57] Rowley used rosin oil thickened with cottonseed pitch and with lampblack as coloring matter.[58]

Residues separated in the recovery of glycerin from spent lyes, in soap making, are suggested by Quick as a base for printing ink.[59] These residues, if acid (from fatty acids) are neutralized by boiling with alkali. Following the latter operation, the resulting products may possess suffi-

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[51] E. Clark, U. S. P. 4102, July 5, 1845.

[52] W. G. Fuerth, U. S. P. 437,588, Sept. 30, 1890, to Redding Ink and Duplicator Co.

[53] Encyclopedia Britannica, Sixth Edition, article on "Ink." W. Savage, *loc. cit.*

[54] S. Sakairi and M. Uchiyama, Japanese P. 111,522, 1935, to Nisshin Seihun K. K.; *Chem. Abs.*, 1936, **30**, 2411.

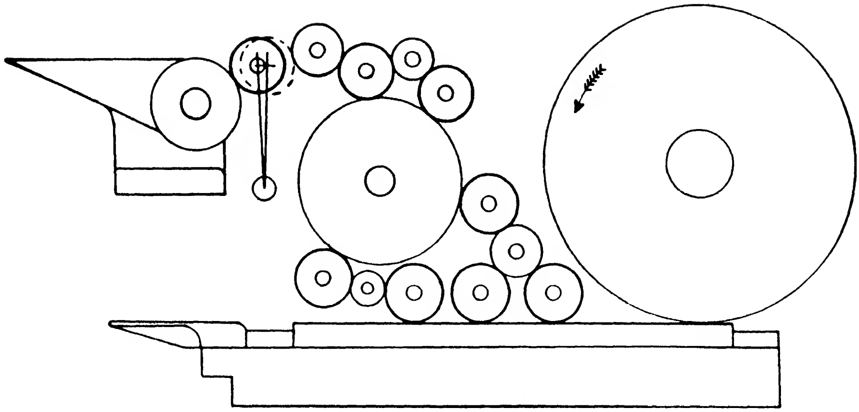
[55] J. W. Leadbeater and W. A. Towler, British P. 228,996, 1923; *Chem. Abs.*, 1925, **19**, 3027; H. E. Rice, *loc. cit.*

[56] S. Horii, Japanese P. 90,585, 1931; *Chem. Abs.*, 1931, **25**, 4724; *Rev. Paint, Colour, Varnish*, 1931, **4**, 250.

[57] E. Strasser, French P. 743,787, 1933, to N. V. Handel Maatschappij "Bayer"; *Chem. Abs.*, 1933, **27**, 4107; *Rev. Paint, Colour, Varnish*, 1933, **6**, 265; German P. 571,856, 1933; *Chem. Abs.*, 1933, **27**, 4428.

[58] J. Rowley, British P. 2854, 1864.

[59] A. S. Quick, British P. 547, 1914; *Chem. Abs.*, 1915, **9**, 1849.



Courtesy Miller Printing Machinery Company

FIGURE 46. Miller Inker Diagram.

cient body to serve as a base for printing ink, in which case they are ground together with carbon black. In the event that the neutralized residues are not sufficiently viscous, thickeners such as barium sulphate, calcium sulphate, kaolin, kieselguhr or chalk are added to produce the desired consistency, and the mixture then is ground with carbon black pigment. Incorporation of lithographic varnish with the material secured by the above treatment produces a printing ink. In one instance, it was suggested that Prussian Blue and barium sulphate (blanc fixe) be ground in glycerol. The dispersion then was blended with a mixture of glycerol and turkey red oil to furnish a printing ink.[60]

Alkaline mucilage, obtained in the refining of cottonseed oil, has been used, together with the acid tar, or sludge from mineral oil refining, to form vehicles for printing inks. Also, in conjunction with the acid tar, the residuum from sulphuric acid refining of linseed or rapeseed oil may be used. Enough of the acid ingredients are employed to neutralize the alkaline cottonseed oil mucilage.[61] Subsequent to neutralization, mineral acid is added in sufficient quantity to cause separation of fatty matter from the liquor. The latter is removed by decantation, and the fatty matter is dried by heating, and then is used as the basis of printing ink. Resins are admixed with the fatty matter and the mixture is boiled until a product is secured having sufficient body to be used in a printing composition. Ink is produced by grinding carbon black with this resinified mass.

It is reported that black printing ink may be prepared with tar from wood distillation as one of the ingredients.[62] An example of such an ink

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[60] R. W. Hochstetter, U. S. P. 928,915, July 20, 1909, to Ault & Wiborg Co.; *Chem. Abs.*, 1909, **3**, 2389.

[61] A. G. Wass, British P. 23,231, 1900, to British Oil and Cake Mills Ltd.; *J. S. C. I.*, 1901, **20**. 1005.

[62] G. Motegi and K. Asakura, Japanese P. 31,189, 1917; *Chem. Abs.*, 1918, **12**, 231.

is one made by heating tar (from wood distillation) in an iron vessel for 5 hours at 100 to 120° C. and afterwards transferring the product to a cooling vat where hemp oil and lampblack are added. The whole is mixed to a uniform consistency and then filtered under pressure.[63]

Synthetic resins which are found to be applicable in the preparation of drying-oil inks include oil-modified phenolics or those prepared from phenols, formaldehyde and drying oils;[64] those resulting from the interaction of substituted phenols (*e.g.*, phenylphenol) and formaldehyde;[65] and drying-oil-modified resins of the glycerol-phthalic anhydride type.[66] Some inks are said to contain approximately twice as much resin as drying oil.

Anti-skinning agents are substances which reduce the oxidation of the ink in the container to a minimum, without, at the same time, seriously slowing down the rate of drying of the material in the film form.[67] Some of these substances are catalysts, such as guaiacol, while others are solvents such as dipentene. Dipentene is considered by some inkmakers to be the best anti-skinning agent. However, methycyclohexanol and pyrocatechol are reported as being satisfactory for this purpose.

A suggested improvement for increasing the adhesive properties of ink is to employ a composition containing 4 pounds of litharge, 2 pounds of lead acetate, and 40 gallons of linseed oil.[68] This mixture is heated at 600° F. for 48 to 65 hours. Heating eliminates "greasiness" from the linseed oil. Four pounds of gum copal are added to each gallon of the heat-treated product, which then becomes "prepared linseed oil."[69] The latter is employed to make a news ink by mixing together 15 pounds of prepared linseed oil, 10 pounds of rosin (common), 2 pounds of brown rosin soap, and 5.5 pounds of lampblack.

A thinner for typographic ink may be composed of varnish, sweet oil and balsam. An illustrative example of such a product is said to contain 1⅓ quarts of varnish, 1⅓ quarts of copaiba balsam, 1 gill of Japan drier, and 1½ quarts of sweet oil.[70] Another composition may be composed of 1 gallon of kerosene, 1 pint of sulphuric ether, 2 ounces of oil of sassafras, and 2 ounces of oil of cloves.[71] The oil of sassafras and oil of cloves are employed to mask the odor of the kerosene which forms the bulk of the thinner.

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[63] Presumably a coarse filter is used.

[64] British P. 408,688, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 6001; *Brit. Chem. Abs.* B, 1934, 546.

[65] R. C. Shuey, U. S. P. 2,073,229, March 9, 1937, to Bakelite Corp.; *Chem. Abs.*, 1937, 31, 3311.

[66] Canadian P. 348,646, 1935, to Canadian Industries, Ltd.; *Rev. Paint, Colour, Varnish*, 1936, 9, 242; *Chem. Zentr.*, 1936, 107 (1), 5022. E. H. Callahan, Canadian P. 332,858, 1933; *Rev. Paint, Colour, Varnish*, 1933, 6, 265; *Chem. Abs.*, 1933, 27, 4428. E. Knebel, A. Hügel and H. Steinmeyer, German P. 591,456, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 2553.

[67] L. Light and T. H. Barry, *Official Printing Ink Maker*, 1934, 12 (3), 10.

[68] C. A. Thompson, U. S. P. 12,733, April 17, 1855. J. Rossman, *Am. Ink Maker*, 1930, 8 (8), 21; (9), 23; (10), 27; (12), 27; 1931, 9 (1), 25.

[69] "Prepared linseed oil" is one which has been heated with litharge and other chemicals.

[70] F. Fisher, U. S. P. 730,897, June 16, 1903.

[71] G. M. Stanchfield, U. S. P. 369,969, Sept. 13, 1887; J. Rossman, *loc. cit.*

DRIERS

Inks which do not dry entirely by absorption or by penetration into the surface or which harden too slowly by oxidation to allow a certain speed of printing are admixed with driers, *i.e.*, substances which catalyze the oxidation of drying oils. Compounds of the type possessing these properties are lead, cobalt and manganese soaps, usually linoleates and naphthenates,[72] lead borate and manganese borate.[73] In some instances, particularly when linseed oil is the liquid vehicle, lead stearate may serve as the siccative.[74, 75] However, "negative" catalyzers may also be employed, *e.g.*, phenols.[76]

Paste driers may be used in inks, in some instances, in order to prevent caking on the press. A lead paste drier may be incorporated in inks for cover printing. For very hard covers, cobalt drier is stated to be the more suitable.[77]

The amount of drier employed is important. It is reported [78] that the addition of more than 15 per cent of drier, whether it be cobalt linoleate, cobalt resinate, paste or other type, will not hasten the drying of ink.[79] Most drying-oil inks, it is stated, cannot be made to dry in less than an hour and a half, no matter how much siccative is added. The common linseed oil inks used for printing [80] require, on an average, 4 to 8 per cent of a good concentrated drier.[81]

PIGMENTS

The pigment content of typographic inks depends upon the special use of the ink.[82] For hard, non-absorbent surfaces such as bank or bond paper, a relatively high percentage of pigment should be employed. A still higher pigment content is required in compositions for printing carton covers. For newspapers and posters, inks possessing a relatively lower percentage of pigment will be satisfactory, since such kinds of papers absorb the ink very rapidly.[83]

For the preparation of a black ink, lampblack probably was the first pigment employed. However, this has been replaced to large extent, if

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[72] W. F. Harrison, *Ind. Eng. Chem.*, 1933, 25, 378; *Chem. Abs.*, 1933, **27**, 2316; *Rev. Paint, Colour, Varnish*, 1933, **6**, 135.

[73] A. Chwala, French P. 780,799, 1935; *Chem. Abs.*, 1935, **29**, 6081.

[74] A. S. Ramage, U. S. P. 1,004,078, Sept. 26, 1911, to Chemical Development Co ; *Chem. Abs.*, 1912, **6**, 302.

[75] A siccative is a drier.

[76] E. Strasser, French P. 743,787, 1933, to N. V. Handel Maatschappii "Baver"; *Chem. Abs.*, 1933, **27**, 4107; *Rev. Paint, Colour, Varnish*, 1933, **6**, 265. German P. 571,856, 1933; *Chem. Abs.*, 1933, **27**, 4428.

[77] E. F. Nurse, *Paper and Print*, 1937, **10**, 166; *Chem. Zentr.*, 1937, **108** (2), 2268; *Rev. Paint, Colour, Varnish*, 1937, **10**, 413.

[78] *Am. Ink Maker*, 1939, **17** (3), 29.

[79] Percentage based on weight of ink.

[80] H. G. Kriegel, "Encyclopedia of Printing Lithographic Inks and Accessories," New York, Superior Printing Ink Co., 1932.

[81] See Chapter 4.

[82] The properties of pigments used in printing inks are discussed in Chapter 6.

[83] E. F. Nurse, *Paper and Print*, 1937, **10**, 166; *Rev. Paint, Colour, Varnish*, 1937, **10**, 413; *Chem. Zentr.*, 1937, **108** (2), 2268.

Courtesy C. B. Cottrell & Sons Co., Claybourn Division

FIGURE 46A. Two-color High-speed Rotary Press, 35" × 47".

not entirely, by carbon or gas black, which may be obtained in various shades of black, depending upon the process used in its manufacture.[84] Incorporation of either pigment into the vehicle or ink composition may be accomplished by grinding,[85] and by the addition of wetting agents.

Preferential wetting of moist pigments by ink vehicles often furnishes the basis of a simple and relatively inexpensive grinding operation whereby the pigment is dispersed in the liquid medium.[86] After the pigment is precipitated in water and filtered, it is pressed into firm, hard cakes. The latter then are ground with a vehicle (*e.g.*, linseed oil) and during this operation become completely wetted by the oily liquid. Water, which is thus displaced, can be removed during the grinding process. Dispersion of the pigment is said to occur without the simultaneous formation of particle agglomerates. In some instances, how-

[84] For a discussion of the manufacture of carbon black, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," New York, Reinhold Publishing Corp., Vol. 1, 1934, and Vol. 2, 1937.

[85] See, for example, M. Wolff, Dutch P. 1424, 1917; *Chem. Abs.*, 1917, 11, 1758.

[86] W. F. Harrison, *Ind. Eng. Chem.*, 1933, 25, 378; *Chem. Abs.*, 1933, 27, 2316; *Rev. Paint, Colour, Varnish*, 1933, 6, 135. See also S. R. Hochstetter, U. S. P. 1,119,960, Dec. 8, 1914; *Chem. Abs.*, 1915, 9, 248; *J. S. C. I.*, 1915, 34, 92.

ever, the pigment may exhibit no preferential wetting by either liquid, *i.e.*, water or oil. In such cases addition of a small percentage of a wetting agent (*e.g.*, lead oleate) will establish preference for the oily vehicle.

In place of grinding, dispersion of the pigment (lampblack or carbon black) can be effected by agitation of the latter in the hot varnish immediately after the boiling or cooking operation is completed.[87] Another procedure involves passing steam into a mixture of oil (linseed, shale, or petroleum), resin (*e.g.*, rosin) and black in a closed vessel to which is attached a condenser.[88] When an apparently homogeneous product is formed, it then may be conducted through a suitable strainer or filter to remove undissolved non-dispersed particles. A modification of the prior method involves simultaneously heating and agitating the mixture of vehicle and pigment.[89] Burning of the liquid ingredient is prevented by placing in the bottom of the heated container an alloy having a low melting point. An example of such a metallic composition is one consisting of 1 part of lead and 2 parts of tin, which melts at 180° C. The melting point may be raised by increasing the proportion of lead, or it may be lowered by addition of mercury or bismuth. In some instances the alloy can be replaced by a saturated aqueous solution of calcium or magnesium chloride.

Jakosky [90] prepares a suspension of carbon in oil (*e.g.*, a hydrocarbon oil) by subjecting the latter to localized heating so that a portion of the liquid is raised to a temperature sufficient to cause decomposition into carbon black and gaseous reaction products. One manner in which such an operation may be conducted is illustrated in Figure 47. The oily mass passes from the supply chamber into a scrubber and from the latter into a preheater where the temperature of the liquid is raised to 200° F. The oil then is conducted into the reaction chamber in which it flows over a high-tension electric arc. The material in direct contact with the arc is decomposed into carbon and gaseous products (*e.g.*, hydrogen and methane). The latter escape from the system through the scrubber (in which any low-boiling substances are dissolved by the incoming oil) and through the pressure valve located above the scrubber. The heat-treated oil drains from the reaction chamber into a storage tank. Increased concentration of dispersed carbon black is said to be obtained by recirculating the oil one or more times from the storage tank to the supply chamber and back through the system.

During the eighteenth century it was customary to suppress the yellow of linseed oil or to give the black inks a deeper and more definite color by the addition of a small quantity of a blue coloring material or toner. For this purpose usually Prussian Blue (also known as Milori

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[87] H. Rahmer and K. Strich, French P. 767,555, 1934; *Chem. Abs.*, 1935, 29, 626. British P. 424,164, 1935; *Chem. Abs.*, 1935, 29, 5682; *Brit. Chem. Abs.* B, 1935, 367.

[88] D. J. Ogilvy, British P. 18,533, 1897; *J. S. C. I.*, 1897, 16, 1012.

[89] D. J. Ogilvy, British P. 14,886, 1900; *J. S. C. I.*, 1900, 19, 1011.

[90] J. J. Jakosky, U. S. P. 1,673,245, June 12, 1928; *Chem. Abs.*, 1928, 22, 2849; *Rev. Paint, Colour, Varnish*, 1929, 1, 173.

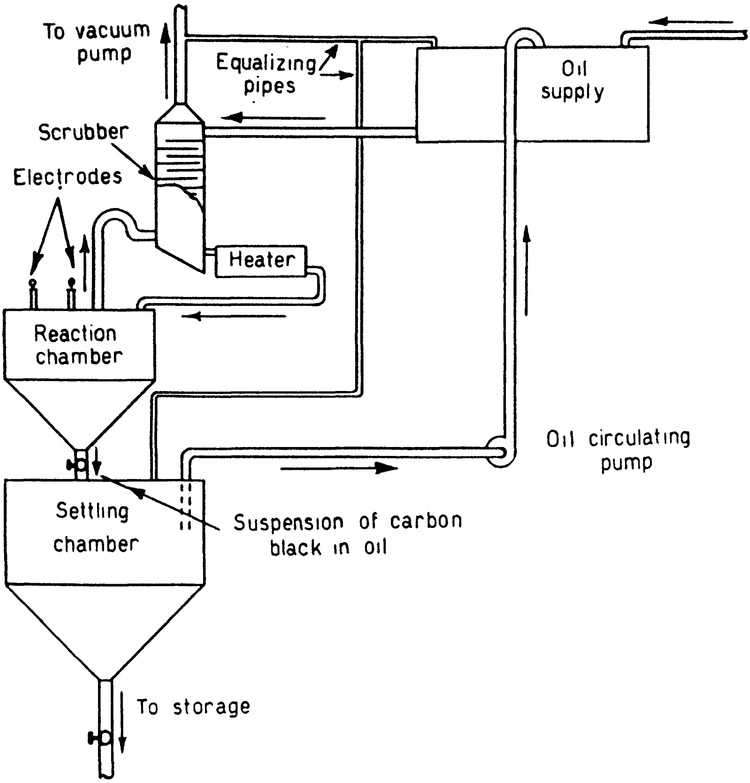

FIGURE 47. Diagrammatic Side Elevation of Apparatus for Producing Printing Inks from Hydrocarbon Oils (J. J. Jakosky).

Blue or Iron Blue), or sometimes even indigo was employed.[91] Bird[92] recommended a certain siliceous earth which was ground with boiled linseed oil. Other toners which are useful include unlaked[93] blue or violet dyes.[94] Inks which are to be overprinted with a cellulose varnish[95] should not contain spirit-soluble toners because of danger of "bleeding." So-called double-toners inks contain, in addition to the pigment, a small proportion of a dye dissolved in the vehicle. When such inks are printed from half-tone screens, the dye tends to spread around the dots thus produced and so develops an additional tone. The vehicle in this case must be relatively slow-drying, since the tone of the dye can develop only during drying of the ink.[96]

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[91] F. L. Burt, *The Inland Printer*, 1919, 64 (2), 190.

[92] J. Bird, British P. 6905, 1835. The mineral earth used was stated to have the following composition: 46 per cent silica, 42 per cent alumina and 12 per cent "coaly" matter.

[93] An unlaked dye is one in the preparation of which no substrate or base is employed.

[94] See Chapter 6.

[95] See Chapter 14 for overprint varnishes.

[96] E. F. Nurse, *Paper and Print*, 1937, 10, 166; *Rev. Paint, Colour, Varnish*, 1937, 10, 413; *Chem. Zentr.*, 1937, 108 (2), 2268.

In the preparation of black printing inks, which are said to be removable from paper by treatment with hydrogen chloride, manganese dioxide may be substituted for lampblack or carbon black.[97] An example of such a composition is one comprising 40 parts of the dioxide ground with 60 parts of linseed oil varnish. To suppress the brownish shade of the manganese pigment, a small proportion of nigrosine is incorporated. Casein or burned magnesia in aqueous solution, olein, soft soap, glycerin, or resinous soaps may be employed as modifying agents for the product[98] just described.

Stephan[99] recommends a composition containing 74.5 parts of varnish, 25 parts of a pigment and 0.5 part of an oil-soluble blue dye. He further points out that the manganese dioxide should possess a bulk density not greater than 0.9 and a moisture content not in excess of 1.5 per cent.[100] Such a composition is made by adding sodium carbonate to an aqueous solution of a manganese salt, subjecting the precipitate to the action of chlorine, and then drying the material until the requisite water content is attained. To deepen the color of the pigment, the latter is impregnated with iron tannate before incorporation into the ink composition.[101]

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[97] German P. 21 408, 1882, to Schmidt Bros.; *J. S. C. I.*, 1883, 2, 243.

[98] W. Reissig, U. S. P. 265,867, Oct. 10, 1882, to Gebruder Schmidt.

[99] K. Stephan, Canadian P. 276,638, 1927, to Chem. Fabr. auf Actien vorm. E. Schering; *Chem. Abs.*, 1928, 22, 2071.

[100] K. Stephan, U. S. P. 1,689,368, Oct. 30, 1928, to Chem. Fabr. auf Actien vorm. E. Schering; *Chem. Abs.*, 1929, **23**, 293; *Brit. Chem. Abs.* **B**, 1928, 937. British P. 270,671, 1927; *Brit. Chem. Abs.* **B**, 1928, 24.

[101] British P. 239,113 1925, to Chem. Fabr. auf Actien vorm. E. Schering; *J. S. C. I.*. 1925, **44**, 891B.

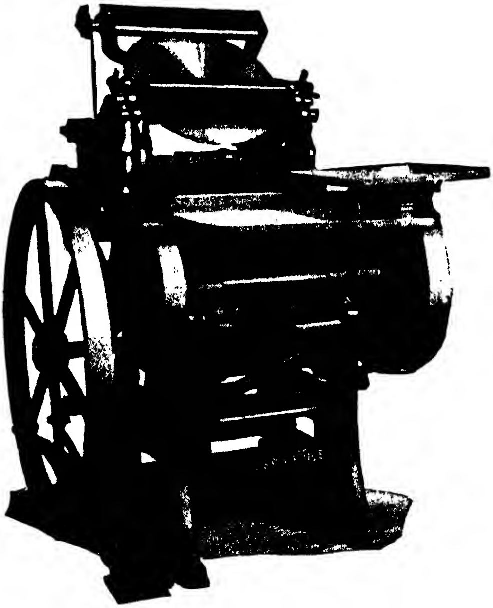

FIGURE 48.

The Chandler & Price New Series Press, 12 × 18.

Courtesy The Chandler & Price Company

Diffusion, instead of grinding, is suggested as a means for attaining minute size reduction, especially if water-soluble organic pigments are to be employed.[102] A paste is prepared containing 3 ounces of carmine, 1 fluidrachm (1 teaspoon) of aqua ammonia and 8 fluidrachms (8 teaspoons) of water. The material is permitted to diffuse for 24 hours (with agitation every 5 hours). Following this operation, about one-half the quantity of ammonia solution and water are admixed with the product. The carmine is now in solution and is dispersed by stirring into a sufficient quantity of varnish to bring the total weight up to one pound.

COLOR PRINTING

The question of transparency and opacity arises in printing involving the use of two or more colors. This is especially to be considered in printing on colored papers, since transparent colors give the resulting color of the ink and paper. In two-color printing the first ink should have as high a pigment content as possible to furnish a desired shade even with a very thin ink film. The first ink also should be sufficiently tacky to insure adherence of the second film of ink. The second ink is usually of softer body and less tacky in order to retain its full color strength when printed upon the first color. The latter usually should be the lighter one.

In three- or four-color printing, the adaptability of inks depends upon tack, transparency and opacity. Difficulty in overprinting a subsequent ink arises, when the foregoing ink dries to a crystallized surface. This may be remedied by incorporating a small percentage of wax into the ink. Colored inks in general should not contain rosin or rosin oils, since these tend to react with certain pigments and destroy their effect.[103]

In "cold color" printing [104] a non-volatile liquid vehicle is used which requires that heat be applied to convert it into a hard state. The vehicle may contain a heat-convertible varnish resin. An example of such a mixture is prepared as follows: 2181 parts (by weight) of raw tung oil are heated at a temperature of 450° F. for 15 minutes. After this operation, 1177 parts of heat-convertible phenol-aldehyde varnish resin, 1002 parts of rosin-glycerol ester, and 105 parts of rosin are stirred into the hot oil. The stirring procedure is continued until the resins are melted, when the mixture is heated at 320° F. for 15 minutes. The mixture is removed from the source of heat, and 755 parts of cooked tung oil, 173 parts of acid-refined linseed oil, and 932 parts of chlorinated diphenyl [105] are added with stirring. When the product is cool, 175 parts of lead naphthenate drier solution (containing 16 per cent lead by weight) and

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[102] C. J. Briedbach and C. Briedbach, U. S. P. 168,134, Mar. 23, 1875.

[103] H. E. Rice, *Paint, Oil and Chem. Review*, 1935, 97 (13), 15; *Chem. Abs.*, 1935, 29, 5680; *Rev. Paint, Colour, Varnish*, 1935, 8, 306.

[104] F. G. Oswald, U. S. P. 2,111,802, Mar. 22, 1938; *Chem. Abs.*, 1938, 32, 3902.

[105] Chlorinated diphenyls boiling between 278 and 360° C. may be employed. Meta and para chlorodiphenyls and 4,4′-dichlorodiphenyl are included in the above boiling range.

2 parts of cobalt naphthenate drier solution (containing 4 per cent cobalt by weight) are added.

Colored inks may be produced by heating together several separately prepared mixtures.[106] The first consists of pigment and alizarine oil;[107] the second contains alizarine oil and an alkali salt or alkaline earth salt; the third is composed of animal fat or oil and naphthalene. After heating the three mixtures together, resins and a small amount of glucose are admixed and the whole is boiled. On cooling, the mixture solidifies, and alcohol is added to give the desired consistency. Such an ink is made as follows. Three mixtures are prepared consisting of:

(1) 100 gms. of basic aluminum acetate and 200 gms. of alizarine (turkey red) oil.
(2) 10 gms. of Biebrich scarlet and 100 gms. of alizarine (turkey red) oil.
(3) 20 gms. of naphthalene and 20 gms. of fish (train) oil.

These are heated together, and a mixture of 50 gms. of Canada balsam, 250 gms. of Venice turpentine (from European larch), 100 gms. of copal resin (from Trachylobium trees), 50 gms. of pine resin, 25 gms. of elemi resin (Buseraceae), and 50 gms. of shellac, is added. During addition of the latter mixture stirring and heating must be maintained, and after addition the whole is boiled to a consistency which will result in solidification upon cooling.

To the above coloring mixture a highly viscous composition is added consisting of 125 gms. of fish (train) oil, 650 gms. of copal resins and 225 gms. of ethyl alcohol (95-per cent), and the resulting product is boiled. If, on cooling, the ink is too thick, toluene may be added to give the desired consistency.

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[106] N. W. Turkin, British P. 23,128, 1913; *Chem. Abs.*, 1915, 9, 973.

[107] Alizarine oil is the neutralized product obtained by treating olive oil, castor oil, cottonseed oils or other glycerides of fatty acids with sulphuric acid.

Chapter 8

Typographic Inks—Mineral-oil and Quick-drying

From the time of the earliest presses, linseed oil has been one of the principal vehicles and binders of ink pigments. Although this oil may vary somewhat in its exact composition, it does contain glycerides of unsaturated fatty acids such as linolenic. These esters slowly absorb oxygen from the air whereby the oil is converted into a tough, elastic film of linoxyn.[1] However, there are definite time limits to the drying of printing inks as a result of oxidation of the vehicle on exposure to air. It has been estimated that a film of oil 0.00012 inch thick, which is the thickest film of ink generally printed on coated papers, requires 50 hours to dry (by exposure to air) when spread upon a hard, non-absorbing surface.[2] Unless care is taken, inks containing drying oils smudge and offset before they are dry. With the steady increase in the use of high-speed printing presses it has become more and more important to effect rapid drying of fresh prints and to produce compositions of the quick-drying type.

Printing inks may dry by absorption, oxidation, polymerization, evaporation of the vehicle, or by the precipitation of certain constituents. If the paper stock is absorbent, the liquid as well as some of the solid ingredients (for example, pigment) may sink into the fibers. Drying by oxidation or polymerization, *e.g.*, exposure of the ink film to air or ozone, usually involves a chemical change in the vehicle. When the latter is substituted in whole or in part by a volatile solvent, quick setting may be effected by evaporation of the more readily vaporizable fluids. In some instances the printed films may be treated by certain agents such as water or alcohol, whereby the binder and pigment are precipitated and a hardened print obtained. Variations and combinations of these methods have been utilized to bring about quick drying of printing inks.

QUICK DRYING BY ABSORPTION

Perhaps the most common application of the principle of drying by absorption is newspaper printing. The paper used for this work, *i.e.*, the so-called "newsprint," has a non-coated, rough surface which allows ink to penetrate into the fibrous material. To facilitate this process, news

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[1] See Chapter 3 for a discussion of drying oils.

[2] C. MacArthur, *Paper Trade J.*, 1937, 105 (15), 37; *Chem. Abs.*, 1937, 31, 8956; *Rev. Paint, Colour, Varnish*, 1937, 10, 413. *Paper Trade J., T. A. P. P. I. Sect.*, 219; *Brit. Chem. Abs.* **B**, 1938, 83; *Rev. Paint, Colour, Varnish*, 1938, 11, 109.

inks are generally quite fluid, though their consistency and composition vary to accommodate the differences in presses and in press speeds. Thus, inks for high-speed presses are very fluid and consist, for the most part, of mixtures of mineral oils and carbon black with a small amount of an oil-soluble toner dye such as induline base.[3] For slower-moving presses the vehicle may comprise resins dissolved in mineral oil and also various proportions of rosin oil, gilsonite, pitch or linseed oil varnish.[4] Although it is probably true that after the ink has entered the paper alterations such as hardening occur by exposure to air, nevertheless the action which makes possible the high-speed delivery of sheets or web is the ready absorption of the fluid ink by the stock.

Newspaper printing, however, is not without its troubles. Most common are the complaints designated by terms "strike through," "show through," "offset," and "flying ink."[5] Since news inks contain mineral oil and are printed on rather thin, rough paper, it is always possible that the oil will penetrate the stock and show as an oily stain or "strike through" on the back of the sheet. This bad feature has been found to depend upon the following factors: color of oil used, consistency of ink, size and dispersion of pigment, character of paper, temperature of ink and paper at impression,[6] length of time and degree of impression, the presence of rosin or rosin oils, and the use of toners. The azo humic acids commonly present in dark asphaltic base oils are very detrimental. Thus, when treated with 2-per cent sulphuric acid to precipitate the pitchy material, followed by filtration through fuller's earth, mineral oils were decolorized and freed of the staining constituent. Although no accurate determinations were made, penetration seemed to vary inversely with the amount of pigment. Inks made with carbon black showed more strike through than those containing lampblack. The fact that the average particle size of lampblack is greater than that of carbon black indicated that finer ground particles permitted deeper absorption than coarse ones. Tests on newsprint showed that reduction of the sulphite pulp content and increase in the proportion of ground wood improved the printability of the paper.[7] When cheap rosin or rosin oil were used, strike through increased. This result was attributed to impurities in the products.

To overcome the brownish tone of the oil and carbon black, several per cent of oil-soluble toner is generally added to the news ink vehicle before incorporation of carbon black. Such toners are made by dissolving about 10 per cent of an oil-soluble dye base, such as Victoria Blue

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[3] See, for example, F. de Braudel and A. de Baudry D'Asson, British P. 8,923, 1901; *J. S. C. I.*, 1902, 21, 782

[4] A. Marzio, British P. 482,489, 1938. *Brit. Chem. Abs.* **B**, 1938, 1454.

[5] B. L. Wehmhoff, *Am. Ink Maker*, 1931, 9 (6), 19; *Chem. Abs.*, 1931, 25, 5581. *Paper Trade J.*, 1932, 94 (13), 39; *Brit. Chem. Abs.* **B**, 1932, 837. B. L. Wehmhoff D. P. Clark and D. H. Boyce, "Newsprint and News Ink," *U. S. Govt. Print. Office Tech. Bull.* No. 18, 1933.

[6] B. Berckmans, *Am. Ink Maker*, 1935, 13 (4), 17; *Chem. Abs.*, 1936, 30, 3665; *Brit. Chem. Abs.* **B**, 1936, 684.

[7] H. Andrews, *Paper Trade J.*, 1929, 89 (22), 63; *Pulp. Paper Mag. Can.*, 1929, 28, 971, 992; *Chem. Abs.*, 1930, 24, 1506.

base, Methylene Blue base, Methyl Violet base, or nigrosene or indulene base, in either oleic or linoleic acid with the aid of heat.[8] The practice of grinding undissolved dye base into the oil simultaneously with the pigment is undesirable as the dye bases are practically insoluble in the oils which make up newspaper inks. Incorporation of toners causes the viscosity of inks to vary irregularly.

Often the oil stain accompanying "strike through" renders the paper more or less transparent so that the pigmented portion of the ink may be seen from the back of the sheet. This is termed "show through" and is primarily a problem of thickness, composition, and surfacing of the paper employed.

"Offsetting" implies that part of the printed image is transferred to another surface which has come into contact with the ink. In newspaper printing this occurs when the ink penetrates at an excessively high rate. The oil soaks into the paper so readily that the pigment is left on the surface without sufficient binding agent. This problem is controlled by the consistency of the ink.

Another result of printing at high speeds with an ink which is too thin is that the ink will "fly." A fine mist or spray of ink is thrown off by the rapidly moving rollers, thereby coating everything in the vicinity of the press with a sticky layer of ink. Flying may be attributed to incorrect ink composition, hard or imperfect rollers, old or uneven blankets or to improper roller settings.

Newsprint is apt to be somewhat discolored and as inks containing colored pigments have their true effect only on perfectly white paper, colored inks are not considered very satisfactory for newspaper work.[9]

Red and red-brown colors combine most successfully with black. The difficulties and cost of multicolor printing result from the necessity of having separate ink ducts and rollers for each shade and from the fact that the photogravure and typographic portions must be printed successively.

News ink making is a difficult problem. Different kinds of paper and the many variables in press room conditions prevent the use of a few set formulas.[10] With high-speed production, paper in the same shipment from one mill may vary in properties. If the fibrous surface becomes too uneven, too porous or too hard and non-absorbent, the prints will be affected. Oftentimes unsatisfactory prints are the results of poor press conditions. Thus, rough or shallow mats, uneven plates, poor rolling surfaces and uneven roller settings, all hamper good printing. From these facts it may be seen that the production of good prints depends upon the skill of the pressmen as well as on the quality of the product of the ink maker.

It has been the desire of many ink makers to find a cheap substitute

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[8] See Chapter 6 for a discussion of pigments, toners and dyes.

[9] See, *Paint Manuf.*, 1933, 3 (9), 255; *Rev. Paint, Colour, Varnish*, 1933, 6, 265.

[10] B. Berckmans, *Am. Ink Maker*, 1935, 13, (4), 17; *Rev. Paint, Colour, Varnish*, 1935, 8, 207.

for the expensive oil varnishes usually employed in making printing inks. Among the materials found applicable to this purpose have been a number of bituminous substances or "bitumens." Unfortunately the definition of these terms and the scope of products to which they refer have not been precise and inclusive. An early terminology, applied principally to naturally occurring products, designated the solid bitumens as "asphalts"; a semi-fluid bitumen was "maltha," and the fluid, mineral oil was "petroleum." In the coarse of time, distillates and residues from pyrogenous treatment of coal and petroleum have been added to the list of bitumens. Destructive distillation of coal and allied substances as well as the distillation, fractionation and cracking of petroleum have yielded tars, asphalts and pitches which are similar in properties to the natural materials. Although it is not always possible to differentiate between the products of these two groups, with the increased knowledge of chemical and physical properties, it has become possible to classify them to a considerable extent. In order to relieve ambiguity in the following discussion, the definitions and classification of Abraham have been kept in mind.[11]

Natural Asphalts. Among the early ink compositions made from naturally occurring bituminous substances was one comprising 40 parts asphalt, 48 parts turpentine, 8 parts methyl violet dye base and 24 parts of the residue remaining from the distillation of rosin oil.[12] A semi-fluid product, "maltha," was used for news, book, and lithographic inks.[13] The inks for these respective uses increase in thickness. In complying with these requirements maltha was altered by removing the more volatile constituents by heat, by adding less fluid bitumens, or by the addition of powdered magnesia or resins. Thus, for news inks the maltha used had a specific gravity of 30 to 36° Bé. and 20 per cent pigment was included; for book inks, maltha of 22 to 28° Bé. with 25 per cent pigment; and for lithographic inks, maltha of 15 to 20° Bé. with 25 per cent pigment. These inks are said to be homogeneous, tough but elastic, and indelible.

A grade of asphalt known as "Assyrian Asphaltum" has been employed in printing inks.[14] In this case the vehicle was made up of 53 per cent asphaltum and 47 per cent mineral oil.[15] Coloring matter, such as an aniline dye or a pigment base ground in mineral oil, was added to the vehicle without application of heat.

Gilsonite is a natural asphaltite which is a brittle solid having a higher fusion point than any of the previously mentioned asphalts. A printing ink has been formed from 70 parts gilsonite, 120 parts fuel oil

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[11] H. Abraham, "Asphalts and Allied Substances," 4th Ed., New York, D. Van Nostrand Co., Inc., 1938. For the compositions of several asphalts used in printing inks, see H. Hadert, *Allge. Oel u. Fett.-Ztg.*, 1933, 30 (11), 561; *Rev. Paint, Colour, Varnish*, 1934, 7, 48.

[12] H. Günther, German P. 9,566, 1879; *Chem. Zentr.*, 1880, 11, 512.

[13] I. Pottawain, British P. 15,839, 1889; *J. S. C. I.*, 1890, 9, 630.

[14] F. J. Baumgardner, U. S. P. 1,259.713, March 19, 1918, one-fourth each to F. L. Phipps and C. G. Gibson; *Chem. Abs.*, 1918, 12, 1517.

[15] C. Krejci, U. S. P. 94,220, Aug. 31, 1869. E. Watson, U. S. P. 458,741, Sept. 1, 1891.

and 12 parts paraffin oil.[16] Inks utilizing the above compositions are said to be non-evaporating and non-skin forming.

Grahamite is a natural asphalt secured from West Virginia. The oil and resinous constituents secured from this substance have been advocated for printing inks.[16a]

Pyrogenous Asphalts. Of the various pyrogenous products, the heavy tar oil residue of the production of anthracene was used at an early date.[17] This oil was boiled with 10 per cent of copper chloride (dissolved in a minimum of water) which imparted a blackish-brown shade to the tar and lessened the quantity of dye base required in the ink. To anthracene oil have been added asphalt, non-drying Greenland train oil (oil from a marine animal, *e.g.*, whale oil), a soap from train oil, and an aniline dye base.[18] To eliminate the disagreeable smell of anthracene oil, it was treated with chlorine at a temperature greater than 212° F. or with an oxidizing agent such as hot nitric or sulphuric acid. Anthracene oil also has been used to extract tar oils from coal, wood, straw or peat.[19] These oils or the resinous residue from the distillation thereof may be used in black printing inks, *e.g.*, 58 parts of coal-extract resin oil, 12 parts lampblack and 30 parts straw extract oil.[20] Such inks were found applicable in quick-running newspaper printing, and are said to dry quickly to a film which adheres to the paper and does not rub off or smudge. Liquid tar, or the heavy oil products from coke ovens, gas producers and water gas plants, has been found to be an excellent vehicle and agglutinant for powdered shale or anthracite coal.[21] When one of the latter substances and a toner or drier were added to such a tar (containing about 40 per cent hard pitch and having a specific gravity of 1.15) a good printing ink was reported formed. Also, the liquid distillation products from ignited mineral or vegetable oils have been advocated as constituents of printing inks.[22] The distillate is admixed with burned corn meal and a small proportion of linseed oil, and the whole heated to furnish an ink.

In inks for lithographic printing, "low-temperature tars" (from the low-temperature distillation of bituminous coals) have been found effective.[23] The nature of the tar varies with the method of distillation and the coal used. Thus, tar from cannel coal possesses a considerable proportion of paraffin waxes and neutral oils with a low percentage of resinous and phenolic bodies. On the other hand, tars from strong coking

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[16] H. A. Barmier, U. S. P. 1,383,512, July 5, 1921; *Chem. Abs.*, 1921, 15, 3758

[16a] H. Wurtz, U. S. P. 67,697, Aug. 13, 1867. U. S. P. 74,188, Feb. 4, 1868.

[17] E. Battley, U. S. P. 54,461, May 1, 1866, to J. Crane. H. Günther, German P. 11,930, 1880; *Chem. Zentr.*, 1882, 13, 591.

[18] H. Günther, British P. 2,868; *J. S. C. I.*, 1882, 1, 182.

[19] British P. 131,588, 1919, to Rutgerswerke A.-G.; *Chem. Abs.*, 1920, 14, 340 British P. 160,467, 1921; *J. S. C. I.*, 1922, 41, 851A. Also German P. 320,056, 1918; *J. S. C. I.*, 1920, 39, 622A.

[20] H. Teichmann, British P. 116,117, 1921, to Rutgerswerke A.-G.; *J. S. C. I.*, 1922, 41, 559A; *Chem. Abs.*, 1922, 16, 351.

[21] R. C. Child, British P. 7,722, 1910; *Chem. Abs.*, 1911, 5, 3632; *J. S. C. I.*, 1911, 30, 1023.

[22] J. C. White, U. S. P. 126,601, May 7, 1872.

[23] R. MacLaurin and I. M. MacLaurin, British P. 312,745, 1928; *Chem. Abs.*, 1930, 24, 979; *Brit. Chem. Abs.* B, 1929, 610; *Rev. Paint, Colour, Varnish*, 1929, 2, 212; German P. 532,249, 1929; *Chem. Abs.*, 1932, 26, 323.

coals are made up largely of phenolic and resinous products with only a small quantity of paraffinoids and neutral oils. These constituents may be separated, but the resinous bodies alone are too sticky for an ink base so that usually the mixture as such is employed. An example of an ink composition consists of: 77 parts tar oil, 1 part caustic soda, 12 parts carbon black and 10 parts linseed oil. The addition of iron hydroxide (or hydrated ferric oxide) tends to blacken the tar and to reduce the quantity of pigment required.

Several types of pyrogenous asphalts resulting from treating petroleum have been employed in printing inks.[24] Rogers [25] used the residuum from an asphalt base petroleum for a "news ink." This substance is heated directly or blown with steam or air until no noticeable odor remains and the product has a density of about 14.5° Bé. In making the ink, 39 parts of thickened residuum is mixed with about 47 parts of a thin petroleum oil such as "300 oil" (an oil fraction of about 27° Bé. and a viscosity of 170), 4 parts rosin, 0.25 part chip soap, and about 10 parts lampblack. The function of the "300 oil" is to act as a thinner and to sink into the fibers of the paper leaving the pigment, rosin, and residuum on the surface. As a result of this type of "drying," newspapers may be printed at high speeds. Metal driers also may be incorporated to accelerate drying. An example of such an ink composition is: 23 parts air-blown asphalt, 17 parts carbon black, 52 parts of a binder (consisting of 41 parts petroleum oil and 11 parts liquid asphaltum), and 8 parts drier such as linoleate of lead.[26]

In some instances, petroleum residues are refined for use in inks.[27] Thus a residue from distillation of petroleum was admixed with 25 per cent by weight of sulphuric acid that previously had been employed in deodorizing petroleum distillates. The mixture was agitated until it became thick and black. The whole then was washed with water to remove sulphuric acid. Calcium chloride was added to the washed oil to neutralize the last traces of acid and to destroy any odor present. The refined product was applicable as a vehicle for printing inks.

A steam-distilled asphalt residue has been differentiated from an air-blown asphalt by the fact that it has a lower melting point.[28] The former also requires less solvent to make a suitable ink vehicle. The incorporation of a volatile petroleum distillate such as "mineral turpentine" (a distillate boiling from 120 to 200° C.) is advocated because it gives drying properties by evaporation rather than by oxidation or by metal driers and because, being composed of petroleum hydrocarbons, it is miscible with asphalt. A newspaper ink was made of the following composition: 48 parts steam-distilled pitch, 37 parts volatile mineral oil, and 15 parts

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[24] O. G. Holt, U. S. P. 424,556, April 1, 1890.

[25] A. Rogers, U. S. P. 1,224,668, May 1, 1917; *Chem. Abs.*, 1917, **11**, 2050; *J. S. C. I.*, 1917, **36**, 724.

[26] J. H. Caughlan, U. S. P. 1,586,947, June 1, 1926; *Chem. Abs.*, 1926, **20**, 2420. Canadian P. 244,684, 1924; *Chem. Abs.*, 1925, **19**, 739. British P. 236,329, 1924; *Chem. Abs.*, 1926, **20**, 997.

[27] G. Duryee, U. S. P. 48,385, June 27, 1865.

[28] J. Azzopardi, British P. 293,238, 1927; *Brit. Chem. Abs.* B, 1928, 681; *Chem. Abs.*, 1929, **23**, 1517.

lampblack. The consistency of this composition was reported to allow rapid drying by penetration and yet to be adherent to the paper.

For jobbing or letter press work, a little thicker ink was prescribed: 42 parts mineral pitch, 39 parts volatile distillate, 1 part turpentine, 1 part rosin, 1 part manganese resinate (solid drier used in paints), and 16 parts lampblack. The extracted products secured by treatment of mineral oils or lubricating oils with sulphurous acid or sulphur dioxide have been suggested for printing compositions.[29] These substances, when mixed with oils, resin, or asphalt produce easily drying inks for book and newspaper work.

Resins and Bitumens. Another method of making substitutes for linseed oil varnishes consists of mixing resins with bituminous substances or alcohols.[30] Many resins are applicable to this purpose,[31] but rosin or colophony has been in most common use.[32] When rosin and paraffin oil are added to coal tar the odorous fumes may be eliminated by treatment with chloride of lime and hydrochloric acid.[33] Glycerol and lampblack are incorporated in the resulting product to form an ink composition. Soap may be admixed in the ink as modifier.[34] Alkaline salts of sodium or potassium also have been suggested;[35] as pigment, pulverized bituminous coal may be substituted for lampblack.[36] By varying the proportions of rosin and mineral oil, compositions of any desired viscosity can be produced.[37] In some instances crude petroleum oil may be used as ink vehicle.[38] The crude oil is heated at 350° F. for three hours with approximately 1 per cent by weight of lime. Subsequently the oil is separated from solid material, and admixed with gum dammar, rosin, and lampblack. For letter press or for lithographic printing a mixture comprising 20 parts rosin, 18 parts petroleum oil (specific gravity 0.880 to 0.920) and 15 parts lampblack is advocated. In another case,[39] a vehicle has been made of 40 to 45 parts of rosin in 25 parts of paraffin oil. The oil contained in cotton waste used for wiping lubricated engine parts has been advocated as ink vehicle.[40] The waste was extracted with carbon disulphide and the latter subsequently removed from extracted

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[29] H. Spath and H. Rebs, Swiss P. 75,552, 1917; *Chem. Abs.*, 1918, 12, 231. Danish P. 22,873; *Chem. Abs.*, 1918, 12, 1601. S. H. Turner, U. S. P. 10,006, Sept. 6, 1853. M. Tully, U. S. P. 113,947, April 18, 1871. H. W. Doughty, U. S. P. 1,439,695 and 1,439,696, Dec. 26, 1922; *Chem. Abs.*, 1923, 17, 1157; Canadian P. 233,933, 1923; *Chem. Abs.*, 1923, 17, 3615.

[30] See, for example, *Muster-Ztg.*, 1873, 22, 34; *Chem. Zentr.*, 1873, 4, 159.

[31] M. Weissberger, U. S. P. 67,697, Aug. 13, 1867; E. G. Acheson, U. S. P. 1,201,991, Oct. 17, 1916; *Chem. Abs.*, 1916, 10, 3169. W. J. McElroy and J. Clarke, U. S. P. 1,450,692, April 3, 1923; *Chem. Abs.*, 1923, 17, 1896. U. S. P. 1,471,746, Oct. 23, 1924; *Chem. Abs.*, 1924, 18, 175.

[32] For synthetic resins used in printing inks see Carleton Ellis, "The Chemistry of Synthetic Resins," New York, Reinhold Publishing Corp., 1935.

[33] M. M. Mathews, U. S. P. 7,686, Oct. 1, 1850. J. H. Wilhelm and F. Bohnstadt, German P. 12,282, 1879; *Chem. Zentr.*, 1881, 12, 512.

[34] S. Steinert, U. S. P. 39,968, Sept. 19, 1862.

[35] J. Ogilvy, U. S. P. 330,613, Nov. 17, 1885.

[36] J. Sangster, A. W. Sangster and W. H. Sangster, U. S. P. 53,379, Mar. 20, 1866, to H. Sangster and T. J. Conroy.

[37] A. G. Wass, British P. 6,061, 1901; *J. S. C. I.*, 1902, 21, 1032. French P. 322,298, 1902; *J. S. C. I.*, 1903, 22, 307. U. S. P. 716,318, Dec. 16, 1902.

[38] M. Connelly, U. S. P. 235,670, July 23, 1880.

[39] H. Brackebusch, German P. 16,227, 1881; *J. S. C. I.*, 1882, 1, 63. German P. 16,237, 1881; *J. S. C. I.*, 1882, 1, 21.

[40] C. T. Bastand, U. S. P. 247,597, July 5, 1881.

oil by distillation. In this manner a product containing lubricating oil, lamp oil and lampblack was said to have been secured.

Albertol resins (modified phenol-formaldehyde type) have been found to be good foundations for black inks.[41] The resin is mixed, at 180 to 200° C., with a mineral oil (specific gravity 0.93 and having a viscosity of 14° E. at 50° C.), and a resin oil (specific gravity 1.02 and viscosity 2-3° E. at 100° C.). By modifying the proportion of these components, inks may be made for job work, illustrative or newspaper purposes. Rosin oil may be employed without addition of rosin modifiers.[42] It was suggested that the gaseous products from distillation of rosin be burned. The resulting carbonaceous material was collected in rosin oil to furnish an ink.

The residual petroleum oil which is commonly known as "fuel oil" likewise has been incorporated into printing inks.[43] For this purpose fractions exhibiting a density of 17° Bé., a flash point of about 150° F. and containing about 30 per cent asphaltum, have been specified. An ink composition illustrative of this proposal consists of the following: 65 per cent of a vehicle base (86 to 95 parts fuel oil, 1 to 10 parts rosin, 0.5 part copper nitrate, 1 part calcium chloride, 1 part sodium hydroxide, 1 part sodium silicate), 4 per cent lead lineolate, 6 per cent Japan drier, and 25 per cent pigment. When the ingredients of the vehicle are heated together, the copper compound reacts with sulphur compounds in the oil, forming a sludge and thereby decolorizing and desulphurizing the product. Resins prepared from petroleum distillates have been advocated for utilization in black inks.[44] For example, a polymer of isobutene, secured by treating the olefin at −40 to −100° F., with 0.1-0.5 per cent by weight of boron trifluoride was said to be a water-white substance with molecular weight between 1,000 and 12,000. In formulating a news ink, 60-70 parts of the above resin were ground with 30-40 parts of lampblack; the ground mixture subsequently was thinned with mineral oil.

Mixtures of rosin and mineral grease or wax have been suggested for ink bases. For newspaper printing the constituents may consist of 65 parts of vehicle (60 parts rosin and 40 parts mineral grease) and 35 parts coloring agent.[45] In the latter component, 30 parts of neutral powders, such as barium sulphate, and 5 parts of aniline dyestuffs were employed. It is also possible to incorporate up to 15 parts of rubber into this composition. These substances, after being thoroughly mixed with the aid of heat, yielded an ink of the consistency of Vaseline and suitable for printing on paper, linen or leather.

In addition to mineral oil and resin, a metallic soap and a mixed color-

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[41] E. Fonrobert, *Farben-Ztg.*, 1931, 36 (No. 31), 1383; *Rev. Paint, Colour, Varnish*, 1931, 4, 153. *Paint Manuf.*, 1931, 1 (7), 196; *Rev. Paint, Colour, Varnish*, 1931, 4, 281.

[42] M. Turly and B. F. Thomas, U. S. P. 105,014, July 5, 1870.

[43] G. W. Herbein, U. S. P. 1,469.414, Oct. 2, 1923; *Chem. Abs.*, 1923, 17, 3923.

[44] E. H. Hillman, U. S. P. 2,154,089, Apr. 11, 1939, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1939, 33, 5686.

[45] T. P. Sanguinetti, British P. 472,684, 1937; *Brit. Chem. Abs.* B, 1938, 693; *Chem. Abs.*, 1938, 32, 1955. French P. 803,031, 1936; *Chem. Abs.* 1937, 31, 2842; *Rev. Paint, Colour, Varnish*, 1937, 10, 173.

ing agent (a lake pigment, a pigment of the Prussian Blue group, and a basic dye) may be used in printing inks.[46] Low-boiling distillates such as naphtha may be employed to effect solution of the fatty acid salt of a heavy metal, *e.g.*, barium stearate.[47] A resin or gum, pigments, and barytes or kieselguhr are added to make a printing composition. For producing such inks, the following procedure has been proposed.[48] Oleic or stearic acid, or the corresponding glycerides, are dissolved in an aqueous caustic soda solution to form soaps. After filtration to remove insoluble material, aluminum sulphate is added to precipitate soaps such as aluminum oleate or stearate. About 10 parts of the heavy metal compound are dissolved in 90 parts of a hydrocarbon oil. The latter is a mixture of a heavy cylinder stock having a gravity of 23° Bé., and a light mineral oil having a gravity of 40° Bé. In the case when "300 oil" (gravity 40° Bé.) is used alone, a larger amount of the aluminum soaps is required, *e.g.*, 25 parts oleate to 75 parts oil. For printing purposes pigments are added to the soap-oil mixture. A composition illustrative of this method consists of the following: 40 parts heavy cylinder oil (23° Bé.), 5 parts light mineral oil (40° Bé.), 5 parts aluminum oleate, and 50 parts pigment (chrome yellow). The oily residue present in spent acid from petroleum refining has been proposed as vehicle for inks.[49] Carbon black was ground into the residue. Instead of oils or asphalts, a mixture of shellac, borax and water was advocated as a vehicle.[50] Also, blends of glue, honey, water and glycerol have been used for the same purpose.[51]

QUICK DRYING BY OXIDATION OR POLYMERIZATION

The use of metal compounds such as cobalt linoleate to accelerate the rate of drying of films of linseed oil varnishes and printing inks is well known.[52] However, for the maximum rate of hardening and for best results, the amount of these substances incorporated in the vehicle is restricted. Other compounds and methods have been suggested for accomplishing this purpose.

ACCELERATORS

Inks containing linseed or other drying oils, may be impregnated with rubrene peroxide.[53] This compound is produced by allowing rubrene ($C_{42}H_{28}$) to absorb a large proportion of oxygen. When heated to

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[46] Eitaro Sato, Japanese P. 109,334, 1935, to K. K. Sakata Syokai; *Chem. Abs.*, 1935, 29, 3863; *Rev. Paint, Colour, Varnish*, 1935, 8, 307.

[47] K. Kawamura, Japanese P. 98,935, 1933; *Chem. Abs.*, 1933, 27, 5995; *Rev. Paint, Colour, Varnish*, 1933, 6, 335.

[48] G. C. Wooley, U. S. P. 1,237,136, Aug. 14, 1917; *Chem. Abs.*, 1917, 11, 2966.

[49] A. Farrar, U. S. P. 100,877, March 15, 1870.

[50] H. A. Buck, U. S. P. 1,421,125, June 27, 1922; *Chem. Abs.*, 1922, 16, 3004.

[51] A. H. Hulot, U. S. P. 47,909, May 23, 1865.

[52] For a discussion of driers see Chapter 4.

[53] T. F. Pinder, U. S. P. 1,842,196, Jan. 19, 1932; *Chem. Abs.*, 1932, 26, 1810; *Brit. Chem. Abs.* B, 1932, 1041.

212° F. or higher, this peroxide is capable of liberating oxygen. Thus on heating a thin film of an ink containing rubrene peroxide, an immediate oxidizing and polymerizing action takes place uniformly throughout the mixture. If chilled ozone is projected upon the surface of the print, further conditioning of the ink surface is effected.

For vehicles containing a bodied drying oil which consists largely of eleostearin (such as tung oil) the use of diacyl peroxides has been suggested.[54] Organic peroxides, of which dibenzoyl peroxide, $(C_6H_5CO)_2O_2$, is a common example, do not dissociate to liberate oxygen. Their action is that of a catalyst rather than an oxidizing agent. Whereas these compounds are very effective with drying oils which consist mainly of eleostearin, they do not accelerate the drying of linseed oil to any considerable extent. This may be attributed to the fact that the drying of linseed oil is by auto-oxidation while that of China Wood oil involves both auto-oxidation and polymerization. Thus, these diacyl peroxides act as auto-oxidation and polymerization catalysts. A quick-drying ink may be made from the following ingredients: 75 parts carbon black, 3 parts indigo, 100 parts tung oil, 5.5 parts rosin oil, and 5.5 parts dilauroyl peroxide, $(C_{11}H_{23}CO)_2O_2$. This ink, when smeared on a glass plate at 100° C. dried in 8 seconds to a film which did not smudge when touched with the finger. Inks containing these diacyl peroxides must be used immediately, however, as they skin after a short time under ordinary storage conditions.

Methods of securing the catalytic effect of these organic peroxides other than by incorporating them in the ink itself have been utilized.[55] The peroxides were dissolved in chloroform or included in a feculose[56] size for treating the paper before printing. On the other hand, solutions of the peroxides in chloroform or dichloromethane may be sprayed upon printed sheets. These methods are applicable for printing on cloth, tinfoil or Cellophane.

The addition of certain synthetic resins to printing inks containing linseed oil causes a rapid drying of the vehicle which has been attributed more to polymerization than to oxidation.[57]

Sheets printed with an ink containing oil and a phenolic resin are reported to dry in much shorter time than those printed with an ink containing a drier and oil but with the resin omitted. Resins prepared by reacting phenol with formaldehyde, hexamethylenetetramine, or other compounds containing an active methylene group, can generally be made

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[54] F. Visser't Hooft, U. S. P. **2,032,554**, March 3, 1936, to Lucidol Corp.; *Chem. Abs.*, 1936, **30**, 2781; *Brit. Chem. Abs.* **B**, 1937, 258; *Rev. Paint, Colour, Varnish*, 1936, 9, 182.

[55] F. Visser't Hooft, U. S. P. 2,109,774, March 1, 1938, to Lucidol Corp.; *Chem. Abs.*, 1938, **32**, 3644; *Rev. Paint, Colour, Varnish*, 1938, **11**, 280.

[56] Feculose is the name by which the various commercial starch esters are designated. They are best formed by treating starch with glacial acetic acid and then washing the product with cold water to free it from uncombined acid.

[57] British P. 408,688, 1934, to Bakelite Corp.; *Brit. Chem. Abs.* **B**, 1934, 546; *Chem. Abs.*, 1934, **28**, 6001. R. C. Shuey, U. S. P. 2,073,229, March 9, 1937, to Bakelite Corp.; *Chem. Abs.*, 1937, **31**, 3311. For information concerning the preparation and characteristic properties of resins used in printing inks, see Carleton Ellis, "The Chemistry of Synthetic Resins," New York, Reinhold Publishing Corp., 1935.

oil-soluble by cooking with rosin for an extended period. Resins made from phenylphenols and formaldehyde possess this oil-soluble property. About one part of oil-soluble resin was incorporated into about three parts of linseed oil for fifteen minutes at 400° F. It has been found that the presence of phenolic resins did not cause the deterioration of such oil-film characteristics as durability and toughness. Furthermore, the resin seemed to aid in keeping pigments such as Peacock Blue suspended in the oil. For some purposes, as in rotary photogravure work, the ink may be diluted with a solvent such as tetrahydronaphthalene, benzyl alcohol, dimethyl and diethyl phthalates, xylene, or amylbenzene. These liquids have boiling points such that they show little tendency to vaporize from the ink at ordinary temperatures. When printed on paper the thinned vehicle is absorbed and the increased surface exposure greatly accelerates the evaporation rate.

The addition of phosphorus tri- or pentachlorides to an ink composition containing a drying oil and an oil-soluble phenol-aldehyde resin has been observed to accelerate the rate of drying.[58] The phosphorus chlorides are added in a diluted form such as 1 or 2 parts in 10 parts of white spirit (a petroleum fraction distilling from 150 to 220° C.) and at a temperature from 80 to 140° F. The drying oil-resin vehicle also may be diluted with white spirit. An ink stated to be quick drying was prepared by admixing pigment, blown tung oil, an oil-resin varnish and a small proportion of α-naphthol, β-naphthol, diphenylguanidine or pyrogallol.[59]

Chlorinated drying or semi-drying oils have been proposed for inks which dry rapidly.[60] The halogenated oil was ground with a pigment and an aqueous paste containing an oxide or hydroxide of zinc, iron, mercury, antimony, copper, tin, cobalt, nickel, chromium or magnesium. Reaction between the chlorinated drying oil and metallic oxide was stated to bring about rapid drying of the ink film.

Ozonation. Ozone is another agent which has been utilized to cause rapid drying of linseed oil vehicles. The time of drying was observed to have been reduced to about half when the oil was exposed to air (or oxygen) containing 0.25-0.4 per cent ozone.[61] Although higher concentrations of ozone further shortened the time of drying, the resulting product was said to be sticky and unsuited for a varnish.

Several types of apparatus have been proposed in which ozone is employed for drying printing inks. In one method[62] the freshly printed web is carried by a rotating, perforated apron through a drying chamber (Figure 49). Here, it is passed between electric heaters and then is sub-

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[58] L. E. Wakeford and L. E. Harris, British P. 447,463, 1936, to Berger & Sons; *Brit. Chem. Abs.* B, 1936, 750; *Chem. Abs.*, 1936, 30, 7365; *Rev. Paint, Colour, Varnish*, 1936, 9, 314.

[59] W. J. Koenig, Canadian P. 377,736, 1938, to Sloan-Blabon Corp.; *Chem. Abs.*, 1939, 33, 2354-5; *Rev. Paint, Colour, Varnish*, 1939, 12, 181.

[60] W. J. Koenig, U. S. P. 2,136,108, Nov. 8, 1938, to Sloan-Blabon Corp.; *Chem. Abs.*, 1939, 33, 1525.

[61] C. Denzler, *Helv. Chim. Acta.*, 1933, 16, 807; *Chem. Abs.*, 1933, 27, 4696; *Brit. Chem. Abs.* B, 1933, 718.

[62] G. L. Clark, U. S. P. 1,668,943, May 8, 1928; *Chem. Abs.*, 1928, 22, 2222.

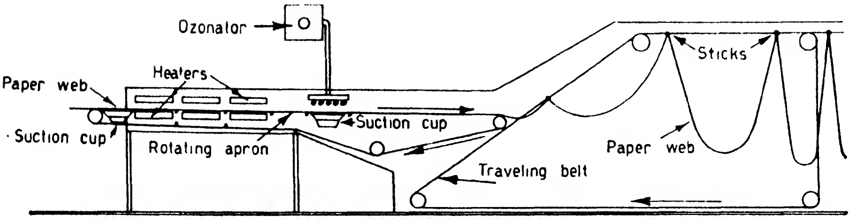

FIGURE 49. Diagrammatic Sketch of Apparatus for Ozonating Printed Sheets to Effect Rapid Drying (G. L. Clark).

jected to ozone. The chamber is thus substantially filled with warm air containing ozone. Further drying is provided in a second, well ventilated chamber which contains a common form of loop carrier. The latter is a system of rotating chains and connecting sticks which pick up the web in such a manner that the paper hangs in the form of loops. The dried material is then wound on a rewind roll.

In the process described by Lawson[63] the printed sheets as they come from the press are subjected to hot air from elevated, electrically heated blowers. As the paper comes to rest for a moment it is swept by a series of electrical point discharges which produce ozone (Figure 50). The ozone generator is in the form of a holder projecting from which are a number of fingers of spirally wound wire. These fingers are connected to one line of a high-voltage electrical supply apparatus operating at 10,000 to 20,000 volts. The holder sweeps the width of the paper with a clearance of $\frac{3}{4}$ to 2 inches.

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[63] A. Lawson, British P. 387,763, 1933, to Sheridan Machinery Co. Ltd.; *Chem. Abs.*, 1933, *27*, 995; *Rev. Paint, Colour, Varnish*, 1933, *6*, 136.

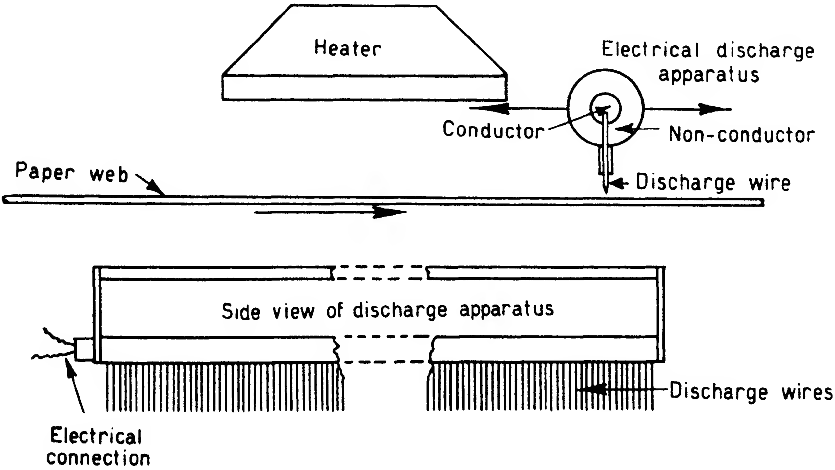

FIGURE 50. Sketch of Apparatus for Ozonating Printed Web by Electrical Discharge (A. Lawson).

In another apparatus, heat is applied by passing the printed web over a drum heated to 175-275° F.[64] Concentric with this drum is an ozonizer with a number of nozzles for projecting ozone upon the paper (Figure 51). The ozone is chilled by a cooling liquid which circulates around the ozone inlet. The web is successively led over a roller at 300-400° F. and a cold roller to bring about solidification of the ink. The ink stock is usually one which has been preconditioned by partial polymerization. This arrangement is useful at each stage of a continuous, multicolor printing process.

Allen and Grammer [65] prefer to pass the printed material through the space between an electrode and a dielectric. One of the electrodes constitutes a row of luminous discharge tubes, the walls of which serve both as containers for the gases of the tubes and as the specified dielectric. Thus high-intensity discharge conditions may be maintained without danger of change to the spark type discharge (Figure 52). The ionizer tubes are generally the width of the paper and the number of them is dependent upon the rate at which the web moves. Also, a corona discharge may be utilized as a source of ozone.[66] A set of conductors having overlapping portions (to permit corona discharge) were placed over the

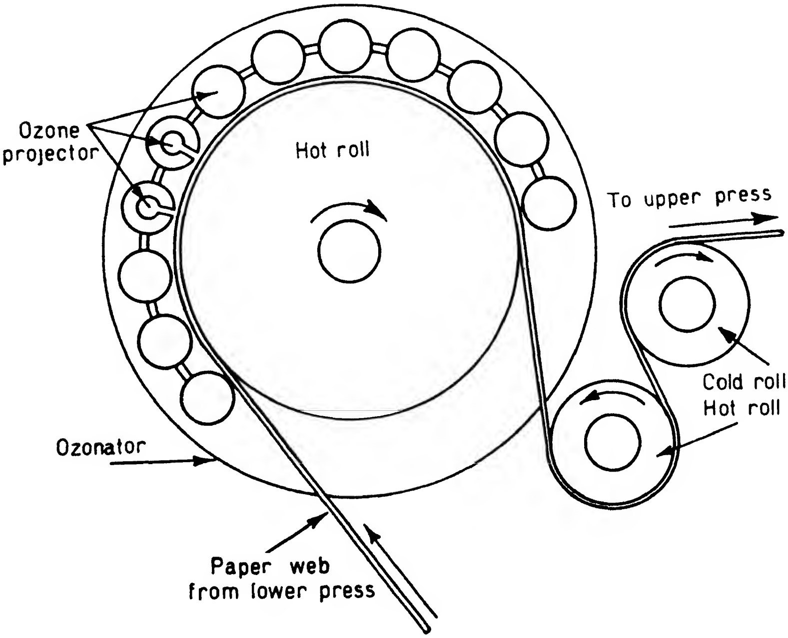

FIGURE 51. Diagrammatic Plan of Ozonator for Multicolor Press (T. F. Pinder).

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[64] T. F. Pinder, U. S. P. 1,842,195, Jan. 19, 1932; *Chem. Abs.*, 1932 26, 1810.

[65] W. W. Allen and A. L. Grammer, British P. 415,885, 1934; *Chem. Abs.*, 1935, 29, 918; *Rev. Paint, Colour, Varnish*, 1935, 8, 26.

[66] J. R. Blarne, U. S. P. 1,503,224, July 29, 1921, to Miehle Printing Press & Mfg. Co.

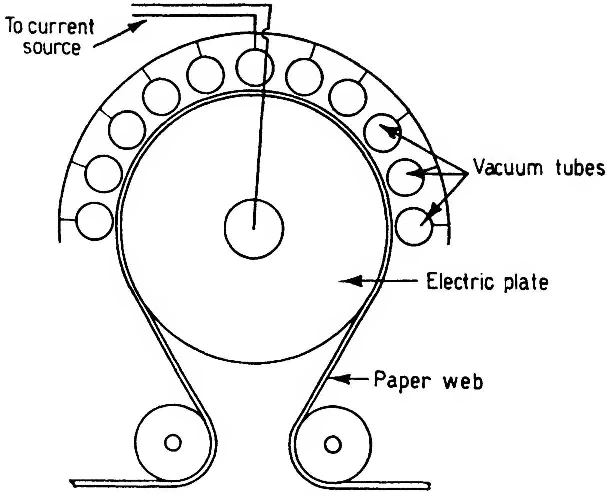

FIGURE 52. Sketch of Apparatus for Ozonating Printed Web to Effect Rapid Drying (W. W. Allen and A. L. Grammer).

conveyor which carries printed sheets from press to the pile table. A transformer, connected to a 110-volt line, was employed to furnish radio frequency current to the conductors. There was said to be no danger of injury from shock to operators who might touch the conductors during operation.

In another method of producing ozone, air has been forced through a number of high-frequency alternating-current ozone generators, charged with current at about 960 cycles per second.[67] These generators are located in the press room but not necessarily close to the press. The ozone and activated oxygen from the generators are piped to the press and delivered to the paper through a perforated pipe extending across and above the drying roll.

A common practice is to collect printed material in stacks of sheets or on a roll, keeping the surfaces separated by means of insert sheets or strips. These inserts are coated or impregnated with wax or oil to prevent offsetting. However, the weight of the pile of sheets, or the tension under which the roll was formed, tends to exclude oxygen from the ink and retard the drying of the oil vehicle. To remedy this it has been proposed [68] to place the sheets or rolls in a confined space which may be evacuated. When subatmospheric conditions have been created, ozone is introduced. By maintaining the atmosphere of ozone in contact with the prints for several hours, drying is accomplished which formerly required several days.

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[67] F. E. Hartman, U. S. P. 1,993,401, March 5, 1935, one-third each to F. H. Montgomery and W. R. Montgomery; *Chem. Abs.*, 1935, **29**, 2763.

[68] P. Aitchison, F. T. Wood, and A. A. Wittnebel, U. S. P. 1,925,429, Sept. 5, 1933, to American Bank Note Co.; *Brit. Chem. Abs.* **B**, 1934, 571; *Rev. Paint, Colour, Varnish,* 1934, **7**, 293. Also British P. 415,261, 1934; *Chem. Abs.*, 1935, **29**, 861.

Indications are that ink on freshly printed sheets dries faster when exposed to rays from a quartz-mercury arc lamp, especially at higher temperatures.[69] As small a concentration as 350 parts per million of ozone greatly accelerated the drying when used in connection with these rays. Monochrome and polychrome prints made with inks containing dyes mixed with drying oils are said to be dried by rays from a quartz lamp.[70]

QUICK DRYING BY EVAPORATION OF A SOLVENT

One of the most common methods of producing quick-drying inks involves the evaporation of a solvent from the composition after the print has been made. The solvents which have been used for this purpose vary from those which are very volatile to those which require the application of heat for vaporization.[71]

Volatile Solvents. Spirit gum, which is formed of spirits of wine (84 per cent ethyl alcohol) and gum arabic has been a constituent of quick-drying writing inks for some time. It likewise has been incorporated in printing inks: 1 part of spirits to 5 parts of ink.[72] The effect of the spirits of wine is to dissolve the organic ingredients of the ink and hold them in solution, making the ink more liquid. By reason of its low-boiling point the spirit volatilizes very rapidly at normal temperature. Ethyl ether, methyl alcohol, and ethyl alcohol are suitable solvents for such gums as shellac or sandarac.[73] Non-hygroscopic agents, for example titanium oxide, zinc oxide or lithopone, are also incorporated in these ink vehicles. The addition of alkylcelluloses is said greatly to improve spirit inks.[74] These inks show good strength of shade, opacity, fastness and at the same time do not penetrate the material. They are said to be suitable for printing from rubber stereos on rotary machines or from metal type. In general the inks for use with rubber stereos are thinner than those for metal type.

In making an ink of this type 5 parts of ethylcellulose and 40 parts of Rotor Green are dissolved in 155 parts of methylated spirit, consisting of 93.5 per cent by weight of ethyl alcohol plus methyl alcohol and a small proportion of pyridine. In place of the ethyl compound, methyl, propyl, butyl or glycol celluloses may be used. The volatile constituent of inks may be hydrocarbons of low boiling range such as naphtha.[75] With the latter, binding agents such as oil-modified alkyd resins have been employed.[76] Mineral oil and drier solution are incorporated in this

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[69] R. A. Brown, *Am. Ink Maker*, 1931, **9**, 21; *Chem. Abs.*, 1931, **25**, 3500.

[70] K. H. Schwimmer, French P. 645 595, 1927: *Chem. Abs.*, 1929, **23**, 2050.

[71] R. F. Bowles, *Penrose Annual*, 1939, **41**, 162; *Rev. Paint, Colour, Varnish*, 1939, **12**, 19.

[72] A. Ruter, French P. 410.635, 1909; *J. S. C. I.*, 1910, **29**, 831. Also British P. 29,389, 1910; *Chem. Abs.*, 1911, **5**, 3923.

[73] W. H. Lawrence, Canadian P. 338,454, 1934; *Chem. Abs.*, 1934, **28**, 2204; *Rev. Paint, Colour, Varnish*, 1934, **7**, 225.

[74] A. A. Harrison and S. Oakeshott, U. S. P. 2,132,468, Oct. 11, 1938; *Chem. Abs.*, 1939, **33**, 417; *Am. Ink Maker*, 1938, **16** (12), 43; *Rev. Paint, Colour, Varnish*, 1939, **12**, 20.

[75] H. Heckel, U. S. P. 1,906,961, May 2, 1933, to Twitchell Process Co.; *Chem. Abs.*, 1933, **27**, 3627; *Brit. Chem. Abs.* **B**, 1934, 157.

[76] D. McBurny and E. H. Nollan, Canadian P. 361,667, 1936, to Canadian Industries Ltd.; *Chem. Abs.*, **1937**, **31**, 1529; *Rev. Paint, Colour, Varnish*, **1937**, **10**, 228.

mixture. After printing, the lacquer is dried at 180-200° F. Subsequently, metal powder is sprinkled over the lacquer and the whole heated to harden the print. Also a mixture of volatile paraffin hydrocarbons and monoethyl ether of butene glycol was said to furnish a quick-drying ink vehicle.[77] Instead of glycol ether, butanol or ethyl lactate may be employed.

Derivatives of rubber have been used as the base for inks which dry by the evaporation of solvents. In one process [78] the principal ingredient consists of the polymerized reaction products resulting from the treatment of rubber in either a benzene solution or plastic mass, with certain amphoteric metal salt compounds containing halogens. Compounds which effect reaction include halide salts of tin, aluminum, antimony, iron, chromium, as well as metal halide acids such as hydrated chlorostannous or chlorostannic acids. An ink is made by incorporating into the base a color agent which may be commercial pigment or lake, and an oil-free, non-oxidizing solvent such as naphtha or carbon tetrachloride. The printed film dries very quickly to a surface which is adherent to paper. Another binding medium consists of a mixture of cellulose derivatives and rubber.[79] To an uncolored printing medium consisting of 10 parts acetylcellulose (dissolved in 40 parts butyl acetate and 40 parts xylene) and 2.5 parts crepe rubber (dissolved in 25 parts cyclohexanone) may be added soluble dyes, lakes, or pigments. The consistency of inks made with the above mixtures may be varied for different types of printing or coating by means of compound thinner such as 1 part butyl alcohol, 1 part toluene, 0.5 part methylethylene glycol, and 0.5 part tetrahydronaphthalene. It is said that these inks produce prints which do not blur or smudge and which are securely bound to fibers of the surface to be printed. Rubber may be mixed also with a synthetic resin to form a coating composition.[80] The resin was prepared in the above case by heating equivalent molecular proportions of glycerin and phthalic acid or anhydride, in the presence of ammonium hydroxide or sodium carbonate, at 200° C. for 20 minutes. The condensation product may be varied by heating for a longer period of time or by including compounds such as citric or succinic acid. A solution of resin in petroleum ether or ethylene dichloride is added to a solution of rubber in the same solvent. Dispersions of these ingredients in water may also be used. The following is an example of an initial coating composition: 10 parts resin, 90 parts crepe rubber, and 40 parts ethylene dichloride. Films of this mixture are flexible, do not peel or crack when creased. To eliminate tackiness a second coat is applied which comprises 30 parts resin, 50 parts cellulose acetate, 5 parts cellulose nitrate and 15 parts plasticizer such as Saniticizer M 17 (Monsanto

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[77] F. Kaufler and H. P. Schmitz, U. S. P. 2,036,480, Apr. 7, 1936, to A. Wacker Ges. für elektrochemische Industrie; *Chem. Abs.*, 1936, 30, 3667.

[78] H. A. Haupth, U. S. P. 2,069,828, Feb. 9, 1937, to Sears Roebuck & Co.; *Chem. Abs.*, 1937, 31, 2158.

[79] H. N. Morris, U. S. P. 2,036,768, April 7, 1936, to Rucel Ltd.; *Chem. Abs.*, 1936, 30, 3667.

[80] J. L. Elliot, U. S. P. 2,116,065, May 3, 1938, and U. S. P. 2,116,066, May 3, 1938, to International Printing Ink Corp.; *Chem. Abs.*, 1938, 32, 5114.

Chemical Co.). These coatings are waterproof, grease-proof and do not deteriorate on exposure.

Mixtures of di- or trichloroethylene with benzene, toluene or xylene have been suggested for quick-drying inks.[81] A resin that has been interacted with nitric acid is admixed with the solvent blend and pigment added. The resulting ink was reported to dry by evaporation of solvent, with no attendant chemical changes of any constituent.

When solvents which have higher boiling points than those considered above are used, there is less tendency for the ink to dry or set upon the inking rollers and type. Also, benzyl alcohol was suggested as an ingredient of quick-drying inks.[82] The alcohol was admixed with pigment and an amyl acetate or acetone solution of a cellulose ester.

Amyl and butyl alcohols have been added to a pigmented polymerization product of linseed or other drying oil.[83] For example, a mixture of 30 parts xylene and 30 parts fenchone has been advocated for use in linoleum printing.[84] To the solvent are added 10 parts nitrocellulose, 25 parts ester gum, 5 parts dibutyl phthalate and 25 parts pigment. The boiling point of fenchone is 193-195° C.

Esters of alcohols such as acetic esters of glycol may be added to inks to accelerate drying.[85]

Inks which dry rapidly when heated above 100° C. may be made of the following ingredients:[86] 0.5 to 0.75 part wax, 0.5 part rosin oil, 1 to 6 parts dry aluminum hydrate, 10 to 14 parts drying oil, 1 to 6 parts varnish-type resin in a low-boiling solvent, 6 to 9 parts pigment, 0.062 to 2 parts drier, 1 to 10 parts hydrocarbon solvent and 1.5 to 2.5 parts organic solvent of boiling point above 100° C. Paraffin wax is advocated, but beeswax, Chinese wax or spermaceti may be used. The varnish type resin may be copal, amber, kauri or glyptals ("Rezyl"),[87] to the extent of 8 to 10 per cent in alcohol or mineral spirit solvent. Also, utilization of saponified rosin in alcohol solution has been proposed.[88] Carnauba wax may be dissolved in phenol and mixed with an aniline dye to produce a quick-drying printing ink.[89]

By including a small proportion of wax the volatility of nitrocellulose

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[81] L. Magnien, British P. 379,094, 1932, to Société anon. Chlorosoda; *Chem. Abs.*, 1933, **27**, 3627; *Rev. Paint, Colour, Varnish*, 1932, **5**, 333. French P. 701,597, 1930; *Chem. Abs.*, 1931, **25**, 4138; *Rev. Paint, Colour, Varnish*, 1931, **4**, 251.

[82] S. Honzyô, Japanese P. 98,838, 1932, to Tuneiti Tanaka; *Chem. Abs.*, 1933, **27**, 5995; *Rev. Paint, Colour, Varnish*, 1933, **6**, 335. See also P. Domange, French P. 41,376, 1930; *Chem. Abs.*, 1933, **27**, 2830. French P. 713,269, 1929; *Chem. Abs.*, 1932, **26**, 1810.

[83] Shinjiro Horii, Japanese P. 101,742, 1933; *Chem. Abs.*, 1934, **28**, 5691; *Rev. Paint, Colour, Varnish*, 1934, **7**, 456.

[84] D. R. Wiggam, U. S. P. 1,996,846, Apr. 9, 1935, to Hercules Powder Co.

[85] B. Kalischer, French P. 644,086, 1927; *Chem. Abs.*, 1929, **23**, 1763; *Rev. Paint, Colour, Varnish*, 1929, **2**, 151. Also British P. 303,200, 1927; *Brit. Chem. Abs.* **B**, 1929, 180.

[86] J. F. Jirousek, U. S. P. 1,951,627, April 10, 1934, to Mir-A-Col, Inc., *Chem. Abs.*, 1934, **28**, 3920; *Brit. Chem. Abs.* **B**, 1935, 110; *Rev. Paint, Colour, Varnish*, 1934, **7**, 196.

[87] See Carleton Ellis: "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., 1935, for preparation and properties of resins.

[88] H. Kurz and K. Albert, Austrian P. 124,742, 1931; *Chem. Abs.*, 1932, **26**, 860; *Rev. Paint, Colour, Varnish*, 1932, **5**, 90; Austrian P. 144,648, 1936; *Chem. Abs.*, 1936, **30**, 3667; *Rev. Paint, Colour, Varnish*, 1936, **9**, 242.

[89] F. A. Putnam, U. S. P. 1,082,099, Dec. 23, 1914; *Chem. Abs.*, 1914, **8**, 830.

lacquers may be reduced so that they may be utilized in printing inks.[90] To provide a surface free from irregularities due to excess wax and yet prevent appreciable evaporation of lacquer solvents at room temperature, the amount of wax should not exceed 2 per cent, on the basis of solvents. A typical composition comprises 40 parts ester gum, 75 parts 0.5-second viscosity nitrocellulose, 140 parts zinc oxide; 90 parts dibutyl phthalate, 150 parts butyl acetate, 150 parts toluene, 30 parts ethyl alcohol and 2 parts ceresin wax. At 70° F. this composition is practically non-volatile, but at 140° F. it dries quickly.

In inks containing nitrocellulose and high-melting waxes, Kelly[91] has used high-boiling plasticizers, plus solvent thinners. These inks dry quickly when heated to 300-400° F. and are applicable to printing on paper, waxed paper or fiber board. A specific example of a red ink contains the following: 41 parts red pigment, 20 parts barium sulphate, 28 parts nitrocellulose of 0.5-second viscosity, 12 parts ethyl alcohol, 123 parts *n*-butyl lactate, 40 parts diethyl phthalate and 10 parts carnauba wax. Nitrocellulose imparts tack or stickiness to the ink while the latter is wet, and binds the pigment to the surface after printing. Other waxes such as Japan, montan, and bayberry, may be employed for lubricating the particles of pigment. As plasticizers, dibutyl phthalate, tricresyl phosphate and as solvents, ethyl lactate, normal and secondary butyl acetates, amyl acetate and cyclohexanol acetate are suggested. After passing over a heated roll, the material printed with these inks may be wound upon a roll without coating the under side with paraffin, to prevent offsetting and sticking.[92]

When an ester or ether derivative of mono- or diethylene glycol and an oleo resin ester or alkyd resin are substituted for the solvent and wax, respectively, in the above inks, several improvements have been noted.[93] The temperature range for drying the inks is lowered to 150-325° F. When the printed web travels at the low speeds of 75 to 100 feet per minute the ink will dry in 11 or 12 seconds when heated to 150° F. Temperatures up to the scorching point of the paper are used when the web moves at 500 feet per minute. In addition to dry pigments, pigments and dyes or dyes alone may be used as coloring matter. With such dyes as Methyl Violet, Malachite Green, Victoria blue, Methylene Blue or Rhodamine, a concentration as high as 15 per cent of the finished ink may be used. The viscosity of the cellulose ester employed in the ink may range from 0.25 to 40 seconds.

Vapor pressures indicate that at ordinary temperatures diethylene glycol monobutyl ether has a low rate of evaporation.[94] However, when

[90] T. F. Bradley, U. S. P. 1,884,553, Oct. 25, 1932; *Chem. Abs.*, 1933, **27**, 1218; *Brit. Chem. Abs.* **B**, 1933, 800.

[91] E. J. Kelly, U. S. P. 2,002,537, May 28, 1935; *Chem. Abs.*, 1935, **29**, 4610; *Brit. Chem. Abs.* **B**, 1936, 608; *Rev. Paint, Colour, Varnish*, 1935, **8**, 403.

[92] See also Chapter 16

[93] E. J. Kelly, U. S. P. 2,070,278, Feb. 9, 1937; *Chem. Abs.*, 1937, **31**, 2457; *Brit. Chem. Abs.* **B**, 1938, 554; *Rev. Paint, Colour, Varnish*, 1937, **10**, 175.

[94] J. E. Brewer and G. S. Gardner, *Ind. Eng. Chem.*, 1937, **29**, 179; *Chem. Abs.*, 1937, **31**, 2058; *Brit. Chem. Abs.* **B**, 1937, 522.

heated to 150° C., this solvent becomes a highly volatile liquid and will evaporate almost instantly. The plasticizing agents, however, are not very volatile even at the elevated temperature; the vapor pressure of dibutyl phthalate is 0.45 mm. at 100° C. and 1.4 mm. at 150° C. Thus, the plasticizing action is maintained after the evaporation of the solvent. With rollers of glue, glycerin and water composition, it is advisable to use diethylene glycol monobutyl ether acetate rather than the ether derivative.[95] The ether tends to extract water and glycerin from the roller composition, eventually rendering it hard and inelastic. The rollers then are unable to carry and distribute the ink evenly and satisfactorily over the printing plates. The acetate has but little affinity for water or glycerin and the demands of the ink vehicle for these compounds may be satisfied by adding a small amount (about 1 per cent) of them to the ink. The quantity of the aqueous mixture which is added does not impair the printing qualities of the ink. Diethylene glycol monobutyl ether acetate shows the same vapor pressure characteristics as the ether derivative, so quick-drying is caused likewise by heating the print to 150° C.

Utilization of water as volatile solvent in quick-drying inks has been suggested.[96] The inks comprised heat-reactive aminoplast resin, liquid vehicles and pigments and had thixotropic properties at room temperature. One heat-reactive resin was secured by interacting urea with formalin (aqueous solution of formaldehyde). Subsequently a portion of the water was removed by evaporation or distillation, leaving as residue a thixotropic syrup. The latter was incorporated with pigment to furnish an ink. Such inks were said to set quickly on heating to 140-155° C. During the heating operation the resinous material changes from a soluble, fusible mass to one which is insoluble and infusible. Instead of water, other solvents such as diethylene or ethylene glycol may be employed.

A thermographic ink which contains no volatile solvent was advocated.[97] Thus a blend of 100 parts dibutyl phthalate, 100 parts paracoumarone resin, 2.5 parts drier and pigment was said to harden quickly on heating at 150° C.

An evaluation of solvents for binding agents utilized in quick-drying inks has been made by Bogin.[98] The binding agents studied included nitrocellulose, ethylcellulose, cellulose acetate and resins (vinyl, methacrylate, polystyrene, alkyd and phenol-formaldehyde).

Nitrocellulose, employed in preparing lacquers and as binding agent in inks, is soluble in a number of substances containing carbonyl groups,

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[95] A. E. Gessler, U. S. P. 2,128,672, Aug. 30, 1938, to Interchemical Corp.; *Am. Ink Maker*, 1938, 16 (10), 43; *Chem. Abs.*, 1938, 32, 8808; International Printing Ink Corp., British P. 442,320, 1936; *Chem. Abs.*, 1936, 30, 4596; *Brit. Chem. Abs.* B, 1936, 463; *Rev. Paint, Colour, Varnish*, 1936, 9, 170. A. E. Gessler, Canadian P. 369,333, 1937, to Interchemical Corp. (formerly International Printing Ink Corp.); *Chem. Abs.*, 1938, 32, 2378; *Rev. Paint, Colour, Varnish*, 1938, 11, 191.

[96] Carleton Ellis, U. S. P. 2,162,331, June 13, 1939, to Ellis Laboratories, Inc.

[97] A. Schneider, U. S. P. 1,992,016, Feb. 19, 1935; *Chem. Abs.*, 1935, 29, 2375.

[98] C. Bogin, *Am. Ink Maker*, 1939, 17 (5), 19, (6), 21.

such as esters, ketones, acids and aldehydes. Also the cellulose derivative is soluble in mixtures of diethyl ether and ethyl alcohol, and in compounds containing an alcohol and ether group in the same molecule. Nitrocellulose is insoluble in hydrocarbons, such as naphtha, toluol or benzol, and in alcohols or ethers separately. Generally, however, solutions of nitrocellulose are diluted or thinned with toluol or naphtha before use in inks. The dilution ratio or tolerance is a measure of the amount of non-solvent that can be added to a solution containing nitrocellulose before precipitation of the latter occurs. This value has been defined as the volumes of any hydrocarbon, or diluent, which can be added to a unit volume of any particular solvent without destroying the ability of the latter to dissolve nitrocellulose. Some properties of nitrocellulose solvents and diluents are indicated in Table 29.

Table 29.—Properties of Nitrocellulose Solvents and Diluents.

Material	Tolerance for Toluol	Tolerance for Naphtha	B. P. (° C.)	Evaporation rate by wt. (*n*-Butyl Acetate =100)
Acetone	4.50	0.65	57.1	920
Ethyl acetate	3.30	1.10	77.	525
Methyl ethyl ketone	4.10	0.85	79.6	465
Isopropyl acetate	3.00	1.10	89.	435
Ethyl alcohol	Latent[99] solvent	Latent solvent	78.5	203
n-Butyl acetate	2.70	1.45	126.5	100
n-Butyl alcohol	Latent solvent	Latent solvent	117.1	45
"Cellosolve"	4.80	1.00	135.	40
Ethyl lactate	5.20	0.70	155.	22
Diacetone alcohol	3.00	0.55	166.	15
Butyl "Cellosolve"	2.60	2.00	170.6	10
Butyl lactate	5.10	2.00	188.	6
Benzene	....	....	79.6	450
Toluene	....	....	111.	195

Ethylcellulose is soluble in toluol. Because of the high viscosities of such solutions, a mixture of 80 parts toluol and 20 parts ethyl alcohol or butanol generally is utilized. Cellulose acetate is soluble in acetone, methyl "Cellosolve," methyl or ethyl lactate and diacetone alcohol. Synthetic resins differ in solubility, depending upon method of manufacture and components. In choosing a solvent, tolerance for thinner and rate of evaporation should be considered as well as solvent action upon the binding agent.

The advent of these printing inks employing high-boiling liquids necessitated that press designers make special provisions for removal of the solvent. In a process developed by Jeuck,[100] the printed web, after

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[99] Latent solvents are substances which do not possess any solvent power for nitrocellulose by themselves, but acquire such power in the presence of true solvents.

[100] F. J. Jeuck, U. S. P. 2,042,432, May 26, 1936, to International Printing Ink Corp.; *Chem. Abs.*, 1936, 30, 5062; *Rev. Paint, Colour, Varnish*, 1936, 9, 316. Also British P. 458,468, 1936; *Brit. Chem. Abs.* B, 1937, 264; U. S. P. 2,129,277, Sept. 6, 1938, to Interchemical Corp.; *Chem. Abs.*, 1938, 32, 8636.

passing over heated rollers, was directed under the flame of a burner which ignited the solvent vapors (Figure 53). The vapors flashed into flame so quickly that neither the web nor the ink was scorched or burned. If the flame extended as far as the rewind roll it was snuffed out as the web was rewound. In this manner the ink was set quickly and was not resoftened by any returning solvent vapor. However, the temperature of metal drums or heating rollers was restricted to about 150° C., above which the paper was said to be injured. Hot air was directed against the web in order to vaporize the solvent. It was soon found, however, that air accumulated and evolved heat so slowly that large volumes were necessary. It was noted that when gas heat was applied directly to the printed material, the time required to volatilize the solvent was materially less than that required to burn or char the paper. Thus if the time of contact is short enough, an intense heat may be applied which will vaporize the solvent without harming the paper or ink. An apparatus utilizing this principle, which is applicable to a printing press of standard construction, has been described.[101] The web, as it emerges, printed side up, from the rollers of the press, forms the bottom wall of a specially

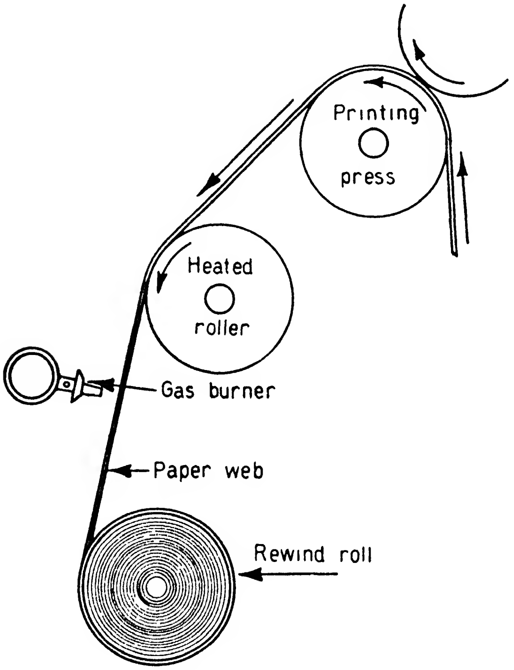

FIGURE 53.

Sketch of Apparatus for Effecting Rapid Drying by Ignition of Ink Vehicle (F. J. Jeuck).

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[101] R. Helmer, U. S. P. 2,127,956, Aug. 23, 1938, to International Printing Ink Corp.; *Am. Ink Maker*, 1938, 16 (10), 43; *Chem. Abs.*, 1938, 32, 8174. Also British P. 466,658, 1936; *Brit. Chem. Abs.* **B**, 1937, 1375.

mounted furnace (Figure 54). The top wall of the furnace contains several rows of cup-shaped burners. The refractory material of these burners is heated to incandescence by burning a gas-air mixture. When the burners are directed toward the moving web, the flames and radiant heat evaporate the solvent from the ink and actually cause ignition of the vapors to take place. The combustion is so rapid that no flame touches the paper, but a temperature of about 1400° F. is maintained. The web next passes a suction duct out of which the vaporized solvent and products of combustion are drawn. In order to retain the tensile strength and original size, as well as to cool the print, the paper is passed over water-cooled rollers before going to the rewind roller. Also, it has been suggested that drying of a printed sheet with radiant heat be effected in an atmosphere of rapidly circulated air.[102] The latter is circulated so that the portion of air in contact with the printed sheet remains at room temperature. In this way, scorching of paper is said to be prevented.

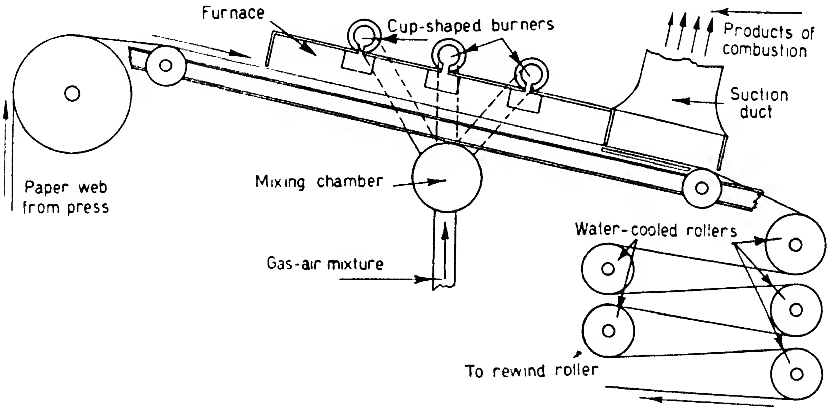

FIGURE 54. Diagrammatic Side Elevation of Furnace for Removing Volatile Vehicles from Inks (R. Helmer).

QUICK DRYING BY PRECIPITATION

In one method of preventing offsetting of sheets or web immediately after printing, the binder and pigment are precipitated from the ink composition onto the paper. Quick-setting of inks which contain certain colloids or binders and a solvent may be brought about by adding an agent which is a diluent for the solvent but not a solvent for the colloid or binder. The binder is thereby precipitated or coagulated to produce a hard, adhesive, non-smearing film which occludes the pigment. The choice of diluent is dependent upon the liquid ingredient of the ink to be treated.

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[102] British P. 474,095, 1937, to Steel Engravers Appliance Corp.; *Brit. Chem. Abs.* **B,** 1938, 194.

The following is an example of an ink in which water may be used as the precipitating agent or diluent[103]: 30 parts Peacock blue, 30 parts 0.25-second viscosity nitrocellulose and 40 parts diethylene glycol monobutyl ether. Another ink consists of 14 parts carbon black, 6 parts Prussian Blue, 47 parts ester gum, 31 parts diethylene glycol monobutyl ether, and 2 parts Syncera wax (*i.e.*, a petroleum wax, melting point 140° F.). When diethylene glycol monobutyl ether acetate is the solvent for the binder, the appropriate diluent is ethyl alcohol or a hydrocarbon. After printing, the web is passed over inclined rollers and while the paper is in this position, the diluent is sprayed upon it (Figure 55). This treatment precipitates the ink binder and renders it free of solvent. The final step consists of evaporating the diluent. When it is desired not to saturate the web or printed material with the diluent, other methods of precipitation have been applied. Thus, a jet of saturated steam may be directed at the prints for one or two seconds.[104] As a result the binder is deposited from solution, thereby effecting adherence of the pigment to the paper.

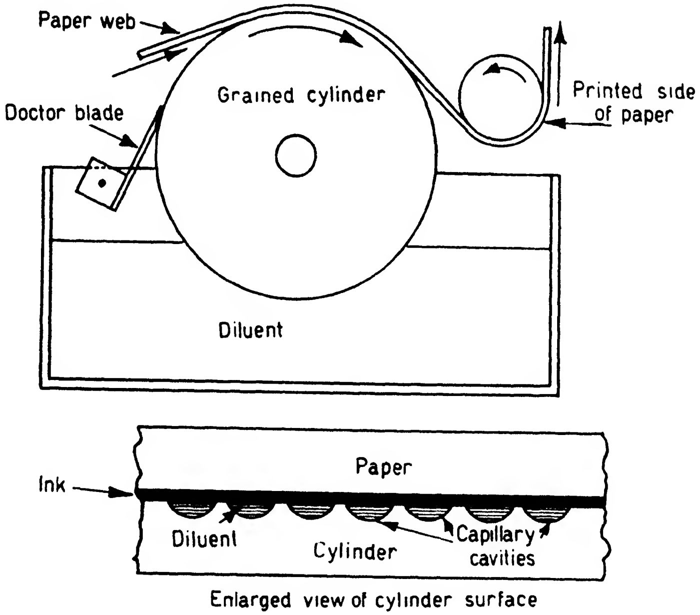

FIGURE 55. Sketch of Apparatus for Effecting Drying by Precipitation (A. E. Gessler, A. F. Guiteras, and C. F. Clarkson).

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[103] A. E. Gessler, A. F. Guiteras, and C. F. Clarkson, British P. 462,924, 1937, to International Printing Ink Corp.; *Brit. Chem. Abs.* B, 1937, 701; *Chem. Abs.*, 1937, 31, 6490; *Rev. Paint, Colour, Varnish*, 1937, 10, 262.

[104] British P. 468,384, 1937, to Interchemical Corp.; *Chem. Abs.*, 1938, 32, 376; *Rev. Paint, Colour, Varnish*, 1937, 10, 413.

Diluting the solvent with molten wax will cause solidification of certain ink mixtures.[105] Inks for use with wax consist of a pigment dispersed in a solution of 0.5-second viscosity nitrocellulose in a high-boiling solvent such as dimethyl phthalate. Immediately after printing, the web is dipped into molten paraffin at 200-300° F. Certain resins are reported to be especially suited for inks of this type.[106] These resins include those of the alkyd type which are synthesized from glycerin, fatty acids and phthalic anhydride, phenol-formaldehyde type, amide-formaldehyde, and oil-soluble gums such as manila gum or shellac. For intaglio printing the following composition has been suggested: 15 parts Prussian Blue, 40 parts Rezyl A varnish, 15 parts Amberol K-12A resin, 30 parts toluene and 50 parts Rezyl 114 in benzene. An ink for use on type has been made consisting of 80 parts Lithol barium toner, 200 parts Lithol sodium toner, 560 parts blanc fixe, 220 parts lithopone, 50 parts chrome orange, 520 parts Rezyl C varnish, 300 parts Santolite varnish, and 85 parts dimethyl phthalate. Materials printed with these inks may be dipped in molten wax, or the latter may be sprayed or brushed on.

Cold Set Inks. Printing from hot plates with inks which are molten at temperatures of approximately 200° F. but which are solids at room temperature has been advocated to secure high-speed printing. Since the ink solidifies when it touches the cold paper web, merely by returning to its natural, solid state, the claim has been made that the faster the paper travels, the faster the ink solidifies. Also, it has been stated that there is no absorption of ink by the paper, no register problems and no washups except to change color.[107] The cold set inks include offset (see page 265), rotary and flatbed inks.

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[105] W. W. Mock, U. S. P. 2,081,949, June 1, 1937, to International Printing Ink Corp.; *Chem. Abs.*, 1937, 31, 5188; *Rev. Paint, Colour, Varnish*, 1937, 10, 342. Also British P. 468,233, 1937, to International Printing Ink Corp.; *Chem. Abs.*, 1938, 32, 376; *Rev. Paint, Colour, Varnish*, 1937, 10, 342.

[106] W. W. Mock, U. S. P. 2,086,428, July 6, 1937, to International Printing Ink Corp.; *Chem. Abs.*, 1937, 31, 6007; *Rev. Paint, Colour, Varnish*, 1937, 10, 342.

[107] *Am. Ink Maker*, 1940, 18 (2), 39.

Chapter 9

Planographic Inks

Planographic printing processes constitute one of the major divisions of printing. These include all the methods of printing from flat or slightly etched surfaces, such as stone or metal plate lithography, offset lithography, and photolithography. These methods are based upon the fact that grease and water are mutually repellent.

The word "lithography" literally means writing on stone. This was the term which Alois Senefelder gave to his invention in 1796.[1] One day he chanced to write a memorandum upon stone with crayon. The stone was of fine-grained laminated limestone still obtained from the Solenhofer quarries near Senefelder's home in Bavaria. The idea occurred to him that he might be able to make an impression on paper by dampening the surface of a design-bearing stone with water and covering the design with printing ink. The process proved successful. Elaborated and perfected, it became available for commercial use.

In the beginning lithography was carried out for the most part on "lithographic stones" of limestone. These were slabs cut about three or four inches thick. The surface was planed, smoothed by grinding with a mixture of sand and water, and finally polished with pumice stone and emery. For some types of work the surface was grained, either by hand with a muller and fine sand or by mechanical agitation using sand and small round marbles. It was found that metal plates could be employed as well as stone. Zinc plates came into commercial use about 1880. In 1898 aluminum plates were introduced.

The thin-rolled plates must be of high purity and free from defects. The surface of the metal plate is grained mechanically so that it will carry a film of water during printing. After graining, the surface is washed with water and then with an alum solution. The latter cleans and sensitizes the plate.

Complete descriptions of the procedures used in lithography may be found in texts on the subject but the following résumé is appropriate before considering planographic processes and planographic inks in detail.[2] The lithographic image may be made upon properly prepared

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[1] See A. Senefelder, "The Invention of Lithography," Translation by J. W. Muller, New York, Fuchs and Lang Manufacturing Co., 1911.

[2] D. Cumming, "Handbook of Lithography," Second Edition, A. & C. Black, London, 1919; H. J. Rhodes, "The Art of Lithography," 2nd ed., New York, D. Van Nostrand Co., Inc., 1924; C. Harrap, *Chem. Trade J.*, 1911, **48**, 590; H. A. Maddox, *Mod. Lithographer*, 1918, **14**, 5, 18, 49, 71; see also Chapter 1.

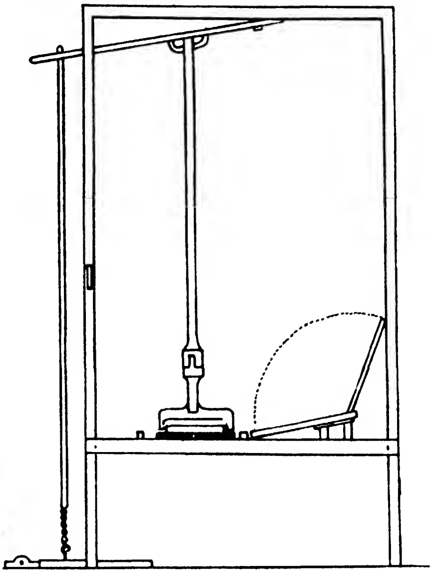

FIGURE 56. (Right)
Senefelder's Lever Press, as Described in a British Patent of 1801.

Courtesy The Penrose Annual

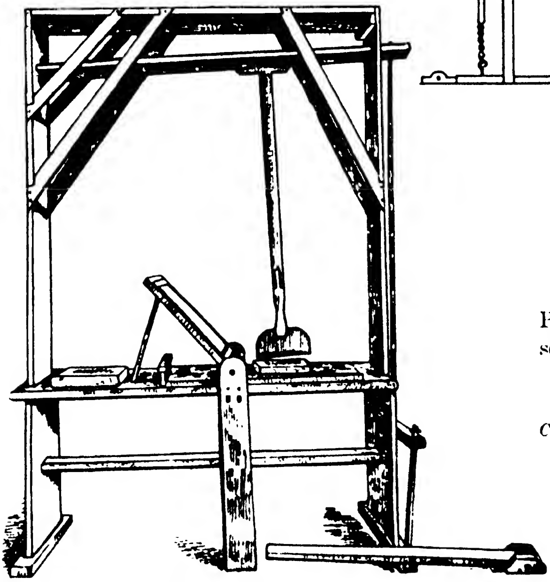

FIGURE 57. (Left)
Senefelder's Original Lever Press, in the Deutsches Museum, Munich.

Courtesy The Penrose Annual

stone or metal surfaces by different methods. The design sometimes is placed directly on the plate by means of a pen, a brush or a greasy crayon (lithographic chalk). Prints made upon transfer paper can be reproduced on the surfaces.[3] Also photographic methods are used for producing the design. In all but the last of these methods it is necessary that the image be produced in a greasy ink containing fatty acids. Subsequently the plate is sponged with an aqueous solution of gum arabic, and dried.

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[3] See Chapter 12.

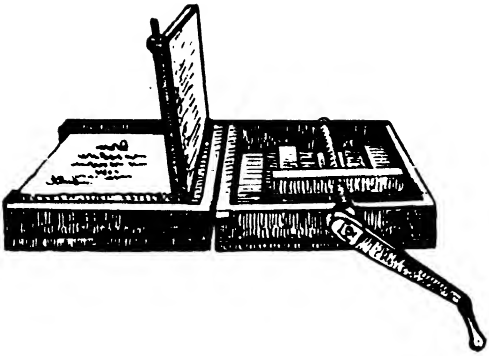

FIGURE 58.

Senefelder's Portable Hand Press, in the Deutsches Museum, Munich.

Courtesy The Penrose Annual

This treatment desensitizes the non-image areas so that, if kept damp, they will not accept ink. The original image or transfer is removed by "washing-out" with turpentine or similar agent and is replaced by rolling up the plate with a heavy ink, usually black. The plate then is etched with an acidic mixture, *e.g.*, one containing phosphoric or nitric acid. Thus the surface of the plate which is not protected by the heavy ink is roughened so as to retain gum arabic and moisture more readily. After being washed to remove the etching solution, the plate again is gummed. The gum arabic sinks into the pores of the stone or adheres to the rough metal surface on the non-image areas. In the printing process the design which is in slight relief receives ink from leather-covered inking rollers.

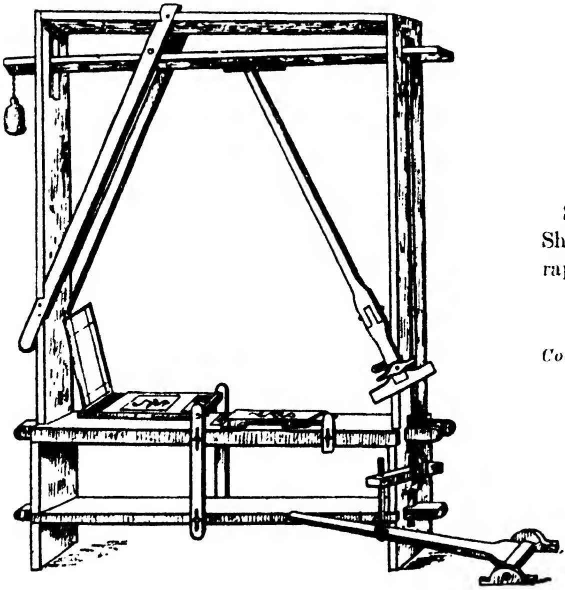

FIGURE 59.

Senefelder's Lever Press, as Shown in his Manual of Lithography in 1818.

Courtesy The Penrose Annual

To prevent the printing composition from spreading to the non-printing areas, the latter are kept moist by means of dampening rollers covered with felt or flannel. The lithographic ink and moisture being mutually repellent, it is possible to print only the desired design or lettering.

THEORY OF LITHOGRAPHIC PRINTING

Lithography was developed to considerable extent by empirical investigations. However, from the advances which have been effected and from several critical studies which have been made, the fundamental principles may be understood.

Limestone, being quite porous, will take up both ink on image areas and moisture on non-image portions. However, with metal plates it is necessary to grain and sensitize the entire surface. The graining process has been described above. To make the plates grease-receptive and grease-retentive, dirt and grease must be initially removed from the surface. Even freshly grained aluminum plates will form a coating of aluminum oxide, or in the case of zinc, a film of basic zinc carbonate, $ZnCO_3 . 3Zn(OH)_2$. If the plates do not contain grease, these corrosion products are not harmful since they are basic and will tend to react with fatty acids of inks. However, it is general practice to sensitize the plate with a dilute solution of acid or acid salts. With aluminum plates, dilute aqueous solutions of sulphuric, oxalic, or citric acids are used. For sensitizing zinc, a water solution of nitric acid and alum is swabbed over the surface. Also, acetic acid and nitric acid, acetic acid and alum, or alum alone may be employed. One such solution comprises potash alum, 4 oz.; concentrated nitric acid, 1 oz.; water, 1 gallon. The thickness of the deposited film of sensitizing material increases with the amount of acid. Utilization of acid in quantities greater than that mentioned renders the film loose and friable. As a result the original image will not adhere to the plate. Properly cleaned metal readily receives the greasy ink of lithographic images.

The action of the gum arabic solution in desensitizing the non-printing areas has been the subject of some discussion.[4] One theory is that an insoluble film of aluminum or zinc arabinate is formed. However, it has been stated that this probability is doubtful. Gum arabic is a mixed calcium-potassium-magnesium salt of arabic acid, containing small amounts of free acid or acid salts.[5] Chemical action between this substance and a metal appears improbable.

An interesting part of the phenomenon is that for effective desensitization the gum film must be dried on the metal surface before the bulk of

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[4] H. S. Blunt, "Gum Arabic," London, H. Milford, 1929. R. F. Reed, P. W. Dorst and S. C. Horning, *Lith. Tech. Found. Bull.* No. 3, 1928. F. J. Tritton, *J. S. C. I.*, 1932, **51**, 299T; *Chem. Abs.*, 1932, **26**, 6163; *Brit. Chem. Abs.* **B**, 1932, 996.

[5] For a resume of the literature on this subject see G. L. Riddell, "A Physico-Chemical Study of Certain Aspects of Lithographic Printing," Thesis, London School of Printing, London, 1929; *Chem. Abs.*, 1931, **25**, 1107.

the gum is washed off again. Tritton[6] found that gum solutions of greater than 30 per cent concentration were equally effective. However, with more dilute solutions, drying before removing excess gum was said to be necessary. It has been suggested that a film of gum is adsorbed by the metal. Gum arabic was found to form an adsorbed film on zinc, aluminum, copper, silver, iron, tin, lead, glass and fused silica. The number and variety of substances upon which this action occurred seemed to preclude the explanation that the gum film might be produced by surface tanning in some way similar to that by which copper tans a gelatin surface.[7] If the film is formed by adsorption, it should, according to theory, be one or possibly two molecules thick.[8] However, experiments were stated to indicate that the films are composed of many molecular layers. Therefore it appears that the desensitizing effect of gum arabic may not be entirely understood.

To produce an image which will reject water and accept a good body of ink, it is essential that inks contain free fatty acids, since these acids are repelled by water. Tests made with a mixture containing 1 per cent acid, calculated as oleic acid, yielded only a moderately strong image.[9] When the acidity was greater than 4 per cent (as free oleic acid), a perfect image was reported to be obtained. In liquid lithographic drawing inks, which normally are made up with soap, the addition of free fatty acids was stated to be unnecessary and undesirable. The soap alone is capable of forming the image since all fatty acid soaps hydrolyze to some extent in water and liberate fatty acids. Addition of fatty acids has been reported to cause livering of coloring matter and neutral greases in the ink. Lithographic crayons, which are used for drawing the design directly on the metal, contain substances such as beeswax, shellac, tallow and lampblack, melted together and formed into pencils. In lithographic crayons and in transfer inks, soaps tend to reduce the water-resisting properties. According to Tritton, these media should contain free fatty acids to produce the image. It has been found that a higher acid value is required to produce a strong image with lithographic varnish than with a neutral ink to which free fatty acids have been added. Oleic acid slowly attacks zinc, with formation of zinc oleate, thus aiding in forming a water-repellent image. In the case of aluminum the chemical reaction is so slow that it was assumed that adsorption of the fatty acid takes place on the metal surface. These observations explain why a higher concentration of fatty acids is required in inks for lithography on aluminum than on zinc. Therefore, to prevent reduction of the image-forming capacity of the inks, addition of large quantities of basic substances such as magnesium carbonate, basic pigments or starch should be

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[6] F. J. Tritton, *J. S. C. I.*, 1932, **51**, 299T (part I), 307T (part II); *Chem. Abs.*, 1932, **26**, 6163; *Brit. Chem. Abs.* **B**, 1932, 966.

[7] H. M. Cartwright and F. J. Tritton, *Phot. J.*, 1927, **67**, 403; *Chem. Abs.*, 1927, **21**, 3568.

[8] See I. Langmuir, *J. A. C. S.*, 1916, **38**, 2221; 1917, **39**, 1848; *Chem. Abs.*, 1916, **10**, 3007; 1917, **11**, 2849.

[9] F. J. Tritton, *loc. cit.*

avoided. Other alkalies which have been proposed as substitutes for magnesium carbonate include lime, chalk, alumina, magnesium oxide or zinc oxide. Although free fatty acids may cause some scumming of lithographic plates, their presence in inks is said to be necessary to produce a satisfactory image.

As has been indicated in the above résumé, the wash-out solution removes the transfer ink with which the image originally is made. The areas to be printed subsequently are rolled up with a heavy machine ink. Wash-out solutions usually consist of bitumen dissolved in turpentine. For example, the solution may contain asphaltum powder 1 part, beeswax 0.25 part, tallow 0.25 part, benzene 1 part, turpentine 5 parts, oil of tar 0.25 part, lavender oil 0.6 part.[10] During the wash-out process, the adsorbed fatty acid layer is covered with a film of bitumen. However, a thin film of asphaltum alone does not readily reject water or gum; therefore wax and non-acid greases are included in the solution. The deposited film is less resistant to nitric acid than lithographic ink. Since neither ink nor bitumen is entirely acid-resistant, the image area generally is dusted with powdered rosin and French chalk before etching.

The initial desensitization of the non-printing areas with aqueous gum arabic was discussed previously. The adsorbed film of gum is said to be the most important agent in preventing the adsorption of fatty acids. A second method of desensitization comprises converting the sensitive surface of the metal, which is basic, into a neutral salt which does not adsorb fatty acids. This is the action of etching solutions. Before the acceptance of the idea of an adsorbed film of fatty acids, the desensitization of metal plates by phosphate etches was not understood clearly. It was suggested that the surface of the plate was roughened, thereby accelerating reaction between gum and metal with formation of zinc or aluminum arabinates.[11] It was thought that the etch created a porous film which took up the gum and kept the non-printing areas moist.[12]

Etches usually contain phosphates and deposit films of aluminum or zinc phosphates. The lithographic processes determine the compositions of the salt deposits. In the case of aluminum, the normal ortho-phosphate, $AlPO_4$, could be precipitated as it is insoluble in acetic acid, but soluble in mineral acids. One etch for aluminum consists of glacial acetic acid and phosphoric acid (85-per cent H_3PO_4) in water. Sometimes phosphoric acid is used alone. Also etches may contain neutral salts which serve to reduce the solubility of the aluminum phosphate. Sodium nitrate and ammonium nitrate have been proposed for this purpose.

Phosphoric acid alone is not entirely satisfactory for etching zinc. The metal effervesces readily in the presence of this acid and the deposit,

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[10] W. C. Browne, "Offset Lithography," National Lithographer, New York, 1922.

[11] H. A. Maddox, *Modern Lithographer*, 1918, **41**, 71.

[12] C. Blecher, "Lehrbuch der Reproduktionstechnik," Vol. I, W. Knapp, Halle A.-G., 1908.

i.e., normal zinc phosphate, $Zn_3(PO_4)_2$, is soluble in the acid. Etches for zinc generally are made by adding ammonium salts to the acid. Zinc ammonium phosphate, $ZnNH_4PO_4$, is deposited on etching. In some instances the etching mixture may contain no ammonium salt. For example, an aqueous solution of sodium and potassium phosphate, sodium and potassium nitrate and phosphoric acid (85-per cent H_3PO_4) has been advocated. Although phosphoric acid causes effervescence with zinc, this action is said to be considerably reduced by the presence of the phosphates and nitrates.

In addition to their application in etching, such solutions may be employed during the printing process. They are considered to be effective in the dampening water for reforming the film if it is damaged or wears away. Also the dampening water is kept somewhat acidic, thereby preventing the formation of soaps through interaction of fatty acids of the ink with alkaline water. If the latter reaction were to take place the ink and water would emulsify. It has been found that when the pH of the dampening water is above 7, the layer of fatty acid which is present on the surface of the dampening water contracts to a half sphere. Since the water film on the metal plate is very thin, the fatty acids may come in contact with the plate and cause scumming. To keep the dampening water below pH 6, additions of etch are advocated. A further use of etches is to remove any scum which has formed. This action depends upon the ability of the solution to penetrate ink, attack the metal or phosphate film, and lift the ink or scum.

The phenomenon designated as "oxidation" frequently occurs in the various stages of lithographic printing. Thus new plates may oxidize on storage. Plates left ungummed after printing or improperly gummed plates may show effects of this action. "Oxidation" has been stated to be corrosion from atmospheric oxygen, and occurs in irregular spots on the plate because of the presence of impurities. The latter, chiefly cadmium, lead or iron in zinc and iron or silica in aluminum, are electrochemically negative with reference to the main metal.[13] Therefore, in the presence of water, couples are set up which cause the zinc or aluminum to be oxidized. The aluminum oxide and basic zinc hydroxide or zinc carbonate which are formed, are ink-receptive. Unless the impurities are removed the reaction will continue until the surface of the plate becomes pitted. Zinc oxidation products may be removed by aqueous "sensitizing" solutions containing nitric acid and alum. Aluminum oxide is not dissolved easily even by "sensitizing" solutions prepared from water and sulphuric, oxalic, or citric acid. Phosphate or gum films temporarily separate the metal plate from atmospheric oxygen but do not prevent oxidation.

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[13] C. A. Kraus, "Properties of Electrically Conducting Systems," New York, Chemical Catalog Company (Reinhold Publishing Corp.), 1922.

LITHOGRAPHIC PRINTING COMPOSITIONS

Lithographic inks are said to be designed to fit the paper.[14] Rough or hard papers may be used, but soft paper, which is sized on both sides, is reported to be satisfactory for lithography.[15]

The lithographic printing compositions are very concentrated, since large volumes of ink cannot be handled practically in this process. As much pigment as possible is contained in a long and tacky vehicle.[16] The inks usually are prepared from water-insoluble ingredients to inhibit bleeding into the water on the non-printing areas of the plate. To prevent bleeding of water-soluble coal-tar dyes, the latter are employed in the form of insoluble lakes.[17] Lakes generally are sufficiently water-resistant so that bleeding does not occur. However, in certain instances, other methods are utilized to render the pigments water-resistant. For example, a small proportion of zinc white (1 per cent by weight) has been suggested to inhibit bleeding of barium lakes of Pigment Scarlet 3B and other azo dyes. Basic lead acetate, as an anti-bleeding agent, is employed with lakes of Naphthol Yellow, Quinoline Yellow and Tartrazine. Tannin, when employed with barium and tartar emetic lakes of Neptune Blue, Acid Green or Patent Blue, is stated to make these lakes insoluble in water. Fine grinding is recommended as an anti-bleeding procedure when using Lithol Red G.

The ingredients of lithographic inks should not emulsify readily with water. If the vehicle is too thin, this phenomenon may occur. When emulsions are formed, greasing and tinting produces a tinted scum on the uninked portions of the printed sheet. On the other hand, if the vehicle employed is too tacky and long, the paper may tear, or transfers may be lifted from the stone.

Smaller quantities of driers are employed in lithography than in typography. Since thinner ink films are utilized in lithography, rapidly drying compositions may require frequent washing of the form, thus decreasing the effective life of the latter. Manganese, cobalt or lead linoleates and tungates do not bleed readily into the water on the non-printing areas of the plate and generally are preferred as lithographic driers. Combinations of driers such as lead and cobalt linoleates and precipitated manganese borate are advocated.[18] For paste inks tereberic acid is recommended as a drier.[19]

The porosity of the paper and the crystalline structure or amorphousness of pigment and dried vehicle are important factors in drying. Uneven drying is said to be caused by rapid dessication of round particles of

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[14] H. G. Kriegel, "Encyclopedia of Printing Lithographic Inks and Accessories." New York, H. G. Kriegel, 1932.

[15] See Chapter 18.

[16] H. J. Wolfe, "Manufacture of Printing and Lithographic Inks," New York, MacNair-Dorland Co., 1933.

[17] For preparation of laked pigments see Chapter 6.

[18] H. J. Wolfe, *loc. cit.*

[19] *Farbe u. Lack*, 1931, 36, 125, 137, 161, 196, 209; *Rev. Paint, Colour, Varnish*, 1931, 4, 152.

drier.[20] The type of pigment influences the rate of drying of linseed oil.[21] Pigments may be divided into three groups with reference to their effect upon oxidation of oils. The first group include inert substances, such as silica (silex). The second group consists of materials which decrease the rate and amount of oxidation, *e.g.*, lithopone, titanium oxide, and barium sulphate. The third group comprises those pigments which retard the initial oxidation of the oil, but cause an increase in the total amount of oxygen absorbed, *e.g.*, white lead carbonates and sulphates.

Lead salts are said to act as pseudo-catalysts which promote the formation of autocatalysts, thereby increasing the rate of oxidation of oil when the latter is exposed to air. The catalyst is stated to be an oxidation product of the oil. Lead driers do not appear to have any effect on the total amount of oxygen taken up by the oil. However when tin plates are utilized lead driers should be avoided because of chemical action between the plate and drier.[22]

Iron salts have been suggested as pigments for use in lithographic compositions.[23] Ten parts of peroxide of iron and 6 parts of protoxide of iron in solution are said to form a printing ink.

Other ingredients have been proposed for use in lithography.[24] Thus, petroleum jelly, paraffin and asphalt are utilized. Turpentine, ethyl alcohol, methyl alcohol and acetone have been recommended as solvents for resinous constituents of inks. Glycerin is used to provide moisture by hygroscopic absorption from the atmosphere. As an ink-preservative, phenol has been recommended. Also, the latter may be reacted with aldehydes to produce resins for use in inks. In some instances camphor is employed as a resin-forming material. Starch is employed as a size and dextrine as an adhesive and binding agent for paper. Gum arabic is utilized to coat the non-printing areas of the plate. Acetic acid is used as an etching solution for the latter. Spermaceti, carnauba, and china waxes are employed as water repellents. Albumin has been suggested as an ingredient to increase the gloss of the printed material.

The coloring materials employed in multicolor printing usually are made from certain basic colors or tints.[25] In some instances, blends of six transparent colors are utilized.[26] These are 1 yellow, 2 reds, 2 blues and 1 gray. From these any desired shade may be produced.[27]

[20] G. Haegens, *Technologie d'Imprimerie*, 1937, **5**, 1131; *Rev. Paint, Colour, Varnish*, 1937, **10**, 186.

[21] *Farbe u. Lack*, 1931, **36**, 125, 137, 161, 196, and 209; *Rev. Paint, Colour, Varnish*, 1931, **4**, 152. F. H. Rhodes and A. E. vanWirt, *Ind. Eng. Chem.*, 1923, **15**, 1135; *Chem. Abs.*, 1923, **17**, 3922.

[22] G. Haegens, *Technologie d'Imprimerie*, 1937, **5**, 1131; *Rev. Paint, Colour, Varnish*, 1937, **10**, 186.

[23] J. Kircher, U. S. P. 110,048, Dec. 13, 1870; U. S. P. 119,154, Sept. 10, 1871; J. Rossman, *Am. Ink Maker*, 1930, **8** (8), 21; (9), 23; (10), 27; (12), 27; 1931, **9** (1), 25.

[24] J. J. Vandevelde, *Koninklijke Vlaamsche Acadamie voor Taal-en Letterkunde*, 1919, 493; *Chem. Abs.*, 1920, **14**, 3130; *Chem. Weekblad*, 1920, **17**, 468; *Chem. Abs.*, 1920, **14**, 3300.

[25] See: H. G. Kriegel, "Encyclopedia of Printing Lithographic Inks," New York, H. G. Kriegel, 1932.

[26] A. Rovira, *Gac. Artes Grafic. Libro Ind. Papel*, 1934, **12** (5), 13; *Chem. Zentr.*, 1934, **105** (2), 1847.

[27] Combinations of three colors have been proposed for trichromatic printing, which is the method employed by some lithographers. (M. Leeden, *Lith. Offset Print.*, 1934, **30**, 162; *Rev. Paint, Colour, Varnish*, 1934, **7**, 376.)

As a vehicle for colored pigments, a mixture of varnish, glycerin, tartar, an alkali salt and a resinous volatile oil has been suggested.[28] The latter substance was said to act as a binding agent for the ink. Also, a composite of drying oil, isinglass (gelatin), graphite and pigment was proposed as a lithographic ink.[29] The gelatin was heated with a polymerized drying oil at 130° C. until a fibrous material had formed. The latter was removed, and graphite incorporated into the clear solution. Pigment then was ground into this vehicle.

Resinous binding materials have been suggested as ingredients of lithographic inks.[30] For example, 150 parts of nitrocellulose, 50 parts of amyl lactate (or benzyl alcohol), 25 parts of an alkylbenzene, 25 parts of amyl alcohol, 325 parts of denatured ethyl alcohol, and 50 parts of lampblack may be employed. In general, the solvents for the resinous materials include compounds boiling between 180 and 350° C., such as alkyl-substituted benzenes or naphthalenes which are liquid at ordinary temperatures. Among the resins which may be employed with these solvents are those prepared from coumarone.[31]

A binder which has been advocated for lithographic inks contains a semi-fluid asphalt or petroleum tar.[32] These substances may be employed with linseed oil. Also, an aqueous solution of potassium dichromate, potassium prussiate, iron tannate, and aniline is stated to aid in binding gelatin inks designed for use on stone or zinc plates.[33]

A lithograph composition for machines having wiping mechanisms, may be prepared from 235 parts of a low-viscosity nitrocellulose, 30 parts of castor oil, 100 parts of phthalic acid diethyl ester, 200 parts of phthalic acid dimethyl ester, 125 parts of ethyl benzoate, 60 parts of dammar resin, and 250 parts of zinc white.[34] This ink is said to produce satisfactory prints when small batches are continuously printed. However, if large batches are to be run, the water on the non-printing surfaces may withdraw soluble substances from the lacquer. The wiping action becomes less effective under these circumstances, and the ink-repellent surfaces may change their characteristics so as to start printing.

Solutions of alkyd resins may be used in lithographic ink.[35] One such ink was prepared by mixing 25 parts of phthalic acid-glycerol and 75 parts of succinic acid-glycerol condensation products. The whole was then dissolved in 100 parts of aceto-ethyl ester and 100 parts of denatured alcohol and ground on a ball mill at 140° C. for 2 hours.

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[28] J. Adelsberger and H. Friedmann, U. S. P. 710,233, Sept. 30, 1902, to S. Wechsler.

[29] W. G. Dewsbury and A. Davies, U. S. P. 2,014,760, Sept. 17, 1935; *Chem. Abs.*, 1935, **29**, 7678.

[30] M. M. Wilson, U. S. P. 2,078,170, Apr. 20, 1937; *Chem. Abs.*, 1937, **31**, 4515.

[31] J. Marcusson, *Chem. Ztg.*, 1919, **43**, 93, 109, 122; *Chem. Abs.*, 1919, **13**, 2607.

[32] O. G. Holt, U. S. P. 412,184, Oct. 1, 1889; J. Rossmann, *Am. Ink Maker*, 1930, **8** (8), 21, (9), 23; (10), 27; (12), 27; 1931, **9** (1), 25.

[33] I. Ramsdell, U. S. P. 345,448, July 13, 1886; J. Rossman, *Am. Ink Maker*, 1930, **8** (8), 21; (9), 23; (10), 27; (12), 27; 1931, **9** (1), 25.

[34] British P. 335,074, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, **25**, 1399; *Brit. Chem. Abs.* **B**, 1930, 1120; *Rev. Paint, Colour, Varnish*, 1930, **3**, 244.

[35] E. Knebel, A. Hügel and H. Steinmeyer, German P. 591,456, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 2553; *Rev. Paint, Colour, Varnish*, 1934, **7**, 196.

Some lithographic inks contain wetting agents with drying oils and pigment. The surface active substances wet the pigment and drying oil, forming a stable dispersion. Wetting agents such as the mahogany sulphonates secured from mineral oils are used. One ink of this type comprises 1 part of Lithol Red and 9 parts of No. 00 varnish containing 5 per cent by weight of mahogany sulphonates.[36]

Refined coal tar has been recommended for use in lithographic ink.[37] To free the crude tar from disagreeable odors, 100 parts of coal tar are treated with 5 parts of caustic soda, followed by washing with 10 parts of hot water. The mixture is allowed to cool, and the water drawn off. The residue then is admixed with pigment and coal oil. Suggested pigments include manganese dioxide, aniline black, and lampblack. Instead of coal oil, turpentine, wax, fat, lard or tallow may be employed.

A paste stated to convert typographic inks into lithographic composition was prepared from 100-160 parts of gum dammar, 25-80 parts of petroleum, 290-430 parts of glycerol, and 120 to 260 parts of linseed oil varnish.[38] The mixture is added to a typographic composition until the whole is sufficiently viscous for lithography. Another composition, one part of which may be admixed with 5 to 15 parts of typographic ink, is said to contain 73 parts of petroleum oil, 21 parts of paraffin wax, 3 parts of magnesium carbonate and 3 parts of oleic acid.[39]

Bronze lithographic inks may contain bronze powder and synthetic resins dispersed in a drying oil. An illustrative example of such an ink is composed of 10 parts of esterified resin (*e.g.*, alkyd resin), 60 parts of linseed oil, 40 parts of tung oil, 5 parts of sodium naphthalenesulphonate, 5 parts of dextrin, 1 part of lead resinate, and 100 parts of aluminum-bronze powder.[40]

Instead of sulphonated wetting agents, turpentine and wax have been advocated.[41] In some instances, the vehicle may contain water in addition to lithographic varnishes. For example, an aqueous solution of borax, cresylic and sulphuric acids was admixed with a lithographic varnish. Flour then was incorporated in the oil-water composite to furnish a vehicle for gold bronze.[42]

Fluorescent inks may be employed for lithographic printing.[43] One such ink was prepared by dissolving 49 parts of dry white shellac, 1 part of Auramine O, 16 parts of butyl acetate, 3 parts of Rhodamine B in

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[36] H. Heckel, U. S. P. 1,906,961, May 2, 1933, to Twitchell Process Co.; *Rev. Paint, Colour, Varnish*, 1934, **7**, 103; *Brit. Chem. Abs.* **B**, 1934, 157. See also Chapter 13.

[37] J. Kircher, U. S. P. 132,840, Nov. 5, 1872; J. Rossman, *Am. Ink Maker*, 1930, **8** (8), 21; (9), 23; (10), 27; (12), 27; 1931, **9** (1), 25.

[38] H. Friedmann, U. S. P. 824,475, June 26, 1906; J. Rossman, *Am. Ink Maker*, 1930, **8** (8), 21; (9), 23; (10), 27; (12), 27; 1931, **9** (1), 25.

[39] O. E. Harder, U. S. P. 1,714,166, May 21, 1929; *Chem. Abs.*, 1929, **23**, 3587; *Rev. Paint, Colour, Varnish*, 1929, **2**, 282; *Brit. Chem. Abs.* **B**, 1929, 610.

[40] Czechoslovak P. 47,430, 1934, to Auerbach, Weissberger and Spol; *Chem. Zentr.*, 1934, **105** (2), 1851; *Rev. Paint, Colour, Varnish*, 1934, **7**, 377.

[41] German P. 604,019, 1934, to Gebr. Jaenecke and F. Schneemann, Kom.-Ges. auf Aktien; *Chem. Abs.*, 1935, **29**, 947; *Rev. Paint, Colour, Varnish*, 1935, **8**, 109; *Chem. Zentr.*, 1935, **106** (1), 1131.

[42] M. Baer, French P. 681,201, 1929; *Chem. Abs.*, 1930, **24**, 4410.

[43] J. L. Switzer, U. S. P. 2,152,856, April 4, 1939.

38 parts methyl alcohol. Thirty-three parts of aluminum hydroxide and 76 parts of saponified linseed oil were admixed with the alcoholic solution on a roller mill until the alcohol evaporated. It has been reported that the ingredients of this ink which fluoresce in the ultraviolet electromagnetic waves are the Auramine O and Rhodamine B. Each of these substances must be present in a certain optimum quantity for maximum fluorescence. If either component is present in a greater or lesser amount, decreased emanation will result. The optimum fluorescences are additive for different substances. Hence, if optimum amounts of Rhodamine and Auramine are employed, a much greater amount of fluorescence is said to result than with either ingredient alone.

For autographic (lithographic) printing, *i.e.*, making facsimiles, special inks have been recommended.[44] The latter may be prepared by heating virgin wax, and adding a mixture of soap, shellac and dragon's blood to the melt. The whole then is ignited for approximately 5 minutes. The ignited mass subsequently is dissolved in hot water. Such an ink may be manufactured from 10 parts of virgin wax,[45] which is heated nearly to ignition. At the high temperature attained in this manner, 8 parts of soap, 16 parts of shellac and 8 parts of dragon's blood are added. The mixture of these several ingredients is ignited for 5 minutes. The product is dissolved by boiling with 150-200 parts of water. The ingredient known as dragon's blood is an exudate from *draoema draco* or *calamus draco* trees. It is described as a red pigment resin, and its main tinctorial component is said[46] to be composed of the benzoic and benzoylacetic esters of dracoresinotannol.

An alternate method of making autographic (lithographic) ink is to fuse gum copal with oil. The product is admixed with wax and tallow. The composite then is ignited. Soap, shellac, mastic and tallow are incorporated with the ignited material, and ignition is continued. Subsequently the flame is extinguished, the whole is cooled, and then ignited again and allowed to burn until the volume is reduced to one-quarter of the original volume. For printing, 1 part of the residue is dissolved in 400 parts of water.

Detection of alterations made in bank checks and other permanent documents often is an aid in uncovering possible forgeries or frauds. An ink which was reported to indicate changes subsequent to printing has been proposed.[47] The printing material comprises copperas (ferrous sulphate), potassium dichromate, hydrochloric acid, sulphur flowers, zinc white and black union dye.[48] The mixture, after removal of water and alcohol, is ground into a lithographic varnish. The ink was stated to

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[44] *Deutsche Ind. Ztg.*, 1870, 26; *Chem. Zent.*, 1870, 1 (3), 87.

[45] Virgin wax is pure white wax. (T. L. Stedman, "Practical Medical Dictionary," William Wood and Co., Baltimore. 1933.)

[46] E. Thorpe, "Dictionary of Applied Chemistry," London, Longmans Green & Co., 1913, Vol. **IV**, 279.

[47] J. Hendricks, U. S. P. 239,954, July 21, 1880.

[48] Black union dye is the alcohol extract of logwood.

print a deep black, and to become red if treated with acids used in ink eradicators.

Gum elemi is suggested for utilization in photolithographic inks.[49] The inks are said to be applicable for printing with zinc plates and stone. For example, the ink may be prepared by melting and mixing together colophony (dissolved in turpentine), asphalt, yellow wax, suet, gum elemi, Marseilles soap, medium linseed oil varnish, and lampblack. Venice turpentine and a transfer ink may be employed as a substitute for the soap. It was stated that the ingredients should be moisture free, and that the vapors should not be permitted to burn during preparation.

Decalcomanias frequently are made by lithographic processes.[50] Briefly, the impression is produced on gum which has a layer of starch between it and the paper.

Lithographic inks are employed for metal, glass, ceramics, Cellophane, plastics, rubber, cloth, food, napkins, blotting paper, shellac surfaces, and vegetable fibers. Some of these compositions require heat treatment after application.[51]

LITHOGRAPHIC SURFACES

As described previously, the process of lithography involves making prints from flat or slightly etched surfaces, which are subdivided into ink-adherent, printing areas and ink-repellent, non-printing portions. Various coatings have been applied to these plates, but they are not considered raised surfaces.

The plates may be of stone, aluminum, zinc or wood.[52] Non-printing areas usually are moistened with water. Greasy ink will be repelled to the printing areas, since the latter attract greasy or fatty printing compositions. Printing areas are coated with ink-adherent material.

The aluminum or zinc plates are "grained" or roughened by grinding or chemical action. This is the first step in preparing either stone, zinc or aluminum plates.

A method of graining zinc lithographic plates with chemicals has been suggested.[53] The plate is treated with a cleansing mixture containing phosphoric acid, butyl alcohol and sulphonated Lorol.[54] Subsequently the printing surface is washed with cold and then with hot water. After rinsing, the plate is immersed for 30 or 40 minutes in an aqueous solution composed of zinc carbonate, ferrous sulphate and zinc dihydrogen phosphate. The temperature of the solution is maintained at 190-200° F.

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[49] K. Kampmann, *Phot. Correspondenz*, 26, 564; *J. S. C. I.*, 1890, 9, 413.

[50] The methods of manufacture are discussed in Chapter 12.

[51] Details of such processes are described in Chapter 14.

[52] A wood plate coated with chromatized gelatin is described by J. N. Lambert, British P. 1,124, 1871; *Chem. Zentr.*, 1872, 3, 254; *Ber.*, 1872, 5, 63.

[53] W. S. Field, U. S. P. 2,126,181, Aug. 9, 1938; *Chem. Abs.*, 1938, 32, 7620.

[54] "Lorol" is the trade name of a commercial product containing a mixture of aliphatic alcohols formed by the high-pressure hydrogenation of coconut oil. (J. R. Ruhoff, *J. A. C. S.*, 1933, 55, 3889.) (Carleton Ellis, "Hydrogenation of Organic Substances," New York, D. Van Nostrand Company, 1930.) (Carleton Ellis, "Chemistry of Petroleum Derivatives," New York, Reinhold Publishing Corp., 1937.)

Aluminum or aluminum alloy lithographic plates may be treated in electrolytic baths so that they will retain water readily on the ink-repellent non-printing areas. The foils are suspended in a 0.5-per cent acid solution containing a mixture of lactic and oxalic acids. The bath has conductor bars connected to an alternating current supply and other bars are connected with positive terminals of a direct current supply. A lead electrode is connected to the negative terminal of the direct current supply. Both surfaces of the printing foils are said to receive treatment by this method.[55]

The methods employed in applying designs to the plates are: by drawing the image with crayon (in reverse), by decalcomania [56] and by photomechanical means.[57] Lithographic chalk, India ink, or Conté pencils may be employed in drawing the designs.

Conté pencils contain no grease and are employed for temporary drawings, whereas lithographic chalk is greasy and is used for the final drawing. The former usually are red in color whereas the latter are black.

Also, India ink may be employed for drawing designs on lithographic stones. The inks generally contain beeswax, soap, shellac and pigment.[58] A number of methods have been suggested for producing this ink. One composition is made by forming a stiff paste of lampblack with an aqueous solution of gum arabic (or tragacanth). Another is prepared by mixing bleached beeswax, water-free grain soap, orange shellac, and carbon black. In some instances India ink may comprise mutton tallow, yellow beeswax, white grain soap, orange shellac, mastic, lampblack, and turpentine. Instead of turpentine and mastic, soda ash sometimes is utilized. Also, tallow soap may be substituted for a grain soap. India inks usually are fused during the mixing process.

Lithographic chalk or crayon is used for making designs on lithographic stones. The chalk may be prepared from yellow beeswax, light grain soap, lampblack, potassium nitrate (dissolved in water), and oil soap. In some instances orange shellac, mutton tallow, and an aqueous solution of soda ash may be incorporated.

In drawing lithographic images on stone or grained metal surface, the figures may be made (in reverse) with a quick-drying, grease-resisting ink.[59] One such ink is reported to contain water, phosphoric acid (dissolved in water-soluble gum), lampblack water-color, lampblack, oxalic acid and glycerol.

When the image is completed the stone and the design are coated with a water-repellent, greasy printing ink. The latter may comprise asphalt, turpentine, black printing ink and ether. Subsequently, the ink-coated

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[55] H. Wolff, British P. 481,252, 1938; *Chem. Abs.*, 1938, 32, 5712.

[56] See Chapter 12.

[57] See Chapter 11 for discussion of photomechanical processes.

[58] H. Hadert, *Farben-Ztg.*, 1926, 31, 2776; *Chem. Abs.*, 1926, 20, 3824.

[59] E. Aurich and F. Wolf, British P. 176,599, Jan. 26, 1921; *Chem. Abs.*, 1922, 16, 2420.

design and stone are treated with phosphoric acid in water-soluble gum. The whole then is washed with turpentine to remove the greasy ink from the image. The latter is somewhat resistant to the composition because of the ink with which it was drawn. The plate and coating are washed with water to remove the ink with which the design originally was made. The design remains as a series of grooves in the gummed coating, the bottom of the grooves being the lithographic stone itself. On printing, a light design on a dark ground is secured.

Various compositions have been proposed for coating the non-printing areas of lithographic plates. Gum arabic or albumin solutions, containing ammonium chromate, have been suggested for this purpose.[60] For example, the solution may be prepared by dissolving 1 part of ammonium bichromate in 16 parts of water and then incorporating in the mixture 60 parts of a freshly prepared clear aqueous solution of gum arabic. The latter solution should have a specific gravity of 1.115 at 60 to 70° F. (14° Bé.). The whole is poured on the plate and rubbed to dryness with a clean rag. The plate then is exposed to a 25-ampere electric lamp, with 0.5-inch white flame carbons, at a distance of 48 inches. For aluminum plates the time of exposure is 8.5 minutes, for zinc plates 10 minutes. The exposed materials are washed with water to remove the non-adherent coatings.

Table 30 indicates the relative proportions of the ingredients employed in chromatized albumin solutions. It may be noted that ammonia is used to keep the albumin in solution.

Table 30.—Relative Proportions of Ingredients in Representative Formulas for Dichromatized Albumin.[61]

Calculated Dichromate: Albumin Ratio	Approximate Solids Content of Solution, Avoirdupois Oz. per Liquid Oz. of Solution	Ammonia Added, Liquid Ounces of 28% Solution for Each Avoirdupois Ounce of Dichromate
.057	.133	0.12
.095	.286	Till Yellow
.14	.125	2.0
.16	.192	Sometimes a little
.25	.164	Till Yellow
.25	.156	0
.25	.104	0
.25	.098	0.8
.25	.078	0
.25	.078	1.2
.25	.078	2.0
.30	.079	0.03
.30	.065	0
.33	.125	0
.33	.111	1.5
.40	.068	0.6
.50	.125	0.75
.57	.172	1.0
.57	.141	1.0
.57	.100	0

A plate oil or varnish, containing rosin, turpentine and linseed oil, has been recommended for preparing lithographic stones or plates prior

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[60] R. F. Reed, *Lithographic Technical Foundation, Research Bulletin* No. 5; *Am. Ink Maker,* 1935, 13 (8), 35; *Rev. Paint, Colour, Varnish,* 1935, 8, 402. *Lithographic Technical Foundation, Research Bulletin* No. 6.

[61] R. F. Reed and P. W. Dorst, *Lithographic Technical Foundation, Research Bulletin* No. 6, 27.

to printing and for diluting the inks.[62] Such mixtures are termed plate oils or plate varnishes. The latter generally are produced by warming 1 part of turpentine and then adding to the hot liquid 1 part of linseed oil and 3 parts of powdered rosin. The product is said to be rapid-drying.

Printing forms for lithographic work may be prepared on matted plates, rolls of glass, porcelain, or enamel. These materials first are washed with an aqueous solution of beet sugar and alum, and the excess liquid is dried. An image made with an ink, containing gallic acid and an iron salt, is transferred to the surface of the plate. After transference the plate is treated with a solution containing glycerol and boric acid. The whole then is rolled over with printers' ink.[63]

A printing surface which has been reported to withstand manipulating has been advocated.[64] The plate may be prepared on zinc. An image is produced on the metal with a fatty transfer ink. Gum then is applied to the non-printing areas and when the gum is dry, the ink is washed out with a fat solvent. A mixture of 80 parts shellac, 30 parts boiled (No. 0) linseed oil, 30 parts castor oil, 600 parts ethyl alcohol, 200 parts turpentine, 10 parts manganese borate, 5 parts aniline, 10 parts of mastic, and 100 parts of xylene subsequently are placed on the gummed inkless surface. The xylene, alcohol, turpentine and aniline evaporate, leaving a hard, metal-adherent substance in the printing areas of the plate.

When printing is done with amalgamated plates, modifying agents are added to the inks to maintain the plates in an amalgamated state.[65] For example, a saturated glycerol solution containing 10 parts of mercurous nitrate and 1 part of silver nitrate may be admixed with lithographic ink in a volume ratio of ink to glycerol solution of 3:1. The amount of mercury on the plate is stated to be kept constant by this method. In some instances linseed oil is saturated with a 5-per cent aqueous solution of mercurous nitrate. The coloring matter is incorporated into the mixture of linseed oil and mercurous nitrate. The mercurized area of the plate is non-printing.

An ink recommended for use in pantome printing (with mercury coated non-printing areas) comprises 52.25 parts of polymerized linseed oil, 35 parts of carbon black, 9 parts of Prussian Blue, 1.5 parts of mercury, and 52.25 parts of an aqueous solution (containing 2.5 to 5 per cent borax and 5 to 10 per cent shellac). The mercury was immersed in linseed oil (fatty acid content of 7.5 to 9 per cent). The mercury in the composition was reported to replace quicksilver lost from the plate and to prevent "scumming."[66] As a diluent, "white spirits" (gasoline) may be employed.

[62] C. Collins, U. S. P. 192,739, June 1, 1876; J. Rossman, *Am. Ink Maker*, 1930, 8 (8), 21; (9), 23; (10), 27; (12), 27; 1931, 9 (1), 25.

[63] German P. 250,203, 1910, to H. Hurwitz Co.; *Chem. Abs.*, 1912, 6, 3501. See also Chapter 12.

[64] A. Schlessinger, British P. 407,047, 1934; *Chem. Abs.*, 1934, 28, 4851.

[65] H. Renck, German P. 646,485, 1937; *Chem. Abs.*, 1937, 31, 6490; *Rev. Paint, Colour, Varnish*, 1937, 10, 342; German P. 561,283, 1929; *Chem. Abs.*, 1933, 27, 1216.

[66] A. R. Trist, British P. 307,535, 1927; *Chem. Abs.*, 1929, 23, 5338; *Brit. Chem. Abs.* B, 1929, 365.

Difficulties arising in lithographic printing with tin plates are said[67] to be caused by grease rather than by the yellow coatings formed thereon. The yellow stain, on tin plates, is mainly produced by anodic oxidation as a result of differential aeration. Dilute aqueous sodium carbonate is stated to remove yellow stains, as well as any grease which may be present on the plate.

To keep the non-printing portions of metallic plates ink-resistant, it has been suggested that an electric current be applied to the plate and maintained at such a voltage that the plate is etched so as to repel the ink.[68] The voltage is applied across the dampening roller and the plate. The roller is of the same metal as the plate, and when the voltage is kept at a low value, metal is removed very slowly from the roller and electrodeposited on the non-printing portions of the plate.

When it is desired to make a sample print (on paper) of a design intended for use on some other material (*e.g.*, linoleum), a special procedure has been advocated.[69] The dots comprising the designs on plates, for paper printing, are larger than the corresponding dots for linoleum. These differences exist because of the different spreading powers of ink on these materials.

It was suggested that the design be printed upon an aluminum (or zinc) plate with the aid of oil pigments. The plate then was etched before the ink dried, and the plate washed free of etching solution. The lithographic plate may be employed for making impressions on paper. The method described above was recommended as general whenever the material of the sheets receiving the printed impression is to be changed.

Dampening Non-printing Areas. The dampening operation in lithography is one which requires careful control. At most, only a thin film of moisture is required on the non-printing areas. To maintain the proper printing conditions calls for skillful pressmanship. Several methods have been suggested to obviate the difficulties of this procedure.

Wechsler[70] proposed an ink mixture which would allow continuous dry printing without the necessity of moistening or wiping the printing plate. This composition consisted of the following: 500-550 parts of glycerin, 5-20 parts sodium carbonate, 12-20 parts of cream of tartar, 150-180 parts of turpentine and 270-370 parts of varnish. After the formation of the image the non-printing areas may be made glycerin-receptive by means of a 0.5-1.0 molar solution of ammonium nitrate and ammonium phosphate.[71] A thin layer of glycerin then is applied to these surfaces. Using a felt or sponge-rubber covered roller and an ink which is somewhat acid, a hundred or more prints were said to have been made

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[67] C. E. Beynon, C. J. Leadbeater, and C. A. Edwards, *Tech. Pub. Intern. Tin Research Development Council,* 1935, Ser. D, No. 1; *Chem. Abs.,* 1935, 29, 6871; *Brit. Chem. Abs.* B, 1935, 458; *Rev. Paint, Colour, Varnish,* 1935, 8, 516.

[68] H. N. Durham, U. S. P. 1,895,125, Jan. 24, 1933.

[69] M. R. Wood, U. S. P. 1,135,749, April 13, 1915; *Chem. Abs.,* 1915, 9, 1551.

[70] S. Wechsler, British P. 12,826, 1901; *J. S. C. I.,* 1902, 21, 782.

[71] G. S. Rowell, U. S. P. 1,976,039, Oct. 9, 1934, to Multigraph Co.; *Chem. Abs.,* 1934, 28, 7561.

before replenishing the glycerin. Tinting or toning of the highlights may occur but this was stated to be cleared up by use of aqueous salt solution. Glycerin was reported to adhere to the metal surface during the removal of excess ink, to act as a protective coating for the plate, and to render the metal less sensitive to chemical reaction with the paper.

One method of applying an extremely thin uniform layer of glycerin to the non-image area utilizes a thixotropic glycerin gel-covered roller.[72] This composition is made by allowing 100 parts of gelatin to soak for approximately 12 hours in 250 parts of water containing 20 parts of chloral hydrate. Three hundred parts of water then are added and the mixture heated at 60-65° C. until solution takes place. The product is mixed with equal parts of dissolved gelatin and glycerin to form the gel. A felt or sponge-rubber covering for the roll is the surface upon which the gel is placed. The thixotropic properties of the gel were stated to allow it to be liquefied by frictional contact with the plate, thereby depositing a thin, unbroken film of glycerin upon the areas which were not to be printed.

In some instances lithographic ink is admixed with a grease-resisting material such as glycerin or glycol and a deliquescent substance, *e.g.*, calcium chloride.[73] The calcium chloride (or calcium nitrate, calcium phosphate, sodium lactate or sodium magnesium chloride) is added to the warmed polyhydric alcohol. Solvents may be used to help mix these substances with the ink. One such composition comprises 40-50 parts of glycerin, 5-10 parts calcium chloride, 2-5 parts potassium phosphate, 2-4 parts carbolic acid, 4-10 parts liquid gum (gum arabic or tragacanth) and 140-180 parts lithographic ink.

Another emulsion-type ink has been advocated to wet the portions of the lithographic stone which are to have ink repelling properties.[74] The need for moistening apparatus was said to be eliminated by emulsifying greasy ink with an ink-repellent aqueous solution. For example, an ink may be prepared by mixing 16 parts of greasy lithographic ink with 0.5 part of a saturated solution of sodium hyposulphite, 0.5 part of glycerin, 0.5 part of rubber cement, and 0.5 part of nicotine (in solution with 0.25 part of benzene).

When this emulsion is applied to a lithographic plate, the greasy ink is stated to deposit upon the printing portion of the plate, while the aqueous phase, which separates from the ink, wets the non-printing areas.

An emulsion ink, containing glycerin, ammonium phosphate, ammonium nitrate, varnish and lampblack, has been recommended for planographic printing. The ink is said to eliminate the necessity for a moistening apparatus.[75] After the plate is grained and the image applied, the

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[72] G. S. Rowell, U. S. P. 1,992,966, March 5, 1935, to Multigraph Co.; *Chem. Abs.*, 1935, 29, 2632.

[73] F. C. Fitzgerald, British P. 150,809, 1920; *Chem. Abs.*, 1921, 15, 2199. Also U. S. P. 1,406,837, Feb. 14, 1922; *Chem. Abs.*, 1922, 16, 1875.

[74] J. V. Mehl, U. S. P. 1,958,311, May 8, 1934; *Chem. Abs.*, 1934, 28, 4255.

[75] V. Diets, U. S. P. 1,892,875, Jan. 3, 1933, to Multigraph Co.; *Chem. Abs.*, 1933, 27, 2262. U. S. P. 1,741,758, Dec. 18, 1929; *Chem. Abs.*, 1931, 25, 3139.

plate is washed with a solution containing 1 part of ammonium nitrate, 4 parts of ammonium phosphate, 20 parts of glycerin, and 75 parts of water. This treatment causes the non-printing portions of the plates to become ink-repellent.

The printing composition consists of an emulsion of glycerin and varnish and is composed of 1 part of ammonium nitrate, 4 parts of ammonium phosphate, 20 parts of glycerin, 52.5 parts of varnish, and 22.5 parts of lampblack. When the ink is applied to the plate, the emulsion is said to be broken. The glycerin goes to the non-printing portions of the plate and is held by the attraction of the inorganic salts for glycerin. The varnish and pigments deposit on the printing portions of the stone.

Also it has been recommended that sulphates be used to moisten the non-printing areas. The method is outlined below. After the ink image has been made upon an aluminum plate, the surface is covered with a 5-per cent aqueous solution of the nitrate or sulphate of aluminum, nickel, iron or copper. Upon drying, a thin layer of crystals or particles is deposited upon the fat-free areas. This film prevents ink from adhering on the non-image areas. The salt crystals are replenished by adding an aqueous solution of metallic nitrate or sulphate (3-8 per cent) to the ink. It was reported to be possible to make tone-free prints, using aluminum plates, without mechanical dampening of the non-image areas.

An ink, prepared especially for work with chilled presses, is said [76] to give better impressions than are obtained with compositions employed on steam-moistened stones. The method involves chilling the press below the dew point of the surrounding air. This results in condensation of atmospheric moisture on the non-printing parts of the lithographic stone. However, inks containing stearic acid, tallow, gum mastic, paraffin and beeswax would not be satisfactory on chilled presses because they would tend to solidify.

A blue ink, said to be applicable under these circumstances, contains 35 parts of Milori blue, 18 parts of plate oil, 1 part of wool fat, and 3 parts of gum arabic emulsion. The plate oil is made by burning linseed oil with hot irons, until some of the greasy characteristics of this liquid are eliminated.[77]

LITHOGRAPHIC INK MODIFYING AGENTS

As thinning agents for photolithographic or collotype inks, terpineol, terpinyl acetate, linseed oil, rosin oil or turpentine have been suggested.[78] Terpineol or terpinyl acetate were recommended for photolithographic compositions containing boiled linseed oil, varnish and pigment. Usually

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[76] J. G. Goedike, U. S. P. 1,935,629, Nov. 21, 1933; *Chem. Abs.*, 1934, 28, 917. U. S. P. 2,110,216, Mar. 8, 1938; *Chem. Abs.*, 1938, 32, 3525.

[77] The ink described above is of the emulsion type. Other lithographic inks of this class are described in Chapter 13.

[78] F. F. Renwick, British P. 472,938, 1937, to Kemitype Co.; *Chem. Abs.*, 1938, 32, 1955; *Brit. Chem. Abs.* B, 1938, 693. French P. 824,938, 1938; *Chem. Abs.*, 1938, 32, 5648.

5 to 25 per cent, by weight, of thinner is recommended for use in inks. Rapid drying is said to result when using the terpinyl acetate because of its volatility. It was stated that white colors are not affected by these thinners.

A thinner for lithographic ink, which is reported to prevent blistering or peeling of the dried ink, to maintain color strength, and to promote the production of smooth impressions, has been proposed.[79] For example, a mixture of 20 parts of tallow, 60 parts of lard, 10 parts of beeswax, 2 parts of lavender, and 8 parts of starch may be utilized. When yellow or red colors are employed, 1 ounce of the thinner, 5 pounds of ink and 1 ounce of varnish are the suggested quantities. For black or brown compositions, 1 ounce of the above thinner to 5 pounds of ink are used.

Another diluent for lithographic compositions comprises 280 parts of varnish, 540 parts of glycerol, 6 parts of alkali salt, 14 parts of tartar, and 160 parts of volatile resinous oil.[80] The resinous oil acts as a binder.

A suggested tone-protecting agent for lithography consists of an aqueous solution of phosphoric acid, tartaric acid, sodium chloride and gum arabic.[81] The composition is recommended for color printing.

Modifying agents, for producing prints with a raised dull finish, were stated to be secured from carbohydrates (sugar), reducing agents (sulphur), bodying agents (alum), and a fusible ingredient (naphthalene).[82] While the prints (on the paper) are moist, a powdered varnish material of the above ingredients is sprinkled over the wet ink, and heat is applied to render the powder soluble in the ink. Lycopodium may be employed as a component of the powder to hasten drying. The ink, after being dusted, is heated so that the naphthalene will melt. Also, heating promotes reduction by the sulphur. Prints made in this manner are reported to resemble work produced by embossing dyes.

Water color effects have been reported obtainable with lithographic procedures.[83] After the print has been made, the picture is covered with varnish and a transparent drying oil. Before this coating has dried, potato meal is applied to the surface. After the absorption of the meal has proceeded as far as possible, excess meal is removed. Images produced in this manner are said to have subdued, plastic and uniform coloring.

SOLVENTS FOR LITHOGRAPHIC INKS

Trichloroethylene has been recommended as solvent for inks for high-speed printing. Also, the halide is non-inflammable. Approximately 42,000 impressions per hour is reported as being a common rate of production with inks containing trichlorethylene. As the paper web leaves the press,

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[79] J. J. Schepp, U. S. P. 669,552, Mar. 12, 1901.

[80] J. Adelsberger and H. Friedmann, U. S. P. 710,233, Sept. 30, 1902, to Simon Wechsler; J. Rossman, *Am. Ink Maker*, 1930, 8 (8), 21; (9), 23, 41, 43; (10), 27, 29, 41; (12), 27, 29; 9, (1), 25, 27.

[81] J. Rull, German P. 240,836, 1911; *Chem. Abs.*, 1912, 6, 2150.

[82] A. J. Nemeo, U. S. P. 1,123,917, Jan. 5, 1915; *Chem. Abs.*, 1915, 9, 763.

[83] C. Fuchs, German P. 243,030, 1911; *Chem. Abs.*, 1912, 6, 2298.

fans remove the vapors of the halide. The latter are absorbed in activated carbon. A recovery of 55 to 65 per cent of solvent is reported. The fans are said to rotate at a rate of 500 meters per minute to evaporate 30 kilograms of trichlorethylene per hour.

Alkyl-substituted benzenes and naphthalenes boiling in the range 180-350° C. have been recommended as solvents for printing inks.[84] These substances are stated to have high solvent power for binders, gums and resins, and to have low surface tension, low viscosity and moderate evaporation rates. An illustrative example of such an ink contains 150 parts nitrocellulose, 50 parts amyl lactate, 25 parts alkyl-substituted benzene, 25 parts amyl alcohol, 325 parts ethyl alcohol and 50 parts lampblack.

A solvent, which is said to be adaptable to lithography, contains petroleum distillates, pine oil, ester gum, and castor oil.[85] The product is reported to have properties practically identical with those of turpentine, except that this solvent is not a dermal irritant, whereas turpentine causes dermatitis.

The ingredients of the above material must possess the following properties:

Substance	Flash Point	Boiling Range
Motor gasoline	Below 32° F.	110 to 400° F.
Benzene	About 95° F.	210 to 400° F.
Stoddard solvent (Naphtha for dry-cleaning)	95° F.	300 to 380° F.
Dry cleaner's naphtha	37° F.	200 to 230° F.
Pine oil (Water-free: sp. gr. .930-.960 at 68° F.)	160° F.	386 to 426° F.

Ester gum must be light in color and have an acidity of from 6 to 7. Castor oil must be refined and free from rancidity.

One such solvent was prepared by mixing 2 lbs. of ester gum and 1 lb. of castor oil in a 2-gallon enameled bucket. Agitation and heat were applied, at a temperature of 200 to 250° F., and stirring was continued until the ester gum was dissolved. The fire was extinguished as soon as solution was achieved, and 10 pounds of anhydrous pine oil were added to the solution, agitation being applied during and after the addition. One pound of the product resulting from the above process was added to 1 gallon of petroleum distillate.

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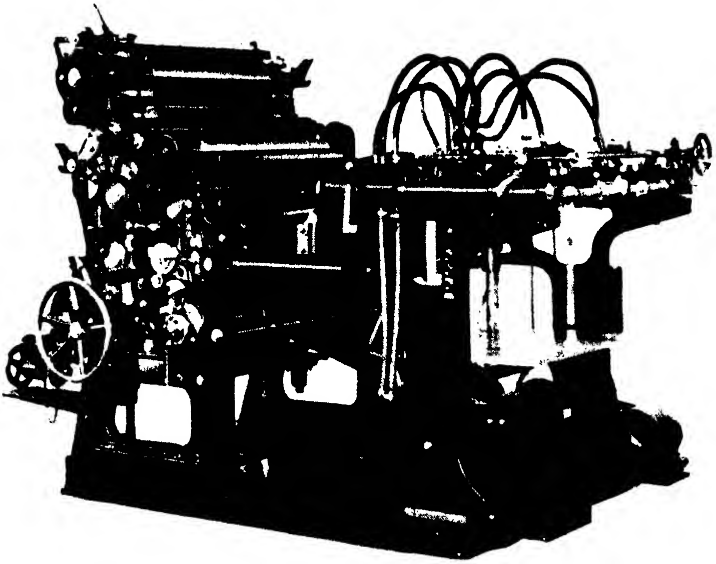
[84] M. M. Wilson, U. S. P. 2,078,170, April 20, 1937; *Chem. Abs.*, 1937, 31, 4515.

[85] R. F. Reed and G. A. Reed, *Lith. Tech. Foundation, Inc.*, Research Bull., No. 7, Research Series No. 8, 1933; *Rev. Paint, Colour, Varnish*, 1937, 10, 184. The trade names for this material are "Lithotine" or "Lithoterps."

OFFSET PRINTING

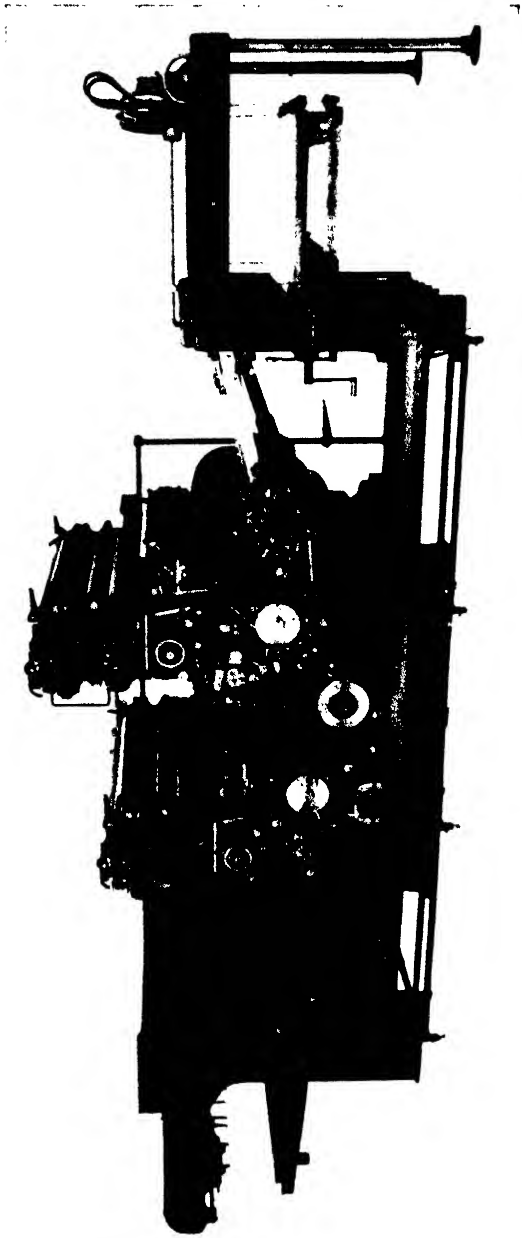
Offset printing is an adaptation of the principles of lithography to printing from curved metal plates. In this process, ink is passed from an etched metal surface to a revolving cylinder covered with a rubber blanket and then is transferred from the blanket to the sheet which is to be printed. Essentially, an offset press consists of three cylinders of equal circumference: the plate cylinder, the blanket cylinder and an impression cylinder. These are placed so that, on revolving, the rubber blanket first comes into contact with the curved etched plate, which is carried by the plate cylinder, and then with the impression cylinder which carries the sheet to be printed. As in flat lithographic processes, one set of felt or flannel covered rollers dampens the plate with water while another set of composition or leather covered rollers distributes the ink on the plate.

The methods of preparation of and the conditions for printing from curved etched plates are practically the same as for the flat surfaces. Zinc is the metal most frequently used. It is economical and for most purposes it is said to be as satisfactory as aluminum. However, aluminum plates are preferred by some lithographers because the brightness of the plate allows observation of tone qualities and color values of images. The fine, lasting grain and water-receptive coating of hydroxide, characteristic of aluminum, are said to make for durable plates, that



Courtesy Harris Seybold Potter Co.

FIGURE 59A. Single-color Offset Press, 17″ × 22″.



Courtesy Harris Seybold Potter Co.

FIGURE 59B. Two-color Offset Press, 26" × 40".

can be stored for long periods of time, without the work "thickening" or "growing."[86] Aluminum has a high resistance to atmospheric corrosion and to many chemicals, with the exception of strong alkalies.

Methods employing transfer papers or photolithography are the more frequent techniques utilized in production of images upon the grained metal. The plates are treated with gum arabic solution, and etched with phosphoric acid, as described previously. The light metal plates are curved and fitted to the plate cylinder. Greater printing speed is attained by employing this rotary process than with stone or metal plates and flatbed presses.

The general characteristics of offset printing inks are similar to compositions used on stone lithographic presses. However, since it is transferred from plate to blanket and then to the paper, the ink must have properties that will permit this operation without loss of any printing characteristics.[87] The type of paper to be printed also determines the properties of the ink. The terms "heavy," "soft," "short," and "long" are employed in describing the characteristics of offset compositions.[88] A long ink is one which is stringy or of molasses-like consistency. Short ink has the consistency of lard. The ink stays in one spot, without creeping. Offset inks are not prepared in standard grades. As a result, it is common practice for the lithographer to buy a heavily bodied ink and to regulate the consistency to fit his particular requirements.

Linseed varnish apparently is the most satisfactory lithographic vehicle. It should be free of acid to minimize chemical action on the plate. A vehicle having the consistency of No. 1 lithographic varnish is used for the majority of offset inks. The viscosity of the resulting ink will vary with the particular pigment to be ground into the varnish. The behavior of the ink during offsetting is the main criterion for the ink's composition. With each revolution of the press, a thin layer of ink is laid on the paper.[89] The ink must adhere to but must not raise fuzz from the surface of the paper. As a general rule, soft surfaced papers take lithographic inks better than hard ones. With soft bond or cheap sulphite paper, a medium bodied ink is employed. If the ink has a heavy body, it should be thinned with number 00 lithographic varnish. If there is a fuzzy surface on the paper, as on newspapers, kerosene may be included in the ink to prevent lifting of too much lint. However, an excess of kerosene, machine oil or hydrocarbon oil in the ink permits too much penetration into the paper. This results in flat, lifeless work. With proper offset paper and ink, the printing is characterized by a softness which is difficult to obtain by direct letterpress printing.[90]

Pigment concentration is of relatively great importance in offset inks.

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[86] E. J. Filler, *Nat. Lith.*, 1935, **42**, 28; *Rev. Paint, Colour, Varnish*, 1935, **8**, 207.

[87] P. Fiech, *The Official Printing Ink Maker*, 1934, **4**, 14.

[88] C. F. Geese, *Nat. Lith.*, 1937, **44** (3), 44; *Rev. Paint, Colour, Varnish*, 1937, **10**, 95.

[89] C. F. Geese, *Nat. Lith.*, 1937, **44** (1), 52; *Rev. Paint, Colour, Varnish*, 1937, **10**, 95.

[90] P. Fiech, *The Official Printing Ink Maker*, 1934, **4**, 14

In printing, a very thin film of ink is transferred from plate to blanket to paper. For this reason, the coloring agents utilized must be tinctorially strong. Further, the quantity of pigment employed is somewhat greater than in other types of inks. In most instances the concentration of pigment is higher than that of vehicle, and the ink is said to have a pigment body rather than a varnish body.[91] Also, pigments for offset printing must be impervious to water and dilute acids. These properties are necessary to prevent bleeding of the pigment on the moistened, nonprinting areas of the plate.[92]

Inks that do not change consistency readily, as a result of absorbing moisture, are said to be desirable for employment on offset presses.[93] It has been stated that good offset inks contain 12 to 15 per cent of water as emulsion at the moment of printing. The emulsions are of water-in-oil type to prevent greasing of the plates. Emulsification makes the inks shorter. However, if the ink becomes too short, piling of the composition on the rollers results, with consequent poor distribution on the plate. Therefore, the quantity of water utilized in preparing inks should be regulated.

Cobalt linoleate is recommended[94] for offset inks because it is stated to prevent leaching out of the paste driers, which results in the coloring of the blanket by chromates. Lead and manganese hydroxides are said to cause such leaching and should be avoided.

Cobalt and manganese driers as well as turpentine are reported to cause oxidation of the rubber surface of offset blankets.[95] Embossing or swelling of the rubber has been observed when ink vehicles or cleaning solvents are absorbed.

Trichromatic color work has certain limitations[96] and requirements. The three colors should be so balanced that neutral gray or black will be produced. Yellow compositions must be complementary to the green and should reflect red and blue-violet as well. Blue compositions should be greenish blue and complementary to the spectrum red and should reflect green, blue and violet.

It is said to be impossible to obtain bright spectrum green in three-color work because no greenish blue pigments or lakes are known which reflect a sufficient amount of green light. Blue or blue-violet shades produce a dull green.

Also limitations are placed upon violets. Muddy violet will result if red does not reflect violet to the same extent as blue. Black is produced instead of violet, when the red employed is vermilion. Bright violets are

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[91] *Am. Printer*, 1939, 108 (5), 22.

[92] For some offset ink formulas see H. J. Wolfe, "Manufacture of Printing and Lithographic Inks," New York, MacNair-Dorland Co., 1933.

[93] A. Grunder, *Am. Ink Maker*, 1936, 14 (3), 25, 27; *Rev. Paint, Colour, Varnish*, 1936, 9, 376; *Chem. Abs.*, 1937, 31, 6034; *Am. Pressman*, 1936, 46 (7), 24.

[94] A. Grunder, *loc. cit.*

[95] R. F. Reed, *Lithographic Technical Foundation, Research Bulletin*, No. 5.

[96] M. Leeden, *Modern Lithographer and Offset Printer*, 1934, 30, 135, 162; *Rev. Paint, Colour, Varnish*, 1934, 7, 376.

said to be impossible because blue does not reflect completely all violet. However, printers have been able to produce brilliant greens or reds by sacrificing certain shades. Brilliant green is obtained if the orange shades are sacrificed. Brilliant red is produced by sacrificing violet tones.

Phosphotungstic colors are suggested for offset printing.[97] These are available in purple, green, blue and red shades. These colors are said to be permanent and strong tinctorially. Another color which is recommended is Syan Blue, which is permanent, strong, and acid or alkali resistant.

The inks used for color printing in offset work require special modifiers.[98] To prevent sticking and smudging of freshly printed superimposed sheets a minimum quantity of an ink containing the lowest practical amount of varnish has been recommended. High-speed machines tend to cause picking, or adherence of paper to the plate. The latter difficulty may be avoided by adding an offset paste and diluent to the ink. The shade of colored inks may be reduced with transparent white. In overprinting with bronze inks, 2 to 3 per cent of chalk is added to improve the appearance of the ink.

Drying of colored inks involves problems somewhat different from those found when using carbon black inks. Blue or violet compositions are said to dry slowly. Potassium chromate inks should contain no driers, since a hard gloss film would be produced, which hinders overprinting with other colors. Driers for color work usually are powders rather than pastes. The latter, if used in a quantity of more than 5 per cent, would lighten the color shade, which is undesirable. Liquid driers should be avoided to prevent lightening of the colors.

Inks which are solid at ordinary temperatures and which are applied hot, in a melted condition, have been recommended for offset printing.[99] These pastes or paints contain a large amount of color pigment and hence produce very intensely colored prints. The paper on which the offset blanket prints must be heated.

An illustrative example of such an ink contains 28 parts of soot, 15 parts of Prussian Blue, 15 parts of medium varnish, and 7 parts of weak varnish. This composition is melted in a pot at a temperature of 130 to 140° C. and is printed without dilution.

Ninety per cent of all offset compositions are reported to contain linseed oil.[100] It is said that offset color printing is a very delicate form of work, and even slight variations in the composition of the ingredients employed in the inks may produce undesirable prints. Some offset printers state that linseed oil, because it is a natural product, varies greatly in

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[97] J. Beckett, *Photo-Lithographer*, 1937, 5, 28; *Share Your Knowledge Review*, 1937, 49; *Rev. Paint Colour, Varnish*, 1937, 10, 512.

[98] *Papier-Ztg.*, 1937, 62 (54), 898; *Rev. Paint, Colour, Varnish*, 1937, 10, 259.

[99] German P. 586,742, 1934, to Chem. Fabr. Halle-Ammendorf Gebr. Hartmann; *Chem. Zentr.*, 1934, 105 (1), 468; *Rev. Paint, Colour, Varnish*, 1934, 7, 102.

[100] J. Beckett, *Photo-Lithographer*, 1937, 5, 28; *Share Your Knowledge Review*, 1937, 49; *Rev. Paint, Colour, Varnish*, 1937, 10, 412.

composition. Hence it is advocated that synthetic vehicles (*e.g.*, synourin oil, paracoumarone resins in a solvent, Tekaolsor, especially processed petroleum derivatives) be employed for color printing since these oils vary to a lesser extent in their properties than does linseed oil.[101] Several other advantages are reported by the users of inks containing "synthetic" vehicles. These are:

(1) The inks will run with a small quantity of acid in the water fountain.
(2) The offset printing compositions will lift cleanly off the blanket and produce stronger impressions with the same film thickness as is employed with inks containing linseed oil.
(3) Dusting bronzes are reported not to adhere readily to ink films containing "synthetic" vehicles.
(4) Drying is more rapid with "synthetic" vehicle compositions than with linseed oil.
(5) The dried films are more rub- and scratch-proof than are linseed oil films.
(6) At 250° F. "synthetic" vehicle inks are said to dry in 6 minutes, compared to 20 minutes for linseed oil inks.

Dry offset color [102] printing may be done with compositions containing vinyl ester condensation products in a glycerol-miscible solvent.[103] A dry offset color of this type was composed of 80 parts of Milori Blue, 12 parts of a moisture-maintaining solution, and 5 parts of a resin solution. The moisture-maintaining solution contains 90 parts of glycerol and 10 parts of potassium tartrate. The resin solution contains 40 parts of vinyl ester resin, 20 parts of diacetone alcohol, and 40 parts of ethylene glycol monoacetate.

Offset gloss inks present many problems to the printer.[104] Among these are prevention of offset and of greasing and scumming of the plates, the development of special papers, and the attainment of greater length and flow. No-offset sprays are a feature in gloss printing. The papers recommended for this work are hard, supercalendered stocks. High-gloss enamel and varnish grade papers which are coated on one side usually are employed.[105] Gloss prints will dry in 0.5 hour, but should be winded [106] at the end of this time to prevent sticking. Scratchproof prints are made with 2 or 4 colors.

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[101] See Chapter 3.

[102] Dry offset printing is a mechanical printing process in which no dampening rollers are employed on the plate. (H. J. Wolfe, "Manufacture of Printing and Lithographic Inks," MacNair-Dorland Co., New York, 1933.)

[103] German P. 609,868, 1935, to Chemische Fabrik. Halle-Ammendorf Gebr. Hartmann; *Chem. Abs.*, 1935, 29, 5283.

[104] R. J. Butler, *Photo-Lithographer*, 1939, 7, 18; *Am. Ink Maker*, 1939, 17 (3), 19.

[105] For further information see Chapter 18.

[106] "Winded" means to separate the prints so that they will be ventilated by air.

In color printing, an overprinting varnish may be employed to produce high-gloss overprints.[107] The varnish is applied to the printed image. This coating composition is transparent and may contain oil-soluble dyes, or be mixed with transparent pigments. An example of such a varnish is composed of 200 parts of linseed oil, 100 parts of hard resin, 15 parts of aluminum stearate and 5 parts of cobalt linoleate. Another varnish of this type is said to contain China Wood oil, hard resin, aluminum palmitate and lead salicylate.

For the reproduction of documents, offset printing has been recommended.[108] An original drawing is made with aniline ink on a sheet or plate. Subsequently, a rubber surface which has been treated with glycerol is impressed on the original. Copies on paper are made directly from the treated rubber. The glycerol compound consists of 75 parts of glycerol, 25 parts of water and 1 part of *spiritus saponitus* (methyl alcohol and potassium oleate). This mixture is smeared evenly over the rubber surface and wiped over with a soft rag until the rubber appears dry.

Offset ink usually is prepared as a highly viscous composition. The printer thins the mixture until the consistency of the ink fits his requirements. It is reported that the thin inks produce good impressions because the ink will enter the recesses of the plate easily.[109]

A thinner or vehicle for offset compositions is reported to contain 15.9 parts of castor oil, 22.1 parts of lithographic varnish, 26.6 parts of stearin, and 35.4 parts of turpentine. This mixture is said to give the proper consistency to offset inks when 14 parts of thinner are admixed with 86 parts of ink. The original ink should contain 35 to 40 per cent of pigment.

An ink, said to be similar to the thinned blend above, comprised 34.4 parts of carbon black, 21.5 parts linseed oil, 33.2 parts of varnish, 2.2 parts of castor oil, 3.7 parts of stearin, and 5.0 parts of turpentine. This ink was recommended for printing wood grain effects.

The addition of modifying agents to offset inks has been advocated to improve the finish, prevent "bleeding," increase the brilliancy, and extend the covering power. To attain the foregoing objectives, it has been suggested[110] that 0.5 to 2.0 parts of a mixture of rosin-modified phenol-formaldehyde resin, tung oil, and wool grease be added to 16 parts of offset ink. The modifying agent is prepared by heating together 4.5 parts of the resin, 4.0 parts of tung oil and 4.0 parts of wool grease. Heat should be applied for 2 hours in the latter process.

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[107] French P. 781,912. 1935, to Chem. Fabr. Halle-Ammendorf Gebr. Hartmann; *Chem. Abs.*, 1935, **29**, 7102. British P. 426,753, 1935; *Chem. Abs.*, 1935, **29**, 6448. British P. 434,450, 1935; *Chem. Abs.*, 1936, **30**, 886.

[108] W. L. Lawrence, British P. 337,455, 1929; *Chem. Abs.*, 1931, **25**, 2255.

[109] C. P. Shaw, U. S. P. 2,043,397, June 9, 1936; *Chem. Abs.*, 1936, **30**, 5436; *Rev. Paint, Colour, Varnish*, 1936, **9**, 315. U. S. P. 1,989,250, Jan. 29, 1935; *Chem. Abs.*, 1935, **29**, 2005; *Brit. Chem. Abs.* **B**, 1936, **30**; *Rev. Paint, Colour, Varnish*, 1935, **8**, 208.

[110] A. J. Gautsche, U. S. P. 2,018,060, Oct. 22, 1935; *Chem. Abs.*, 1936, **30**, 309; *Rev. Paint, Colour, Varnish*, 1936, **9**, 93. U. S. P. 2,018,060, Oct. 22, 1935; *Chem. Abs.*, 1936, **30**, 309; *Brit. Chem. Abs.* **B**, 1936, 1109; *Rev. Paint, Colour, Varnish*, 1936, **9**, 93. Carleton Ellis, "Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

Rubber offset blankets usually contain a small proportion of excess sulphur from vulcanization processes. The sulphur may be removed by printing inks. This was stated to be avoided by employing sulphur-containing washing solutions in the printing compositions. The quantity of wash added generally is 10-15 per cent of the total amount of ink. One such wash comprised a solution of 2 parts of sulphur in 100 parts of aniline. An alternative composition contained 2 parts of sulphur, 50 parts of *o*-toluidine, and 50 parts of furfural.[111]

The question of deterioration of offset rubber blankets has been studied.[112] In Figure 60 is shown a method of making a test for the effect of linseed oil upon offset blankets. Linseed oil is said to emboss rubber blankets, and tackiness is reported to be the result of simultaneous oxidation of absorbed varnish and rubber. The latter phenomenon is an irreversible process, and is not caused by devulcanizing. Dusting the blanket with sulphur was stated to afford only temporary relief. Cobalt salts and turpentine are said to oxidize the rubber blankets in a manner similar to that of linseed oil. To counteract oxidation by cobalt salts, turpentine and linseed oil, with resulting formation of glazed, tacky or engraved surfaces, an antioxidant wash solution was developed. The latter is prepared by dissolving 1.75 ounces of hydroquinone per gallon

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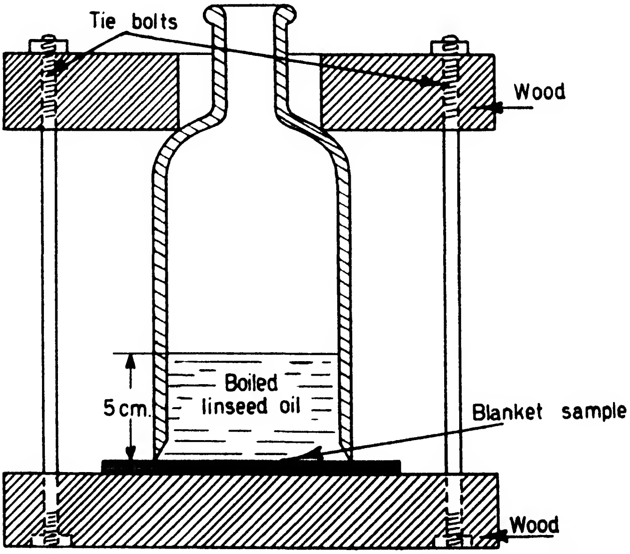
[111] J. Scheiber, German P. 608,383, 1935; *Chem. Abs.*, 1935, 29, 2632.

[112] R. F. Reed, *Lithographic Technical Foundation, Inc., Research Bull.* No. 5; *Am. Ink Maker*, 1935, 12 (8), 35.



Courtesy Lithographic Technical Foundation, Inc.

FIGURE 60. Sketch of Apparatus for Testing Effect of Vehicles on Offset Blankets (R. F. Reed).

of acetone. Each gallon of acetone solution of hydroquinone then is mixed with 9 gallons of benzene.

Phenol, as a modifier for offset inks, is said[113] to provide good adhesion of ink to metallic plates and to eliminate the necessity for special fixing agents. Ten parts of phenol were admixed with 90 parts of ink. The latter contained 6 parts of asphalt, 6 parts of lampblack, 2.7 parts of pitch, 28.8 parts of petrolatum, and 56.5 parts of turpentine oil.

Offset coloring mixtures may be prepared by introducing 0.3 to 0.5 per cent of calcium hydroxide or barium hydroxide into an aqueous pigment paste.[114] The hydroxides must be in a dry state before admixture. The combination of paste and hydroxide is added to polymerized oil and stirred until a good mix is obtained. Polymerized glue is suggested as a substitute for the oil.

A method of lithographic or offset printing, involves the employment of inelastic unsized gutta percha tissue[115] to receive the impression of an original design.[116] If the original work is a negative, the gutta percha impression is applied to a lithographic stone and the final print is made by the latter. The same method may be employed for offset printing as well. The original negative is impressed upon the gutta percha sheet. The positive produced is applied to a second layer of gutta percha which in turn prints the image upon a stone, and the latter superimposes the design on a rotary rubber blanket from which the final prints are made.

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[113] British P. 478,776, 1938, to Chemische Forschungsgesellschaft m. b. H.; *Rev. Paint, Colour, Varnish*, 1938, 11, 110; *Chem. Zentr.*, 1938, 109 (1), 744; *Chem. Abs.*, 1938, 32, 2378. French P. 817,406, 1938; *Rev. Paint, Colour, Varnish*, 1938, 11, 110; *Chem. Zentr.*, 1938, 109 (1), 744; *Chem. Abs.*, 1938, 32, 2378.

[114] N. I. Kozlov, Russian P. 45,700, 1936; *Chem. Abs.*, 1938, 32, 5648; *Chem. Zentr.*, 1936, 107 (2), 877; *Rev. Paint, Colour, Varnish*, 1936, 9, 316.

[115] Gutta percha is the inspissated juice of a saponaceous evergreen tree (*Dichopsis Gutta*), found in the Malay archipelago. It is a brownish-red, horny solid which is insoluble in water but will dissolve in ethers.

[116] G. Ruthven, U. S. P. 1,364,523, Jan. 4, 1921; *Chem. Abs.*, 1921, 15, 767.

Chapter 10

Intaglio Inks

It has been estimated that the annual consumption of intaglio inks amounts to more than forty million pounds.[1] This figure represents an appreciable fraction of the total production of printing inks. Intaglio inks dry mainly by evaporation (also, in part, by penetration) and for this reason differ from ordinary lithographic inks in containing a large proportion of a volatile solvent, *e.g.*, toluene or xylene, and in being free from drying oils and therefore siccatives.

In discussing intaglio inks a distinction must be made between copperplate inks (which term is here used to include also steel-plate and photogravure inks) and rotogravure inks, since the latter are especially compounded to dry with sufficient rapidity to correspond to the high rate of output attained in the rotogravure process.[2]

The leisurely progress of the copper plate processes (as compared to rotogravure) makes very few demands upon the ink used. The latter should wipe cleanly and easily from the plate to leave what is called a good wipe; it should possess sufficient cohesion to pull out readily from the depressions in the plate and transfer to the material receiving the imprint without spreading laterally. Further, the pigment should not bleed in water since in these processes slightly dampened paper is generally used.

The requirements of a good gravure ink, on the other hand, are much more exacting, due to the rapid rate of printing and the purely mechanical nature of the rotogravure process. (1) The ink should possess a low viscosity and surface tension. These properties govern what is generally known as the "flow" qualities. Good flow is necessary if the ink is to fill the etched cells of the plate completely and rapidly and flow back into the ink duct from the doctor blade. Low viscosity and surface tension also control the ease with which the ink will "wet" the paper. (2) The ink should have sufficient cohesion to remain in the cells against the centrifugal force set up by the rotating cylinders. (3) It must have low adhesion so that it may be wiped cleanly from the cylinder. (4) In drying, the ink should "harden" immediately without first passing through a "sticky" period. (5) The solvent should be volatile, non-inflammable and non-toxic.[3]

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[1] *The Official Printing Ink Maker*, 1934, 4 (3), 12.

[2] See Chapter 1 for a description of the important intaglio processes.

[3] G. L. Riddell, *Modern Lithographer*, 1934, 30, 114; *Rev. Paint, Colour, Varnish*, 1934, 1, 293.

The gravure inks (employing as solvents toluene or xylene) now in general use fulfill fairly well the requirements enumerated above with the exception of the properties of non-toxicity and non-inflammability. There is considerable difficulty in obtaining a solvent which is cheap, volatile, non-inflammable and non-toxic. There are a number of materials which are non-inflammable and volatile (such as chlorinated products of methane and ethane[4]) but most of them are rather toxic and costly.[5] An objection to the use of chlorine derivatives of methane and ethane in particular is that in the presence of moisture they hydrolyze and form small amounts of hydrogen chloride which reacts with the copper of the plate or cylinder.[6]

In considering inflammability, the flash point must be taken into account.[7] Thus, benzene is an excellent solvent but is not generally employed (in the United States) because of its low flash point (−5° F.). Xylene, on the other hand, although also inflammable, has a higher flash point (75° F.) and consequently is much safer to use.

In preparation of the ink certain precautions must be observed. It must not contain any compounds (as for example a dye or pigment containing sulphur) which will react chemically with the copper of the cylinder. The chief disadvantage in the use of chlorinated ethane and methane, as previously mentioned, is the fact that in the presence of moisture slight traces of hydrogen chloride are formed.[8] Many acid resins exert a deleterious effect on the etching, and care must be exercised when employing hydrocarbons which may have been refined by washing with sulphuric acid (or other acids) since traces of the latter may be present. The pigments should be free of abrasive substance which would scratch the cylinder and they must have a sufficiently low specific gravity to remain dispersed in the fluid medium. On the other hand, pigments should not be in too fine a state of division since the ink, in that case, will not wipe cleanly from the cylinder but will be retained in the minute scratches made during the polishing operation.[9] The relative amount of solvent and pigment depends of course to a certain extent on other factors, such as the speed of printing and type of paper used.[10]

Although much work has been done on the development of water-base inks, the chief objection to these is that the surface tension is too high and the resulting prints are inferior to those obtained with other gravure inks. The advantages of low cost, non-toxicity and non-inflammability are, however, so decided that probably water-base inks will find application in cheaper publication work where high quality is not required.[11] For

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[4] See G. E. Lang, French P. 713,155, 1931; *Chem. Abs.*, 1932, **26**, 1810.

[5] G. L. Riddell, *loc. cit.*

[6] H. N. Morris, *Brit. Print.*, 1937, **49**, 235; *Rev. Paint, Colour, Varnish*, 1937, **10**, 96.

[7] R. B. Warne, *Modern Lithographer*, 1935, **31**, 132; *Chem. Abs.*, 1936, **30**, 4024.

[8] H. N. Morris, *loc. cit.*

[9] G. L. Riddell, *Lith. Offset Print.*, 1934, **30** (6), 114; *Rev. Paint, Colour, Varnish*, 1934, **7**, 293.

[10] *Printing*, 1937, **5** (52), 28; *Rev. Paint, Colour, Varnish*, 1937, **10**, 95. Cf. *Deutscher Drucker; Chronique Graphique*, 1938, **13** (103), 3993; *Rev. Paint, Colour, Varnish*, 1938, **11**, 107.

[11] G. L. Riddell, *Modern Lithographer*, 1934, **30**, 114; *Rev. Paint, Colour, Varnish*, 1934, **7**, 293.

high speeds and all kinds of paper, the printer must at present depend to a large extent on toxic and inflammable thinners.[12]

The use, quite common in Europe, of a closed type of press which does not allow the vapors to escape into the press room renders the use of these inflammable solvents quite unobjectionable.[13] In one type of such a press part of the solvent is removed before the imprint is made.[14] A current of air is drawn over the region between the doctor and the impression point, the vapor-laden air passing into a condenser where the solvent is recovered.

The use of inflammable solvents in rotogravure printing (multicolor) is avoided in a rather unique method employing normally solid vehicles.[15] This method of multicolor printing involves first heating an ink whose vehicle consists of a normally solid, readily liquefiable, amorphous substance to a temperature at which it melts, and becomes fluid. The ink then is transferred to the heated roller, printed and cooled at once so that it solidifies. Afterwards, the paper is passed over the second cylinder and receives the impression of an ink which melts at a somewhat lower temperature than the first. After a cooling operation, the printing process may be repeated. In every instance, each ink has a congealing temperature lower than that of the preceding ink. The vehicles are low-melting solids such as hydrogenated vegetable oil, *e.g.*, soybean oil or castor oil. A yellow ink, which may be employed in such an operation and which melts at 180° F., consists of 20 parts of chrome yellow dissolved in a vehicle made up of 75 parts of hydrogenated castor oil and 5 parts of WW rosin.

GRINDING OF ROTOGRAVURE INKS

After pigment and vehicle have been prepared they are mixed together and ground in a mill. The method for effecting the latter operation has undergone considerable modification in the last two decades and a short description of it will be given.

Rotogravure inks were originally ground in iron pots or on buhrstone[16] mills or roller mills. The product went to the printer in the form of a heavy paste which he had to thin to the proper consistency.[17] Pebble or ball mills are used now almost exclusively since these are best adapted

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[12] H. N. Morris, *loc. cit.*

[13] The incentive to the development of such presses however, is the solvent recovery made possible by their use. For this reason, most progress in their development has been made in Europe where the high price of petroleum solvents has been the greatest deterrent to the more general use of the rotogravure process. A solvent recovery of 75 per cent is quite common. (H. N. Morris, *loc. cit.*)

[14] C. H. Siebel, British P. 449,112, 1936; *Rev. Paint, Colour, Varnish*, 1936, 9, 316.

[15] W. L. Jones and E. H. McLeod, U. S. P. 2,147,651, Feb. 1, 1939, to Interchemical Corp.

[16] Buhrstone is a hard, tough rock, white or creamy in color, consisting of chalcedonic silica with a cellular texture. The best variety (French buhrstone) occurs in deposits near Paris.

[17] R. Rullman and D. M. Wilhelm, *Am. Ink Maker*, 1934, 12 (11), 21; *Rev. Paint, Colour, Varnish*, 1934, 7, 491.

Courtesy Industrial and Engineering Chemistry

FIGURE 61. Ink Mill Grinding Colored Ink (A. Linz).

to the needs of the rotogravure ink maker. Both pigment and vehicle are placed in the mills which are rotated for several hours, no attention being required during the grinding operation. The finished product is discharged in the proper consistency for use. As the grinding is carried out in a closed container there is no evaporation of the solvents and no obnoxious or poisonous odors in the grinding room.

The mills were originally lined with French buhrstone and provided with pebbles imported from France and Denmark. About 1929 a synthetic silicate replaced these buhrstone linings and balls of the same material began to be used. This resulted in a better product, free of grit. About 1932-33 a still newer type of ball mill was introduced in which both beads and shell were made of steel alloy containing a high percentage of chromium, manganese, and some nickel. Because of the greater density of the steel, the balls are made smaller and more efficient grinding action is thus obtained.

Although the steel mills are used in general for the production of such colors as brown, black, green and blue and some of the reds, the silicate-lined mills equipped with the silicate balls are employed, for the most part, in the production of the delicate pastel shades, such as yellow, the lake colors, and white.

Courtesy Industrial and Engineering Chemistry

Figure 62. Ink Mixer (A. Linz).

Intaglio Ink Compositions

To facilitate their discussion, intaglio inks may be grouped according to the liquid bases (solvents) and the binders employed in their preparation. The inks are thus most conveniently classified under the following headings:

1. Aromatic hydrocarbon-base inks
2. Paraffin hydrocarbon-base inks
3. Water-base inks
4. Inks employing resin binders
5. Inks employing cellulose derivatives as binders.

If, as is often the case, the inks fall into more than one of these groups, the more prominent or unusual feature will decide the classification under which it is discussed.

Aromatic-Base Inks. As already pointed out, toluene and xylene, despite their objectionable features, are the most common solvents for intaglio printing inks. Benzene, the most satisfactory base of this group, judged solely by the printing results obtained, is employed rarely in this country because of its high inflammability and toxicity. Its use in Germany, however, is reported to be widespread.[18] The binding agents ordinarily employed with these solvents are gilsonite (for dark-colored or black inks), or dammar and synthetic resins (for bright-colored inks). If resin alone is the binder, a short ink with a tendency to liver is often produced. This defect (tendency to liver), however, may be remedied by incorporation of dammar. Another shortcoming of resin inks, it may be noted, is that when unpigmented their low cohesion and high adhesion renders them unsatisfactory for many purposes.[19]

Either a glossy or a matt finish may be secured with varnishes containing the binders mentioned above dissolved in an aromatic solvent. Thus, if pigments are absent, and a fat-soluble dye is substituted therefor as a coloring agent, gilsonite varnish dries to a highly glossy finish. Dammar also imparts a high gloss to the print which is, however, undesirable in multicolor printing. To obtain a matt finish, a matting agent such as alumina, magnesium carbonate, blanc fixe, chalk, or wax is added. Soluble waxes (*e.g.*, montan wax) often serve as matting agents since inorganic compounds tend to smother the sharp outline of the print.

For copper-plate printing in Germany the benzene hydrocarbons (usually toluene) act as satisfactory solvents. For rotogravure work, however, the solvent generally consists of nearly equal portions of toluene and a low-boiling paraffin hydrocarbon fraction (*e.g.*, benzine). For example, a copper-plate ink varnish comprises 60 parts of toluene and 40 parts of gilsonite, whereas a similar rotogravure ink varnish contains 15 parts of toluene, 17 parts of light benzine and 33 parts of gilsonite.

In preparing the varnish, the solid material, asphalt or resin, is ground to about the size of hazelnuts and gradually added to the vigorously agitated solvent. Introducing the solid in this manner avoids the formation of lumps and allows the material to dissolve, the latter step requiring from 8 to 10 hours. Dyestuff is then incorporated and the whole mass ground in a mill.

Photogravure inks, containing only the more volatile aromatic hydrocarbons, because of the high rate of evaporation of the solvent, tend to form a "skin" between the ink and the paper, thus hindering penetration of the ink into the paper and allowing the ink to dry mainly by evaporation.[20] It is reported that the formation of such a skin may be obviated

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[18] See, E. Max, *Farben-Chem.*, 1933, 4, 336; *Chem. Abs.*, 1933, 27, 5557. H. Hadert, "Die Tiefdruchfarben-Herstellung," Publ. by the author at Olwanstrasse 4, Berlin-Frohan, 1933; *Official Printing Ink Maker*, 1934, 4 (3), 12.

[19] G. L. Riddell, *loc. cit.*

[20] Wm. E. Wornum, Brit. P. 423,751, 1935, to Mander Bros., Ltd.; *Chem. Abs.*, 1935, 29, 5682; *Brit. Chem. Abs.* B, 1935, 367.

and drying effected by penetration as well as evaporation by adding to the solvent at least 10 per cent of a high-boiling petroleum fraction (boiling point above 160° C.) rich in aromatic hydrocarbons. If a petroleum fraction with a boiling range of 150 to 250° C. is used as a solvent, drying by penetration dominates. A yellow ink of the latter type may be prepared by incorporating a pigment composed of 72 parts of chrome yellow and 90 parts of extender (barytes) in a medium consisting of 60 parts of dammar resin dissolved in 98 parts of a high-boiling petroleum fraction. The ink may be thinned if the work to be done renders this step necessary.

Paraffin Hydrocarbon-Base Inks. The use of a paraffinic liquid alone as solvent yields an unsatisfactory printing ink. Kaufler and Schmitz reported, however, that by adding a small proportion (*e.g.*, 3 to 8 per cent) of an alcohol or liquid ether or ester containing 3 to 7 carbon atoms, a satisfactory base is obtained.[21] To 95 g. of benzine may be added for instance, 3 g. of butanol or dibutyl ether, 8 g. of ethylene glycol monoethyl ether, or 4 g. of ethyl lactate. In the preparation of intaglio inks a volatile hydrocarbon such as benzine should be used.[22] (Benzine boiling between 70 and 100° C. for instance has a rate of evaporation from paper almost as great as that of benzene.) To such a liquid, addition of about one-third its volume of carbon tetrachloride is said to yield a non-inflammable mixture.[23]

Knight[24] prepared a quick-drying ink consisting substantially of a mineral spirit or solvent naphtha solution of gilsonite with which were admixed pigments and resin varnish. Thus, 8000 cc. of mineral spirits and 4000 g. of gilsonite are heated together at 150° C. for about one hour. 1000 cc. of linseed oil-resin varnish may be added before this heating operation or before the heated mixture is cooled. An oil drier may also be added. The resulting vehicle is milled with pigment to yield the finished ink.[25]

Mock[26] describes a printing ink composed of a solution of 15 to 30 per cent gilsonite in a liquid component containing 85 to 95 per cent petroleum naphtha and 5 to 15 per cent of a ketone, both the naphtha and ketone being more volatile than benzene.

Water-Base Inks. The vehicles for intaglio inks here designated as water-base inks are for the most part mixtures of water, a water-soluble solvent, a natural resin, an alkaline reacting compound (either organic

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[21] F. Kaufler and H. P. Schmitz, U. S. P. 2,036,480, April 7, 1936; *Chem. Abs.*, 1936, 30, 3667. British P. 371,202, 1932, to Alexander Wacker Ges. für Elektrochemische Industrie G. m. b. H.; *Chem. Abs.*, 1933, 27, 3627; *Brit. Chem. Abs.* B, 1932, 721. French P. 752,492, 1933; *Chem. Abs.*, 1934, 28, 1206; *Rev. Paint, Colour, Varnish*, 1934, 7, 103.

[22] British P. 390,641, 1933 to Alexander Wacker Ges. für Elektrochemische Industrie G. m. b. H.; *Chem. Abs.*, 1933, 27, 5994; *Brit. Chem. Abs.* B, 1933, 667.

[23] A. Schwenterly, U. S. P. 1,447,734, March 6, 1923; *Chem. Abs.*, 1923, 17, 1723.

[24] G. D. Knight, U. S. P. 1,722,925, July 30, 1929, to Emory Winship; *Chem. Abs.*, 1929, 23, 4582; *Rev. Paint, Colour, Varnish*, 1929, 2, 282; *Pine Inst. American Abs.*, 1929, 3, 178.

[25] For a comparison of German asphalts and gilsonite and their solutions, see *Farben-Ztg.*, 1938, 43 (12), 302; *Rev. Paint, Colour, Varnish*, 1938, 11, 192.

[26] W. W. Mock, U. S. P. 2,139,242, Dec. 6, 1938, to Interchemical Corp.; *Chem. Abs.*, 1939, 33, 2354; *Rev. Paint, Colour, Varnish*, 1939, 12, 181.

or inorganic) and a dispersing agent (*e.g.*, a colloid such as casein or glue).[27, 28, 29] These vehicles are reported to be not only relatively non-inflammable, but also non-toxic.

Drey and Freedland[30] suggest an organic alkaline substance such as diethanolamine. Their vehicle is prepared by dissolving a natural resin of an acid character in a solvent miscible with water, adding the water to this solution after the introduction of an alkaline substance to either the water or resin solution. For example, a solvent mixture is prepared consisting of one pint of triethanolamine, four pints of industrial methylated spirits and three pints of cyclohexanol. Six pounds of shellac are then dissolved in one gallon of this mixture and the whole diluted with two gallons of water. To obtain the printing ink the resulting mix is ground with 2.5 pounds of carbon black.

An inorganic base such as an alkali or ammonium hydroxide may be used as saponifying agents in the preparation of inks. The binding agent (acaroid, dammar, colophony, gum lac or a synthetic resin) is dissolved in a solvent soluble in water, such as ethanol or other alcohol or acetone, after which the resin is saponified, at least in part, by alkali or ammonia. To this is then added a solvent of high boiling point which mixes with the ethanol or other solvent used, *e.g.*, turpentine oil or methylcyclohexanol. Water is added during or at the end of the above-mentioned steps.[31] For example, 10 parts of colophony are dissolved in 5 parts of spirit (96-per cent ethyl alcohol) and 2 parts of turpentine oil. Next are added 3 parts of concentrated aqueous ammonia and 2.5 parts of soft potash soap (to prevent livering) while stirring the cold or moderately heated mixture. The pigment is rubbed up with this binding medium. The addition of water is advantageously effected before the rubbing operations.

This procedure may be modified by first saponifying the resin with an aqueous solution of alkalies or ammonia and then adding the alcohol or other water-soluble organic solvent or a solution of resin in such a solvent.[32, 33, 34] To illustrate, 100 g. of rosin and 20 g. of ammonia are dissolved in a solution of 10 g. of soap in 200 g. of water and 50 g. of alcohol, and afterwards 5 g. of turpentine are added. Oxidation of rosin before use in intaglio inks was reported to furnish a rosin product which

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[27] K. Albert, *Penrose Annual*, 1932, 34, 95; *Phot. Korr.*, 1931, 67, 46; *Chem Abs..* 1932, 26, 1140.

[28] H. Hadert, *Nitrocellulose*, 1932, 3, 80; *Chem. Abs.*, 1932, 26, 4189.

[29] Zenzi Kosizima and Kazuo Siba, Japanese P. 90,910, 1931; *Chem. Abs.*, 1931, 25, 5048. French P. 788,406, 1935, to P. Chouanard & Fils Co., (Soc. veuve); *Chem. Abs.*, 1936, 30, 1595.

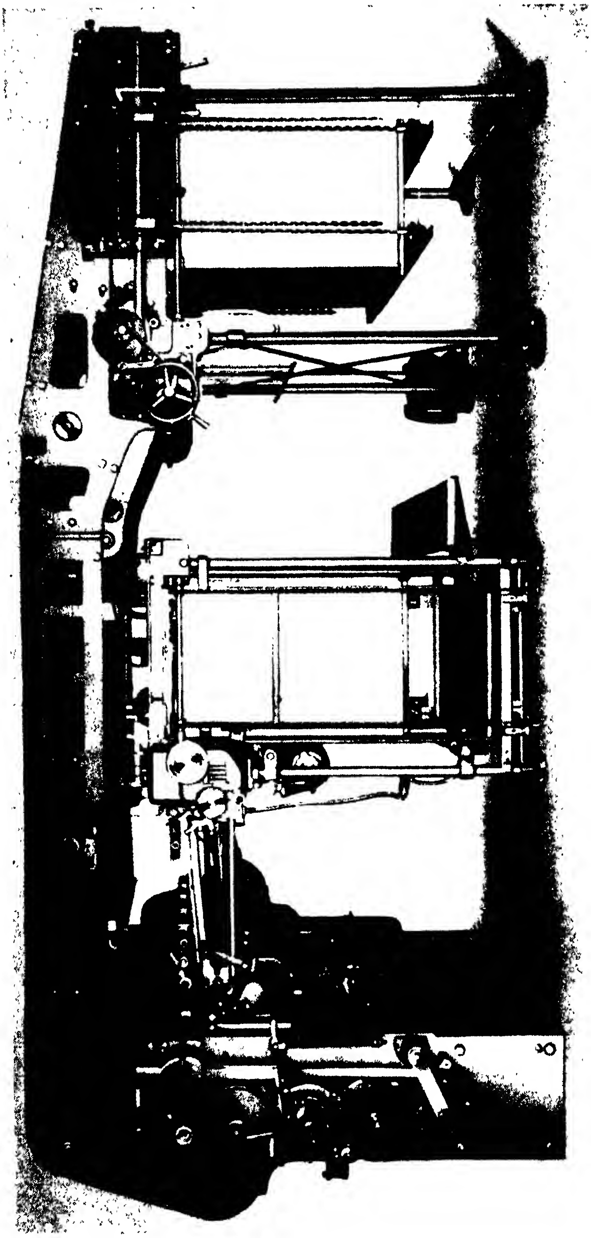
[30] N. Drey and I. Freedland, British P. 376,413, 1932; *Chem. Abs.*, 1933, 27, 3627; *Brit. Chem. Abs.* B, 1932, 947.

[31] H. Kurz and K. Albert, French P. 711,613, 1931; *Chem. Abs.*, 1932, 26, 1810; British P. 371,527, 1932; *Chem. Abs.*, 1933, 27, 3627; *Brit. Chem. Abs.* B, 1933, 687; German P. 547,442, 1933; *Rev. Paint, Colour, Varnish*, 1933, 6, 266; See also, D. Schultz, *Farbe u. Lack*, 1933, 31, 368.

[32] H. Kurz and K. Albert, British P. 396,654, 1933; *Chem. Abs.*, 1934, 28, 1206; *Brit. Chem. Abs.* B, 1933, 879; Addn. to British P. 371,527, 1932; *Chem. Abs.*, 1933, 27, 3627; *Brit. Chem. Abs.* B, 1932, 687.

[33] H. Kurz and K. Albert. French P. 43,145, *Chem. Zentr.*, 1934, 105 (1), 3131; Addn. to French P. 711,613, 1931; *Chem. Abs.*, 1932, 26, 1810; *Am. Ink Maker*, 1934, 12 (6), 15; *Rev. Paint, Colour, Varnish*, 1934, 7, 295.

[34] German P. 650,092, 1937, to Berger and Wirth, (Addn. to German P. 547,442); *Farben-Chem.*, 1937, 8 (12), 422; *Rev. Paint, Colour, Varnish*, 1938, 11, 110.



Courtesy Miehle Printing Press & Manufacturing Company

FIGURE 62A. Miehle Intaglio Press.

dissolves in ammoniated water to a clear solution.[35] The latter was stated not to be affected by subsequent addition of soap. Oxidation of rosin was carried out, using a mixture of hydrogen peroxide and water as oxidizing agent.

Kurz and Albert also found [36] that the use of a water-soluble organic solvent is not essential for an intaglio ink. Their binder consists essentially therefore of a resin dissolved in aqueous alkali, the latter being present partly as fixed alkali and partly as ammonia. In many cases the addition to this solution of a colloid, such as casein or glue, will aid in maintaining the pigments in suspension. Further, it is necessary to remove the property of frothing associated with alkaline resin solutions, like all soap solutions which depend upon their surface activity. This can be effected by means of a defrothing agent, for instance, by adding a small amount of ethereal oils (since these dissolve satisfactorily in alkaline resin solutions). Colophony is the resin generally used, but it may be partially replaced by resins which yield soluble ammonium compounds, such as shellac, or which will be peptized by the alkali resinate present. The latter is necessary to peptize the ammonium resinate which is insoluble in water. The vehicle proposed consists of the following ingredients: 2.0 kg. of colophony, 1.6 kg. of 10-per cent aqueous potash lye with about 0.1 kg. of casein, 0.24 kg. of ammonia solution (d. 0.91), mixed with 4.0 kg. of water and 0.2 kg. of turpentine oil. The ink obtained is noteworthy in that it is not water-resistant when freshly printed but gradually passes into a water-insoluble state and then no longer can be effaced. A colloidal maturing process seems to be involved here, since such inks yield directly water-resisting inks if the binder has previously been heated for a long time at an elevated temperature.

Addition of a few per cent of tannin to the water-base inks described above will impart a gloss to the print.[37]

Another type of water-base ink consisting primarily of an aqueous emulsion of casein plus coloring matter has been proposed by Knight.[38] Carbolic acid and formaldehyde are used as preservatives, and oil of citronella is employed to mask any objectionable odors. Addition of glycerin gives body to the vehicle without interfering with the free-flowing quality so essential to an ink of this type. Moreover, it prevents bubbling in the fountain and is reported to give the print a better finish. An alkaline peptizer, usually borax, is required to emulsify the casein.

Preparation of such an ink may be carried out as follows: To 1000 cc. of skim milk are added about 85 g. of casein. After the latter is stirred into the milk, about 60 g. of borax are incorporated and the mixture

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[35] G. W. Miles, U. S. P. 1,401,348, Dec. 27, 1921; *Chem. Abs.*, 1922, **16**, 1013. U. S. P. 1,410,211, March 21, 1922; *Chem. Abs.*, 1922, **16**, 1875.

[36] H. Kurz and K. Albert, U. S. P. 1,962,823, June 12, 1934; *Chem. Abs.*, 1934, **28**, 4923. French P. 746,863, 1933; *Chem. Abs.*, 1933, **27**, 4698; *Rev. Paint, Colour, Varnish*, 1934, **7**, 103.

[37] H. Hadert, Dutch P. 56,423, 1936; *Chem. Zentr.*, 1936, **107** (2), 877; *Rev. Paint, Colour, Varnish*, 1936, **9**, 316.

[38] G. D. Knight, U. S. P. 1,724,603, Aug. 13, 1929, to Emory Winship; *Chem. Abs.*, 1929, **23**, 4836; *Rev. Paint, Colour, Varnish*, 1929, **2**, 332.

agitated until the casein is colloidally suspended. To this suspension is added a few drops of formaldehyde, about 10 cc. of a 10-per cent solution of carbolic acid, approximately 5 cc. of citronella oil and about 50 cc. of glycerin (in the order named) while the mixture is in constant agitation.

Instead of adding more casein to the skim milk, a gelatin, especially animal glue, may be incorporated as binding agent.[39] The vehicle is made up of 70 to 80 per cent of skim milk, 10 to 20 per cent of glue, 2 to 4 per cent of potassium dichromate (a preservative), 3 to 4.5 per cent of vegetable oil, 1 per cent of citronella oil, and 1 per cent of hydrocarbon thinners. The vegetable oil increases the viscosity of the emulsion and allows the ink to pull more readily from the intaglio plate or cylinder in the printing operation. In one instance, gelatin and glycerol were utilized for aqueous inks.[40] A resin may be added to this type of mixture to impart more body.[41] In place of skim milk an ammoniacal solution of casein containing approximately the same proportion of the latter may serve as base. However, the minerals and other materials present in skim milk seem to affect the properties of the ink favorably.

A number of intaglio inks, which may be technically described as water inks, consist of an emulsion in water of a solution of asphalt or resin in a high-boiling petroleum hydrocarbon.[42] A solution of gilsonite in a petroleum hydrocarbon (boiling point 130 to 180° C.), for example, is dispersed in a water solution containing the reaction product of ethylene oxide and dodecyl alcohol (as emulsifying agent) and a suspension of the pigment (*e.g.*, carbon black or Milan Blue).[43] For bright-colored inks an oil-soluble alkyd resin [44] or colophony is generally used. For example, a glycerol-phthalic anhydride-linseed oil resin dissolved in a hydrocarbon solvent is emulsified with Hansa Yellow GT paste, using the condensation product of oleic acid and ethylene oxide as emulsifier.[45]

A fast-drying ink of the same type consists of approximately 22 parts of gilsonite in 51 parts of hydrocarbon solvent dispersed in 22 parts of water containing 5 parts of glue. This dispersion is ground with a pigment to furnish a homogeneous composition.[46]

In some instances a water ink for copper-plate engraving work may contain flour as a bodying agent.[47] The vehicle is made of 48 parts of flour and 16 parts of magnesia mixed with a solution of 1 part of sodium carbonate and 2 or 3 parts of yellow soap dissolved in 160 parts of water. A soluble dye serves as coloring material and a small amount of dextrin

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[39] G. D. Knight, U. S. P. 1,816,978, Aug. 4, 1931, to Emory Winship; *Chem. Abs.*, 1931, **25**, 5584; *Brit. Chem. Abs.* **B**, 1932, 518; *Rev. Paint, Colour, Varnish*, 1932, **5**, 173.

[40] J. Macdonough, U. S. P. 52,869, Feb. 27, 1866.

[41] Zenzi Kosizima and Kazno Siba, Japanese P. 90,910, 1931; *Chem. Abs.*, 1931, **25**, 5048.

[42] See Chapter 13 for a discussion of emulsion inks.

[43] French P. 765,378, 1934, to I. G. Farbenind A.-G.; *Chem. Abs.*, 1934, **28**, 7042. British P. 414,801, 1934; *Chem. Abs.*, 1935, **29**, 1269; *Brit. Chem. Abs.* **B**, 1934, 932.

[44] For the preparation of such resins, see Carleton Ellis, "The Chemistry of Synthetic Resins," New York, Reinhold Publishing Corp., 1935.

[45] British P. 439,524, 1936, to I. G. Farbenind A.-G.; *Rev. Paint, Colour, Varnish*, 1936, **9**, 93.

[46] G. D. Knight, Canadian P. 304,857, 1930; *Chem. Abs.*, 1931, **25**, 833.

[47] R. Webb, British P. 26,992, 1896; *J. S. C. I.*, 1897, **16**, 1012.

assists in the drying. Chlorinated rubber has been proposed as binding agent for water-base intaglio inks.[48] This binder was stated to furnish a lustrous, elastic ink, highly resistant to chemical or physical changes.

Alcohols find occasional[49] use as solvents for quick-drying gravure inks. Shellac, being the most common satisfactory binder soluble in alcohols, is generally employed. Pigments are dispersed in this solution to produce the ink.[50, 51]

Kawabata suggests the use of a volatile (essential) oil as solvent.[52] The lake pigments kneaded with rosin oil are added to a gum solution in the oil. Fillers such as aluminum hydroxide or magnesium carbonate may be incorporated.

Synthetic Resin Binding Agents. The use of synthetic resins as binders in intaglio inks is proposed by Fleischmann and Jordan.[53] The resins suggested by them are condensation products obtained from urea or urea derivatives and an aldehyde, in particular, formaldehyde; from organic vinyl esters; or from organic dibasic acids and polyhydric alcohols.[54] These resinous products are dissolved in a volatile organic solvent, especially those which contain hydroxyl groups, as for example aliphatic alcohols having one to five carbon atoms per molecule, glycol monoalkyl ethers or ketones, and also in some esters or benzene hydrocarbons. The binding agents are easily soluble in mixtures of the above-mentioned liquids with each other or with some other substances of a resinous or oily character. In some cases the resins may be formed directly in the solvent.

The ink is made by incorporating a finely dispersed pigment in the varnish. In addition, other resinous materials such as coumarone resin, colophony, and also cellulose derivatives (*e.g.*, nitro- or acetylcellulose esters or ethers) may be incorporated. The following example will serve as an illustration of the procedure: a solution of 40 parts (by weight) of a condensation product of urea and formaldehyde, 40 parts of isobutyl alcohol and 20 parts of 80-per cent ethyl alcohol is mixed with 10 parts of lampblack and 5 parts of the calcium salt of the azo-dyestuff of aniline and 2,6-naphthalenesulphonic acid. The mixture is repeatedly ground in a three-roller mill, adding a small proportion of alcohol during the grinding operation. After dilution with alcohol to the desired consistency, an intaglio ink ready for printing is obtained. The finished prints are reported to have good fastness to water and rubbing.

Nitrated natural resins dissolved in a solvent having as bases di- and

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[48] H. Hadert, *Am. Ink Maker*, 1933, 11 (11), 9; *Rev. Paint, Colour, Varnish*, 1933, 6, 335.

[49] See section on cellulose derivative inks in this chapter.

[50] W. H. Laurence, Canadian P. 338,454, 1934; *Chem. Abs.*, 1934, 28, 2204.

[51] German P. 636,311, 1936, to Kast and Ehinger, G. m. b. H., *Chem. Zentr.*, 1937, 108 (1), 1294; *Rev. Paint, Colour, Varnish*, 1937, 10, 119.

[52] Iwao Kawabata, Japanese P. 69,035, 1926; *Chem. Abs.*, 1928, 22, 2850; *Rev. Paint, Colour, Varnish*, 1928, 1, 173.

[53] H. Fleischmann and O. Jordan, U. S. P. 1,787,239, Dec. 30, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 833. British P. 307,877, 1928; *Chem. Abs.*, 1930, 24, 252; *Rev. Paint, Colour, Varnish*, 1929, 2, 151. French P. 671,082, 1929; *Chem. Abs.*, 1930, 24, 1996.

[54] Methods for preparing such bodies are discussed by Carleton Ellis, "The Chemistry of Synthetic Resins," New York, Reinhold Publishing Corp., 1935.

trichloroethylenes are said to provide a suitable vehicle for printing inks.[55] The resin is nitrated by means of nitric acid of 36° Bé. at 160° C. until it is saturated. The product is added to the solvent and after dissolution the coloring matter is added and the mixture stirred until it is homogeneous. The solvent may be either quick- or slow-drying. The quick-drying solvent contains 70 to 100 per cent dichloroethylene and 30 to 0 per cent benzene whereas the slower-drying solvent consists of 70 to 100 per cent trichloroethylene and 30 to 0 per cent toluene or xylene.

The use of the resin Beckacite (a tar acid-formaldehyde resin) has been recommended.[56] This binder is dissolved in xylene or toluene and aluminum hydroxide suspended in this mixture (for example, 40 kg. Beckacite 120G. hard, 65 kg. xylene and 55 kg. aluminum hydroxide). Coal-tar dyes are used as coloring material. By adding a large proportion of the dye an intense hue is obtained which may be used as a standard mixture for coloring inks.

Cellulose Derivatives as Binders. Solutions of cellulose derivatives find important applications as vehicles for some intaglio inks used in printing on various non-absorbent substrates such as metal foils, glazed paper, and on Celluloid or various acetylcellulose products. These inks serve also for transparent printing and are reported to give very good printing results where unpigmented resin inks, because of their shortness and high adhesion, are inadequate. Because of their high cost, however, they find only limited use.[57]

The liquid component of the vehicles consists of mixtures of highly volatile solvents with which, however, a higher-boiling liquid is often admixed to reduce the volatility. A solvent including a large fraction of ethanol, for example, may be employed. One such ink comprises a solution of alcohol-soluble cellulose esters (*e.g.*, acetylcellulose or nitrocellulose) and coloring matter in a solvent containing at least 70 per cent of ethanol.[58] In addition to ethyl alcohol other solvents or diluents are employed. These solvents should not, of course, nullify one of the advantages, *i.e.*, pleasant odor and lack of injurious physiological action of the ink. Esters, ketones, dioxane, glycol ethers and benzine, for instance, may be added in small amounts. Various modifying agents, such as resins,[59] pigments, plasticizers, fillers, are of course incorporated, depending on the particular use to which the ink is to be put.

An intaglio printing ink for metal foils is prepared as follows: 450 parts of a rolled mass of 200 parts of nitrocellulose (containing 11 per cent of nitrogen and soluble in ethyl alcohol), 50 parts of diethyl

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[55] L. Magnien, British P. 379,094, 1932, to Societe Anonyme Chlorosoda; *Chem. Abs.*, 1933, 27, 3627; *Brit. Chem. Abs.* B, 1932, 997. French P. 701,597, 1930; *Chem. Abs.*, 1931, 25, 4138. German P. 557,626; *Paint Var. Prod. Man.*, 1933, 9 (9), 23; *Rev. Paint, Colour, Varnish*, 1933, 6, 266.

[56] H. Hadert, *Farben-Chem.*, 1935, 6, 135, 171; *Chem. Abs.*, 1935, 29, 6079; *Rev. Paint, Colour, Varnish*, 1935, 8, 207.

[57] G. L. Riddell, *Modern Lithographer*, 1934, 30, 114; *Rev. Paint, Colour, Varnish*, 1934, 7, 203.

[58] British P. 339,733, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2865; *Rev. Paint, Colour, Varnish*, 1931, 4, 208. French P. 700,427, 1930; *Chem. Abs.*, 1931, 25, 3855.

[59] For high rates of printing, little or no resin should be present, according to French P. 734,287, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1216; *Rev. Paint, Colour, Varnish*, 1933, 6, 135.

phthalate and 200 parts of chromium yellow are dispersed in a mixture of 360 parts of 90-per cent ethyl alcohol, 30 parts of ethylene glycol monoethyl ether, 50 parts of colophony, and 50 parts of diethyl phthalate.

Another ink employed for printing Celluloid, ethylcellulose foils, or glazed paper consists of 270 parts of nitrocellulose containing about 10.7 per cent nitrogen, which has been moistened with about 35 per cent of its weight of isopropyl alcohol, 150 parts of diethyl phthalate, 30 parts of castor oil and 40 parts of colophony. These ingredients are ground in a ball mill with 95-per cent ethyl alcohol and 200 parts of Milori Blue.

Harrison and Oakshott[60] describe an ink which consists essentially of a solution of a cellulose ether (*e.g.*, methyl, ethyl, propyl, butyl, and glycol cellulose) and spirit-soluble dye in alcohol. An illustration is a composition comprising 40 parts of Green Y Rotor, 5 parts of ethylcellulose and 155 parts of denatured alcohol. To this are generally added a spirit-soluble adhesive, such as shellac, and an additional high-boiling solvent, such as methylcyclohexanol acetate or methylcyclohexanone. Titanium oxide increases the opacity of the ink without impairing the brilliance which the spirit-soluble dye imparts. These inks, because of their brightness and depth, may be utilized for printing on colored paper or paper to be subsequently waxed.

Diethyl- and dimethyl-1,4-dioxane have been proposed as solvents for the cellulose derivatives.[61] One vehicle of this kind consists of 100 parts of pyroxylin dissolved in a mixture of 600 parts of diethyl-1,4-dioxane, 50 parts of butanol and 250 parts of ethanol. Resins, dyestuffs, gelatinizing agents subsequently are incorporated to produce the ink. The inclusion of a small amount of these dioxane derivatives facilitates the dissolution of any resins which may be incorporated and further tends to impart a pleasant odor.

Arzt[62] employs a solvent consisting mainly of benzene. One such ink comprises a solution of 10 parts of ethylcellulose in a mixture containing 130 parts of benzene and 13 parts of alcohol, in which are suspended 5 parts of lampblack. Such compositions, according to Arzt, exhibit a strong resistance to mechanical and chemical action.

A printing ink particularly for printing foils, films and other articles of organic derivatives of cellulose includes a pigment, a cellulose acetate (plasticizable base) and at least five times the amount of the latter of a plasticizer.[63] A brown intaglio ink has the following composition:

Cellulose acetate	24 parts	Triacetin	400 parts
Carbon black	50 parts	Acetone	40 parts
Red oxide of iron	180 parts	Benzene	25 parts
Benzyl alcohol	157 parts	Alcohol	18 parts

[60] A. A. Harrison and S. H. Oakshott, British P. 425,218, 1935, to Imperial Chemical Industries Ltd.; *Chem. Abs.*, 1935, 29, 5682.

[61] British P. 326,824, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 4945; *Brit. Chem. Abs.* B, 1930, 624.

[62] H. Arzt, German P. 540,997, 1932; *Chim. et Ind.*, 1932, 28 (2), 405; *Rev. Paint, Colour, Varnish*, 1932, 5, 276.

[63] Wm. H. Moss, British P. 456,898, 1936, to British Celanese, Ltd.; *Rev. Paint, Colour, Varnish*, 1937, 10, 25; *Brit. Chem. Abs.* B, 1937, 159.

In some instances, aluminum stearate has been utilized.[64] One such composition, for example, is made of 15 parts of wax, 10 parts of aluminum stearate, 14 parts of castor oil, 15 parts of nitrocellulose dissolved in 70 parts of butyl acetate and 30 parts of toluene. The pigment in this instance is 15 parts of carbon black.

An ink especially adaptable for intaglio printing on surfaces such as paper, rubber, cellulose and fabrics, and containing rubber and cellulose as binders, is described by Morris.[65] The prints produced with these inks are keyed, that is to say, they penetrate into the surfaces of the material and thus yield a fast print which is not removable. In making these inks a "rubber-cellulose medium" is prepared and to this a paste of the coloring matter, solvent and thinner is added. The "rubber-cellulose medium" is a concentrated solution of the celluloid derivative and rubber or rubber-like medium, such as balata or gutta percha. One such medium, for example, consists of 10 parts of acetylcellulose dissolved in 40 parts each of butyl acetate and xylene mixed with a solution of 2½ parts of crepe rubber in 25 parts of cyclohexanone. The constituents may be mixed in any order so that it is possible for the printer to prepare the colorless ink of the correct consistency and then add the color paste in the well of the press until just the right shade is obtained. A thinner recommended for such solutions comprises 2 parts of toluene, 2 parts of butyl alcohol, 1 part of methylethyleneglycol and 1 part of tetrahydronaphthalene. White or other effects may be obtained by printing with the uncolored or colored medium and subsequently dyeing by means which will not take where there has been such printing. Also, chlorinated rubber and latex may be used in ink compositions either with or without cellulose derivatives.[66]

Practically all the inks previously described in this chapter dry mainly by evaporation and to some extent by penetration. For printing on absorbent paper, Hydeman[67] recommends a non-drying composition which will dry entirely by penetration or absorption. This ink may be used in printing service checks, such as those issued in hotels, restaurants and garages, which can be used at once without undue smearing of ink or soiling of the hands. The base may be oleic acid, castor oil, or mineral oil, in which the pigment has been incorporated.

Ussolzew[68] describes a gravure ink the drying of which is brought about by gelation. The ink in bulk is a sol, the binder of which consists of an aqueous dispersion of a colloidal body obtained by the mixture of

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[64] French P. 806,594, 1937, to Auerbach, Weissberger a Spol; *Chem. Abs.*, 1937, 31, 4837; *Rev. Paint, Colour, Varnish*, 1937, 10, 341.

[65] H. N. Morris, U. S. P. 2,036,768, April 17, 1936, to Rucel Ltd.; *Chem. Abs.*, 1936, 30, 3667; *Rev. Paint, Colour, Varnish*, 1936, 9, 243. British P. 320,410, 1928; *Chem. Abs.*, 1930, 24, 2622; *Rev. Paint, Colour, Varnish*, 1929, 2, 333.

[66] French P. 806,594, 1937, to Auerbach, Weissberger a Spol; *Chem. Abs.*, 1937, 31, 4837; *Rev. Paint, Colour, Varnish*, 1937, 10, 341.

[67] J. E. Hydeman, U. S. P. 1,721,397, July 16, 1929; *Chem. Abs.*, 1929, 23, 4310.

[68] S. S. Ussolzew, British P. 481,911, 1938, to Aktieselskabet Drubin; *Chem. Abs.*, 1938, 32, 7294; *Brit. Chem. Abs.* B, 1938, 694. French P. 810,509, 1937; *Chem. Abs.*, 1938, 32, 814.

the secondary alcohols of the borneol type and derivatives of furan (*e.g.*, furfuraldehyde). A typical preparation of this kind contains 10 parts of borneol, 2.5 parts of an aldehyde of the furan group, and 50 parts of water, in which vehicle are incorporated 0.5 per cent of carbon black and 9 per cent by weight of pigment. The sol thus produced in bulk gelatinizes upon being printed, due to external influences (*eg.*, air, temperature), and sets to a water-fast coating.

Chapter 11

Photomechanical Preparation of Matrices

Although this book deals essentially with printing inks, it has been thought desirable to incorporate at least a short discussion of the preparation of printing matrices. The requirements of printing inks are so closely dependent upon the printing processes in which they are used that a short exposition of the basic principles involved in the preparation of printing surfaces should find a place in a book of this kind. In Chapter 1, a number of mechanical and photomechanical methods of preparing printing matrices already have been described, and it is intended here to discuss somewhat more fully the more important photomechanical reproduction processes. All these processes involves the use of sensitized surfaces so that the actions of these will be first discussed. The preparation of intaglio, relief, copy relief, and lithographic plates then will be described.

Photosensitive Compositions

All photomechanical processes are based on one phenomenon, the change in solubility or distensibility produced in a photosensitized colloid by the action of light. Of the colloids now in use the more important are gelatin (photogravure); fish glue (relief processes); albumin (lithography and relief processes); and gum arabic (lithography). The sensitizing agents generally are alkali or ammonium bichromate, although silver salts occasionally find application. The sensitized film is obtained by pouring a thin emulsion of the colloid over a properly prepared base, drying the film and allowing it to come to (hygroscopic) equilibrium at operating conditions. Under ordinary conditions the water content of a "dry" gelatin or albumin film is 10 to 15 per cent, and in this state, if it contains a sensitizer, the film is photosensitive. Neither the emulsion nor the completely desiccated mixture of colloid and bichromate will react under the influence of light. The effect of the light is to harden or tan the sensitized gel and render it insoluble in water. The degree of tanning depends on the time and intensity of illumination.

The wide applicability of gelatin—it is used in the collotype and copy relief processes as well as the gravure—makes this colloid of particular interest. Gelatin is a complex protein derived from collagen, a substance present in the muscles, bones, and connective tissue of veterbrates. Upon treating this animal matter with hot water, steam or slightly acid solution, the collagen is hydrolyzed to gelatin which passes into solution. The clear filtrate from this solution forms a colorless transparent gel on cooling to room temperature if sufficient gelatin (more than 2 per cent) is present. If gelatin is placed in cold water it absorbs a considerable amount of liquid and swells. The quantity of water taken up increases with temperature and, at approximately 30° C., the swollen gelatin goes into solution. It is generally believed that gelatin, in absorbing water, dissolves the latter and retains its own molecular structure expanded but otherwise unchanged. Instead of expanding radially however, it swells almost entirely in a single direction, that is, along the axis on which it shrank from the original solution. It is this property of gelatin which allows its use in collotype and the preparation of copy relief in which, as described below, the untanned gelatin is swollen but not removed from the plate. Both fish glue and albumin are more or less soluble in cold water and cannot be used, therefore, in these processes. The presence of a bichromate salt does not modify the behavior of the gelatin to any great extent in the absence of light although a slow hardening occurs even in the dark.

In applying the sensitive film a warm solution of the gel, either plain or containing the requisite quantity of bichromate salt, is poured over the carefully leveled plate or backing[1] and dried in an oven at low heat. A gravure tissue, on the other hand, may be suspended vertically and excess solution allowed to drain off. If the sensitizing salt has not been included, it may be introduced by soaking the coated plate in an aqueous bichromate solution of the proper concentration, and the coat once more dried. The plates generally are used within a few days of their preparation, because of their gradual deterioration. According to Rowell,[1a] deterioration may be retarded by covering the freshly dried colloid film with a thin coating of water-insoluble but water-permeable material. A composition consisting of 1.5 parts beeswax, 3 parts tallow and 20 parts turpentine is applied to fresh films which have been dried in non-actinic light. It is reported that plates which were treated in this manner and stored a year or more in light-tight envelopes were found, upon removing the wax, to be in good condition and still sensitive.

TANNING

The phenomenon of tanning is not very well understood. It is known that the hardening of chromatized gelatin is brought about by the action of insoluble chromium chromate, $Cr_2O_3 . CrO_3$. The reduction of the

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[1] Sometimes the sensitive coating is prepared first on a flexible backing and then transferred to the metal plate. One method comprises coating a thin sheet of material such as paper with an aqueous solution of starch or sugar. This is dried and the gelatin composition applied. After this has set, transfer to the metal surface is made. The backing sheet is removed by moistening it. The water penetrates the paper and softens the starch or sugar coating and allows the paper to be stripped off. Then the carbohydrate itself is rinsed off, leaving the clean surface of gelatin. (H. Neumann, U. S. P. 1,989,017, Jan. 22, 1935; *Chem. Abs.*, 1935, 29, 1908.)

[1a] G. S. Rowell, U. S. P. 1,992,965, Mar. 5, 1935, to Multigraph Co.; *Chem. Abs.*, 1935, 29, 2632.

bichromate proceeds, although very slowly, in the absence of light. Illumination serves merely to accelerate this reaction. The addition of a reducing agent to the gel causes reduction of the bichromate and tanning of the gelatin. However, small amounts of mild reducing agent are sometimes incorporated for the purpose of rendering the gelatin more sensitive. Potassium ferrocyanide, for example, is frequently used.[2] The presence of small quantities of certain salts, which do not exhibit any reducing action, however, has been found to enhance the sensitivity of the coating. Chlorides of copper, cobalt, and nickel in low concentration (0.1 to 0.5 per cent) increase the sensitivity of the film two to threefold. The objection which has limited the general use of copper chloride, and to a lesser degree also nickel and cobalt salts, is that gelatin coats become too tough to allow clean and easy development in water. On the other hand, cerous and lanthanum chlorides are described as excellent accelerators.[3] They show no tendency to toughen the gel and the exposure required is one-third to one-half the usual time.

The tanning of a simple chromatized gelatin is attributed, as already mentioned, to the action of chromium chromate. However, any insoluble chromate (and many other salts as well) exhibits the same tanning action.[4] It is to the formation of these chromates that Tritton [5] ascribes the accelerating action of the heavy salts. It appears probable that photodecomposition of bichromate proceeds by stages, the first of which is the formation of chromate ion which then is followed by reduction to chromium chromate. In the presence of a soluble salt which precipitates a chromate the hardening compound is formed at the end of the first stage and further reduction to produce insoluble chromium chromate is unnecessary. The choice of cation is greatly restricted. Thus, any salt which precipitates the chromate from a solution of the bichromate cannot be used since such a salt would tan the gelatin at once. The following considerations indicate the conditions a good accelerator must meet.

In a solution (or a water-retaining gel) of a bichromate or chromate salt, both the bichromate and chromate ions are present. The equilibrium between the two ions and the equilibrium constant K may be represented respectively by the equations:

$$2CrO_4^{--} + 2H^+ \leftrightharpoons Cr_2O_7^{--} + H_2O \qquad K = (Cr_2O_7^{--})/(CrO_4^{--})^2(H^+)^2 = 1.2 \times 10^{14}$$

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[2] See, for example, A. Weingarten, U. S. P. 1,564,161, Dec. 1, 1925; *Chem. Abs.*, 1926, 20, 343.

[3] F. J. Tritton, *Photographic Journal*, 1929, 69, 281; *British Journal of Photography*, 1929, 76, 381; *Chem. Abs.*, 1929, 23, 4629.

[4] This fact is applied in the preparation of printing plates similar to collotype by non-photographic methods. Briefly, it consists of making a sketch on paper say, with a pencil containing a tanning salt (*e.g.*, alum) and mounting this on the unsensitized gelatin. The printed portions of the subject tan the gelatin so that on treating the latter with water and ink-repellent (*e.g.*, bile), the tanned portions are unaffected and remain ink-retaining whereas the distensible portions swell and become ink-repellent. See V. Dietz, U. S. P. 2,023,669, Dec. 10, 1935, to Erwin B. Elliott and Maurice C. Boyd; *Chem. Abs.*, 1936, 30, 793; U. S. P. 2,044,156, June 16, 1936; *Chem. Abs.*, 1936, 30, 5334. H. Wienke, British P. 448,520, 1936; *Chem. Abs.*, 1936, 30, 8441.

[5] F. J. Tritton, *loc. cit.*

The mechanism involves the two equilibria:[6]

$$HCrO_4^- = CrO_4^{--} + H^+ \qquad K = 7 \times 10^{-7}$$
$$2HCrO_4^- = H_2O + Cr_2O_7^{--} \qquad K = 60$$

Inspection of these equations shows that the concentration of chromate ion decreases with increasing hydrogen ion concentration or decreasing pH. The greater the insolubility of a chromate the lower the pH of the solution from which it will precipitate. The pH of a gelatin film is usually 7 to 8. The addition to such a gel of a salt which deposits the chromate from solutions of lower pH will result in immediate tanning of the gelatin because of the formation of the insoluble precipitate (unless the salt is added in such small quantity that the solubility of the chromate is not exceeded). Thus copper chloride is ordinarily an unsatisfactory sensitizer since it precipitates the chromate from solution with a pH of 5.5. Cobalt and nickel chromates form in solutions with pH of 6.8 and 6.6, respectively, and for this reason, salts of these cations are also objectionable. Even in small quantities these sensitizers react to some extent and toughen the gelatin. A satisfactory sensitizing agent is obviously one which forms the insoluble chromate in a solution with a pH slightly higher than 8. This salt would not form the chromate in the original bichromate gel but would precipitate as soon as any additional chromate had been synthesized by the action of light. Cerous and lanthanum chlorides deposit the chromates from solutions with pH of 8 and 8.5, respectively, and are recommended as sensitizing agents. The salt may be incorporated in the sensitizing bath. Such a bath used in the preparation of gravure tissue has the following composition: 2.5 parts potassium bichromate and 2 parts of a 10-per cent cerous chloride solution in 100 parts of water. On the other hand a normal bichromated gelatin may be exposed for one-third the usual time and then soaked, preparatory to mounting, in a 2-per cent cerous chloride solution in place of plain water.

What has been said regarding gelatin holds to a large extent also for albumin and fish glue. This is to be expected since they all are protein compounds.[7] In photolithography, albumin (and occasionally gum arabic) is the colloid employed. Ammonium chromate is the chromatizing agent generally used with albumin. Its sensitivity in the latter is about twice as great as that of the potassium salt. Reed and Dorst[8] state that for best results the ratio of bichromate to albumin (dry) should be 1:3. The amount of moisture retained (10 to 15 per cent) after the film has set depends on the humidity of the surrounding air, and greatly influences the quality of the print obtained. Humidity is therefore an important factor in preparation of the plate.

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[6] W. M. Latimer and J. H. Hildebrand, "Ref. Book of In. Chem.," New York, The Macmillan Co., 1934, p. 281.

[7] Fish glue, a gelatose, is a further hydrolytic product of fish gelatin.

[8] R. F. Reed and P. W. Dorst, *Bulletin, Lithographic Technical Foundation, Inc.*, 1932, No. 6. The albumin process is fully described in this bulletin.

Sensitized films employing certain synthetic resins in place of the usual albumin, gelatin or gum arabic have been proposed. Polyvinyl alcohols [9] and ammonium bichromate, for instance, are stated to form a photosensitive body which requires only one-third of the exposure needed by corresponding albumin coatings. A film of this kind is prepared by pouring over a clean zinc plate or other backing a heated aqueous solution containing 5 per cent moderately polymerized vinyl alcohol and 4 per cent ammonium bichromate and subsequently drying the layer thus formed. The exposure is made, the plate developed, dyed, etched and washed out to produce the finished matrix. The polyvinyl alcohol coatings are said to exhibit a toughness and elasticity exceeding that of the protein films.

Synthetic resins, together with shellac, dissolved in a weakly alkaline bichromate solution dry to a photosensitive film which may be used in the autotype and similar processes.[10] Development of the plates after exposure is effected with alcohol.

The use of asphalt or bitumen of Judea (sometimes referred to as "Syrian Asphalt") as a photosensitive material was quite general before the introduction of chromatized gelatin, albumin, and fish glue. This asphalt is much less sensitive than the bichromated protein colloids, although it is said to give somewhat superior printing results.[11] The introduction of sulphur increases the sensitivity of the bitumen.[12] A method of incorporating sulphur is to dissolve 100 parts of Syrian asphalt in 500 to 600 parts of carbon disulphide. To this solution are added 6 to 8 parts of sulphur chloride diluted with 20 parts of carbon disulphide, and the whole heated to boiling in a flask fitted with a condenser. Hydrogen chloride and carbon disulphide distill off. The residue is diluted with 2000 parts of anhydrous benzene and the mixture filtered. After the addition of 2 per cent oil of lavender, the filtered solution is ready for use. Turpentine is used in the development since asphalt is insoluble in water.

PRINTING PROCESSES

The three classifications of printing, *viz.*, intaglio, relief and planographic, are based solely on the nature of the printing matrices employed (see Chapter 1). In considering the preparation of these matrices it is found more convenient to make the following division of the subject: intaglio processes, relief processes, copy-relief processes, photolithographic processes and the collotype process.

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[9] British P. 451,009, 1936, to Chemische Forschungsgesellschaft m. b. H.; *Rev. Paint, Colour, Varnish*, 1936, 9, 306; *Chem. Abs.*, 1937, 31, 332. French P. 795,361, 1936; *Chem. Abs.*, 1936, 30, 5138.

[10] F. Besemann, German P. 650,151, 1937, to I. G. Farbenind. A.-G.; *Chem.-Tech. Ubersicht*, 1938, 62, (1/3), 3; *Rev. Paint, Colour, Varnish*, 1938, 11, 50; *Chem. Abs.*, 1938, 32, 874.

[11] C. W. Gamble, "Modern Illustration Processes," London, I. Pitmans and Sons, Inc., 1933, 1938.

[12] E. Valenta, *Phot. Korr.*, 1910, 47, 238; *Chem. Abs.*, 1910, 4, 3044; *J. S. C. I.*, 1910, 29, 783.

Intaglio Processes. An important difference between intaglio prints and prints produced from planographic and relief matrices is that in the first-named the tone of the print is rendered by various thicknesses of ink or pigment, whereas in the latter two the illusion of tone or shade is created by dots of different size.[13] In intaglio prints effects are thus obtained in the same manner as in a painting, and the intaglio processes are, for this reason, adjudged by many to afford the ideal method of photomechanical reproduction.

The most direct photointaglio process is the Woodbury type,[14] although the method is seldom used. The printing plate consists of a sheet of lead which is impressed with a series of cavities, the variation in depth of which corresponds to the light and dark portions of the picture it represents. A sheet of paper coated with bichromated gelatin containing carbon or other pigment in suspension[15] is exposed under a negative. The gelatin is tanned to different depths depending on the intensity of illumination. The film is then transferred to a support consisting of a thin layer of collodion on a plate of glass. (In "transferring" the film is mounted on another surface so that the upper face—the tanned portion—of the film rests on this surface and is properly affixed thereto. By sponging the paper backing with warm water, it is loosened and may be stripped off. The soluble gel next is washed away, leaving the contoured surface of tanned gelatin. This is generally treated with alum solution to completely harden it.) The collodion sheet then is stripped off the glass plate. This sheet with the pigmented gelatin is known as the Woodbury "relief" and is nothing more than a carbon print mounted on collodion rather than on paper. It constitutes a reproduction of the subject in which the tone or shade is produced by various depths of pigment, the amount of the latter being proportional to the thickness of the gelatin layer. The relief is placed on the bed of a hydraulic press, a piece of pure, smooth lead placed on it and uniform pressure applied. The tanned gelatin is hard enough to withstand this pressure and a perfect impression of the gelatin mold is produced in the lead. In making a print, the metal matrix is carefully levelled and a pigment-gelatin solution poured into the mold. A sheet of paper is placed on top and pressure evenly applied. Excess gelatin is in this way squeezed out. After the emulsion has set, the paper is pulled off carrying with it the gelatin mold. The latter is a reproduction of the relief from which the matrix was made (provided that the same amount of pigment is present in both). Although this method is no longer in use, the Woodbury type process yields results which are said to compare favorably with those obtained by any other method of photomechanical reproduction.[16]

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[13] This is only partly true for collotype (a planographic process), which is described below.

[14] W. B. Woodbury, British P. 1,918, 1866.

[15] Paper coated with such a pigmented gelatin is known as "carbon tissue." "Gravure tissue" is a paper coated with sensitized gelatin and containing no pigment.

[16] C. W. Gamble, "Modern Illustration Processes," London, I. Pitmans and Sons, Inc.. 1933. 1938.

The Woodbury type is a bridge between the purely photographic carbon process and the photointaglio process exemplified by rotogravure. In the latter process the printing surface is reticulated with narrow lines of unetched copper. The purpose of the reticulation is to provide a bearing surface for the doctor blade with which the ink is removed from the unetched portions of the surface. If a surface with relatively large recessed areas uninterrupted by such reticulation were wiped, much of the ink would be removed from the cavities and accurate reproduction rendered impossible. In rotogravure, reticulation rather than stippling (as in photogravure) is used to prevent lateral flow of ink.

The usual procedure of preparing a rotogravure plate is described in Chapter 1. This comprises exposing a gravure tissue under a diapositive[17] and an intaglio screen successively; transferring the film to printing plate;[18] removing tissue backing and soluble gelatin; etching the plate and removing the gelatin coating. The depth of the cavities in the gravure plate is controlled by the thickness of the gelatin deposit. When the ferric chloride solution is applied the salt diffuses through the gelatin and attacks the metal beneath. The time of etching is so controlled that the metal surface corresponding to white portions of the image is not attacked.

In producing text (line drawings and the like) in combination with gravure pictures the negatives of the continuous-tone matter and of the print or line work may be combined to produce a positive. The complete image is then obtained on the gravure tissue and transfer of the latter to the copper plate is made. The two portions of the plate containing the line work and the picture are etched separately, one portion being covered with asphalt while the other is etched. The separate treatment is necessary bcause the time required differs for the two sections.[19] Another method is to print the text portion (properly layed out) on a thin sheet of celluloid, with a tacky ink. The surface is then dusted over with bronze powder and the print thus rendered opaque. Exposure of the gravure tissue is then made through this sheet and through the diapositive of the continuous-tone matter.

A method of preparing a gravure plate which obviates the necessity of using a gravure tissue has been proposed by Pearson.[20] In this process, according to his description, the image to be reproduced is twice photographed to produce a continuous-tone and a screened negative and from these the corresponding transparencies are made. The presensitized printing plate is then exposed to light passing through the screened positive, and the plate developed to establish an acid-resisting coating. The plate

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[17] For a description of the preparation of a photogravure plate by means of the web collodion process see *British and Colonial Printer*, 1932, 3 (New series No. 207), 344; (208), 372; *Nitrocellulose*, 1932, 3, 228; *Chem. Abs.*, 1933, 27, 1526.

[18] For a method of centering the subject on the plate see V. E. Royle, U. S. P. 1,964,599, June 26, 1934.

[19] See C. W. Saalbury, German P. 236,022, 1910; *Chem. Abs.*, 1912, 6, 1890.

[20] A. A. Pearson, U. S. P. 1,901,468, Mar. 14, 1933; *Chem. Abs.*, 1933, 27, 3157.

is once more sensitized directly over this coating and exposed, this time to light passing through the continuous-tone diapositive with the image on plate and on positive in register. After developing this coating the plate is etched with a copper solvent.[21]

If a rotogravure plate is to be used for long runs, it is often provided with a hard surface, usually of chromium or steel. The layer of metal is produced by filling the depressions with a non-conducting paste and electrolytically depositing a thin layer of a tough metal on the flat portions of the plate. Such a chromium-faced plate may be more deeply etched[22] if this proves necessary on taking a print, the chromium remaining unattacked by the copper-etch solution. Also, nickel has been recommended for this purpose.[23]

Relief Processes. In relief printing, the ink is taken from the supply roller and transferred to the surface being printed by those portions of the matrix which are in relief. This method is of great commercial importance since relief and typographic matrices may be combined and printed simultaneously, the manner of inking and transferring being the same for both. (The term "relief process," as used here, includes only the photoengraving processes of producing line and half-tone plates.) In the reproduction of line work a simple negative is used. Continuous-tone subjects, on the other hand, are rendered by half-tone plates which are obtained by means of a "broken-tone" negative. This negative is obtained by exposing the subject through a half-tone screen. The screen, or its equivalent, is essential in both relief and lithographic processes and its function will be described briefly.

In a half-tone print the illusion of gradation in tone is obtained by dots of various sizes. Thus the dots, which are distributed regularly over the surface, are very small in the highlights and large in the dark portions of the image and these, with dots of intermediate size, produce the effect of tonal variation. The illusion is possible because of the imperfect resolving power of the eye. Thus, if a white sheet covered with black spots is regarded from a distance of 100 cm., the sheet will appear gray and no individual spots will be apparent to the normal eye. Further, the shade of gray will depend upon the size of the spots (the number per unit area remaining constant) until a black is obtained when the spots completely merge.

To obtain a half-tone matrix the screened negative is used. This screened negative is obtained by interposing a half-tone screen[24] between the film and the continuous-tone positive so that a broken-tone negative

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[21] See N. Ludvigsen (U. S. P. 1,944,354, Jan. 23, 1934; *Chem. Abs.*, 1934, **28**, 1944) for another photogravure process in which the exposure is made directly on the sensitized printing plate.

[22] British P. 446,793, 1936, to Soc. anon. de publications periodiques (Imprimeries E. Desfosses); *Chem. Abs.*, 1936, **30**, 6857.

[23] A. A. Leucher, U. S. P. 2,127,824, Aug. 23, 1938; *Chem. Abs.*, 1938, **32**, 7886.

[24] The evolution of the "screen" into its present form may be said to have begun in 1852 with F. Talbot (British P. 565, 1852), who employed gauze. Other more orthodox types of screens were proposed by E. J. Bullock (British P. 2,954, 1865) and J. W. Swan (British P. 2,969, 1879). After this, work on the screen was carried on by Meisenbach Co. Works. For details see Ch. W. Gamble. "Modern Illustration Processes," London, I. Pitman & Sons, 1933, 1938.

is obtained. The screen generally used consists of a transparent plate ruled diagonally with opaque lines, the distance between them and their thickness being approximately equal. The appearance of such a screen is that of clear, transparent squares on an opaque background. Light on passing through a small aperture tends to spread. When the light from the bright portion of the positive passes through these squares in the screen, neighboring rays more or less overlap so that only the centers of intersection (in a properly adjusted screen) of the opaque lines are pictured on the negative as transparent spots. In those parts of the image through which less light passes, the overlapping of the beams will be less and eventually only a small beam will pass through the screen. The portions of the negative illuminated will become opaque, the unilluminated parts remaining clear. On exposing the sensitive surface through this negative the colloid acted on by light will be rendered completely insoluble, the remainder staying soluble.

The sensitized film applied to the plate is generally chromatized albumin or fish glue (in the so-called enamillene method). Ammonium chromate, because of its great sensitivity, is the usual sensitizing agent. Processing of the plates subsequent to exposure differs depending on which of the two coatings (albumin or enamillene) is used. With the albumin film the procedure is as follows: The plate is covered with transfer ink[25] and placed in water. After a short period, the soluble gel is removed by rubbing the plate with a piece of cotton wool. The insoluble portion, to which adheres a thin coating of transfer ink, remains. After drying the plate it is dusted over with finely ground bitumen powder which sticks to the ink. The whole then is warmed to fuse ink and bitumen. Subsequently the portions in relief are covered with a film of gum arabic solution. The plate then is ready for etching.

In the enamillene method, the exposed plate is placed in water and the unaffected fish glue dissolved (fish glue readily dissolves in cold water), leaving the hardened gel on the surface. The tanned gel or image, which is difficult to see, is made visible by flowing a solution of methyl violet over the plate. The plate then is washed clean and dried. Any retouching is made at this stage. The plate subsequently is heated over a low flame. This operation, called "burning in," renders the gel hard and impervious to the etching solution. Because of this last operation, copper rather than zinc (which is preferable in the albumin process) is used, since the zinc, upon being heated, forms crystals and thus produces a rough, uneven surface. A disadvantage of copper, on the other hand, is that it tends to scum (*i.e.*, insolubilize) the gel. From the description, it will be seen that the enamillene is the simpler of the two methods, and it is for this reason that it is preferred in commercial work, particularly for half-tone plates.

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[25] The printing surface may be slightly roughened by incorporating phenol in the transfer ink. This roughened surface causes the ink to be more readily retained on the plate (British P. 478,776, 1938, to Chemische Forschungsgesellschaft m. b. H.).

Etching. Following the preparation of the resist, the plates are submitted to a short, preliminary etch. If the etching were prolonged, the cavity formed between the resist would be attacked not only vertically but also along the sides so that "undercutting" of the resist would occur. This is prevented (in the roller process) by rolling up the surface with ink, powdering over with colophony, and warming so that resist mixture flows down the sides of the cavity and protects them from further action. This is repeated until the etching is completed. A method of modifying the plate, known as "fine-etching," employs controlled undercutting to change the size of the half-tone dots. The operation consists of successively stopping out the portions which are not to be treated further, and undercutting the remainder. The process of fine-etching often constitutes an important step in the production of half-tone plates.

Hurst and Meulendyke[26] describe a method of preparing plates for relief, intaglio or planographic printing which eliminates a number of the steps required in the usual processes. The procedure for making a half-tone plate is as follows: a copper sheet is coated with a thin layer of silver, chromium or nickel and upon this base is deposited a film of gelatin emulsion containing a photosensitive silver salt. The purpose of the metal layer is to avoid contamination of the emulsion by copper. The gelatin then is hardened by treating with a tanning solution. The next step is to expose the plate to the subject through a half-tone screen (60 to 133 line screens afford a practical range). The exposed plate then is developed. Any developer such as metol-hydroquinone can be used. Following this, the plate is rinsed and placed in an oxidizing bath which is generally a 3-per cent hydrogen peroxide solution. The oxidizer has the effect of softening the gelatin directly surrounding the silver dots so that the gelatin dissolves out under the selective control of the silver image. After the solubilized gelatin has been dissolved, the image resist remains on the plate. The addition of a light-restraining agent was found to aid in the control of exposure and processing. The silver emulsion (as most sensitized emulsions) is sensitive largely to light of rather short wave-length, *i.e.*, blue and violet light. A satisfactory light-restraining agent is the yellow dye "tartrazine" which acts as filter to hold back penetration of the blue and violet light.[27]

Preparation of Intaglio and Relief Printing Surfaces from Copy Reliefs. By copy relief is meant the swollen gelatin from which intaglio or relief matrix is cast. In preparing such a relief for an intaglio plate, a so-called copy plate, for example, covered with a thin film of sensitized gelatin is exposed through a diapositive of the subject and then through a ruled screen of transparent lines on an opaque background.[28] The copy plate is then inserted in cold water, the gelatin swelling or

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[26] R. E. Hurst and C. E. Meulendyke, U. S. P. 1,938,290, Dec. 5, 1933.

[27] See also F. H. Bloom, U. S. P. 2,122,404, July 5, 1938; *Chem. Abs.*, 1938, 32, 6775.

[28] E. Sauer (U. S. P. 1,811,971, June 30, 1931, to Ernst Sauer Process, Inc.; *Chem. Abs.*, 1931, 25, 4984) employs a screened positive so that only a single exposure of the copy plate is required.

rising to form the copy relief. This resembles in appearance a reversed rotogravure plate, *i.e.*, a network of sunken lines on a field of varying thicknesses. In this treatment, also, all unreacted bichromate is dissolved out so that no further reaction can take place. If a copy relief for a half-tone plate is desired, a broken-tone negative is used in place of the diapositive and intaglio screen, but the same general procedure is followed.

After the copy relief is removed from the water it is allowed to dry and a cast is made of it. The plate is laid flat, gelatin surface up, and across one end a plastic ("dope") material is poured. A backing sheet of celluloid, for example, is then placed above the gelatin relief and, by means of a heavy roller, is squeezed down upon the copy relief. The bulk of the viscous liquid composition gradually is pushed forward toward the other end of the plate and the excess of the liquid composition pushed out and discarded. The moldable composition is then allowed to harden and set to the final cast. After about 15 minutes the backing paper is stripped off. The backing, with the cast on it, constitutes the printing matrix. After complete solidification of the cast, it is mounted on a plate or roll.

The plastic coating materials are generally cellulose derivatives dissolved or dispersed in volatile liquids. One such mass consists of finely ground acetylcellulose containing 53 to 55 per cent acetic acid mixed with benzene and ethyl alcohol.[29]

Plastic masses employing cellulose nitrate are described by McKee.[30] The compositions are made of cellulose nitrate, plasticizer and a mixture of solvents and contain approximately 25 per cent solid and 75 per cent solvent. The plasticizers (with cellulose nitrate, tricresyl and triphenyl phosphates or dibutyl phthalate are used) impart the desired consistency and toughness to the cast. Acetone, ethyl acetate and other solvents commonly are used. A composition of this type contains 20 per cent cellulose nitrate and 5 per cent triphenyl phosphate dissolved in a mixture of 43.5 per cent amyl acetate and 31.5 per cent butyl acetate. This mixture is reported to yield a cast of great hardness and durability which will faithfully copy the finest impressions. In general a mixture of nitrates of different viscosity are used. The addition of a gum or resin, such as gum dammar, increases the hardness and life of the cast. These gums, which should be insoluble in the inks used, delay hardening and setting of the product somewhat. The compositions harden first by absorption of the solvent by the backing, secondly by precipitation processes when the plastic composition comes in contact with moisture carried by the water-swollen gelatin copy relief, and finally by evaporation of the residual solvent when the cast is removed from the mold and exposed to air.

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[29] German P. 605,995, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1907.

[30] R. H. McKee, U. S. P. 2,116,536, May 10, 1938, to Cellu-type Plate Co., Inc.

Another type of plasticizable mass for casting from copy relief comprises a solution of polyvinyl chloride (containing 65 per cent chlorine) in a solvent such as methyl alcohol.[31]

A somewhat novel method of casting the printing matrix was proposed by Sauer.[32] Instead of using a plastic material, a celluloid solvent (*e.g.*, acetone, ethyl acetate) is poured over the copy relief and a sheet of Celluloid pressed down until only a thin film of solvent remains. This solvent makes the under surface of the celluloid sheet plastic so that an impression of the relief is made. After the mass has set, the celluloid sheet is pulled off and mounted in the customary manner.

A method of producing a rubber matrix from a copy relief is described by Browne.[33] Instead of swelling the exposed gelatin with water, the surface is immersed in rubber latex. As water is absorbed from the latex, the concentration of rubber in the dispersion contiguous to the colloid surface increases to such an extent that a fairly thick film of gelatinized rubber is deposited on the mold. After being withdrawn from the solution, the rubber film is re-enforced by pouring on it a coat of latex and allowing the latter to dry.

Schultz [34] points out that smudges of ink often appear on the uncolored portions of printed matter and encircle the outer margins of the printed image. These defects, he states, are due to the presence of the screening relief which extends into the uncolored portions of the picture and beyond the picture margin. By blocking out the white portions and the margins on the negative, the screen lines are eliminated in the clear portion of the image and from the margins.

Lithographic Processes. The lithographic printing processes are based on the ink repellency exhibited by moist surfaces on the one hand and ink receptiveness exhibited by greasy, water-repellent surfaces on the other. In the (non-photographic) lithographic process, a porous stone generally is used.[35] The calcium-magnesium limestone from the Solenhofer quarries, first used in 1796 by Senefelder, the originator of lithographic printing, still remains one of the best stones for the purpose. The design is drawn on the clean, smooth stone surface with a greasy ink. Upon wetting the stone, water is adsorbed by the uncovered stone, leaving it moist, but repelled from the greasy design. When the wetted stone is next rolled up with fatty ink, the latter is repelled by the moist stone but adheres to the greasy portions making up the design. When an impression is taken, this ink is transferred and the print of the design drawn on the stone is obtained. In most photolithographic processes a

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[31] German P. 614,358, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, 30, 793.

[32] E. Sauer, U. S. P. 1,811,071, June 30, 1931, to Ernst Sauer Process. Inc.; *Chem. Abs.*, 1931, 25, 4984.

[33] T. C. Browne, U. S. P. 2,022,183, Nov. 26, 1935; *Chem. Abs.*, 1936, 30, 902.

[34] O. R. Schultz, U. S. P. 1,980,443, Nov. 13, 1934.

[35] A. R. Trist (British P. 475,902, 1937: *Chem. Abs.*, 1938, 32, 3706) states that a mat surface of electrolytically deposited chromium in a crystalline state may be used for lithographic plates. Such a surface is made grease-receptive by treatment with acids, *e. g.*, hydrochloric or hydrobromic acid, and then is rendered grease-repellent by further treatment with an oxidizing agent, *e. g.*, nitric acid or hydrogen peroxide.

metal, generally zinc or aluminum (in zincography and alagraphy, respectively), is employed in place of stone. The non-image portion of the metal is rendered water-receptive by graining. Water is retained in the minute crevices of the grained surface which is thus rendered grease-repellent. Such a surface is obtained by placing the plate in the shallow tray of a graining machine, moistening the surface, covering it with fine abrasive material and small round marbles. A rapid reciprocating motion is produced which causes the marbles and abrasive material to roll over the plate and produce a finely-grained surface.[36] A roughened surface is also necessary to hold the colloid firmly to the plate.

A process of preparing photolithographic plates employing a transfer paper is described in Chapter 1. This is the so-called "indirect" method. In another, the "direct" method, exposure is made directly on the sensitized printing plate and the latter processed to yield the printing surface. In the direct process a zinc or aluminum plate generally is employed. The metal surface is grained, moistened, and coated with a thin film of fish glue or albumin sensitized with ammonium chromate. A uniform, thin coat is obtained by means of a "whitler." The plate is placed in this machine and revolved at a speed of between fifty and ninety revolutions per minute. The emulsion is poured on the center of the plate and is evenly distributed by the slow whirling motion. The coat is dried by gentle heating. The plate next is exposed through a reversed negative. For reproduction of a gradated tone subject a broken-tone negative is employed. The latter is prepared by exposing the film under a diapositive and screen. Another method, which finds some application in the preparation of litho-plates for offset printing, consists of preparing a half-tone plate, filling in the etched portions with magnesium carbonate to produce a white background and photographing this surface to obtain the broken-tone negative.[37] This expediency is sometimes resorted to when retouching of the diapositive will not produce satisfactory results.[38]

After the proper period of exposure, the plate is covered with a greasy photolithographic developing ink. This is a special composition which adheres only to the exposed portions of the plate. When the ink has dried the plate is placed in a trough or sink and covered with water at about 40° C. The surface then is swabbed with a piece of cotton to remove the unaffected colloid. The plate is removed from the trough, rinsed and given an ammonium phosphate-nitrate etch. After washing and drying, the plate is ready for mounting.

Cornell [39] proposed a double-coated sensitized plate in which the first sensitized layer (nearest the backing or support) consists of a chroma-

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[36] See W. T. Hagelin (U. S. P. 2,040,129, May 12, 1936, to Multigraph Co.) for another method of graining lithographic plates. See also M. Leeden, *Offset Printer*, 1929, 2, 216; *Rev. Paint, Colour, Varnish*, 1929, 2, 342.

[37] See also A. Ya. Baitzurov, Russian P. 34,316, 1934; *Chem. Abs.*, 1935, 29, 2632.

[38] See the description of "dot etching," however, in a subsequent section of this chapter.

[39] A. W. Cornell, U. S. P. 1,912,693, June 6, 1933, to Forbes Lithographic Manufacturing Co.

tized albumin and the other layer of a photosensitive silver salt emulsion. The silver emulsion takes the place of the negative generally employed in lithographic processes. The screened negative image is produced in this emulsion by a short exposure. After it has been developed and fixed, the sensitized surface is again exposed so that the corresponding positive is formed on the albumin layer beneath. After stripping off the top emulsion, the albumin is processed in the customary manner to produce the printing surface. The sensitized plate (see Figure 63) comprises the support, which generally takes the form of a metal plate such as aluminum, on which is applied the layer of bichromated albumin. This layer is provided with a very thin protective coating of paraffin, to the face of which is secured a pellicle of Celluloid. Upon this in turn is imposed a light-sensitive layer which may be an ordinary wet plate emulsion embodying silver iodide. Such compound plates, it is stated, may be used to particular advantage when large images (ten feet square, for example) are to be produced. In the customary method an enlarged negative is made on a silver emulsion supported on a glass plate (lighter transparent mountings being in general unsatisfactory because of shrinkage and trouble in handling). A plate of such size is unwieldy apart from its fragile character. Employing the compound plate, the exposure is taken through a diapositive and the enlarged latent image produced on the silver emulsion (Figure 63). Because of the short exposure and composition weakness of the illumination, the albumin layer is not affected. The plate next is developed, the wax (paraffin) protecting the albumin from the reagents during this operation. The compound film is illuminated (Figure 63) and a print made from the negative layer to the colloid coat underneath. The negative on its celluloid carrier then is stripped off, any adhering wax being sponged off the colloid with turpentine. After this has been done the printing surface is developed in the usual manner.

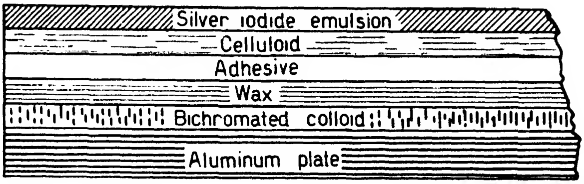

FIGURE 63. Sketch of Double-Coated Sensitized Plate (A. W. Cornell).

Other Methods of Preparing Lithographic Matrices. One of the earliest methods of preparing lithographic printing surfaces employing a bichromated gel as ink-receptive surface was described by Lambert.[40]

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[40] J. N. Lambert, *Ber.*, 1872, **5**, 63; *Chem. Zentr.*, 1872, **3**, 254. British P. 1,124, 1871.

A planed surface of birch, elm or boxwood is used as support. On this surface a sketch is made with an ink composed of a mixture of gelatin, albumin and lampblack in a saturated potassium bichromate solution. This plate is left in the sun for 2 to 24 hours, during which period the gelatin is fully tanned. The surface then is covered with glycerin or gum arabic so that the non-printing areas are rendered ink-repellent.

A zincographic printing process, developed by Droege,[41] is stated to be particularly applicable in reproduction of technical drawings. A positive, such as an India ink tracing on linen, is employed instead of the usual negative. The plate is grained, moistened and coated with a bichromated albumin emulsion which then is dried over a low flame. The tracing is laid upon the plate and an exposure of 2 to 3 minutes made. A composition composed of 1 part of printer's black and 4 parts of oil of turpentine is evenly distributed over the plate and allowed to dry. The surface then is rubbed over with a wad of cotton wool so that the soluble gelatin is removed and the drawing appears in metal on the black background (Figure 64). The drawing at this point appears on the zinc plate as a negative. To transform this into a positive a solution of shellac in alcohol is applied to the plate and dried so that it sets to a thin film over the whole plate (Figure 64). The plate then is washed with a paraffin solvent, a soft brush being used, until the covering or coating, that is, the shellac and printer's black, has been dissolved and removed from the unexposed parts of the plate. This step leaves the plate covered with shellac—corresponding to the black portion of the image—and albumin. All traces of fat or oil are cleared from the surface by rubbing the latter with an aqueous solution of gum arabic. The albumin is removed by treatment with nitric acid and the exposed zinc cleaned and partly corroded with dilute sulphuric acid. The ink-repellent moisture-retaining background is obtained by etching with a solution containing 2 parts each of nitric, hydrochloric and phosphoric acid, together with 1.2 parts of sodium bichromate solution and 50 parts of water. Durable plates, capable of being used for long runs, are said to be secured in this process.

A method of obtaining a positive image from a negative image in gelatin is described by Beebe and Murray.[42] A light rubber blanket is placed in contact with the exposed surface holding the undeveloped negative (as would be obtained by exposure under a screened positive). When the blanket is withdrawn, the soft gelatin is removed from the film adhering to the lower surface of the blanket, forming a reversed positive image on it. The image is transferred to a lithographic surface. The soft gelatin is hardened by treatment with tanning solution and rendered ink-receivable.

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[41] K. Droege, U. S. P. 1,959,947, May 22, 1934; *Chem. Abs.*, 1934, 28, 4616.

[42] M. C. Beebe and A. Murray, U. S. P. 1,618,505, Feb. 22, 1927, to Wadsworth Watch Case Co.; *Chem. Abs.*, 1927, 21, 1169.

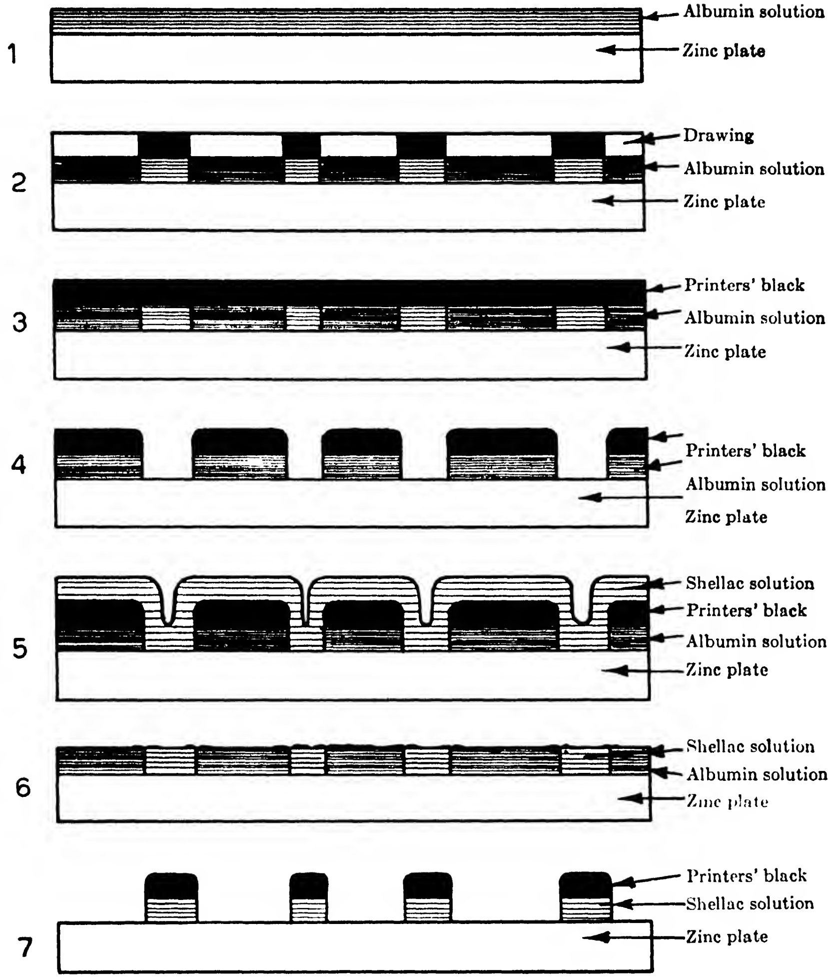

FIGURE 64. Sketch of Method for Preparing Zinc Printing Plates (K. Droege).

1. Plate covered with sensitized solution
2. Drawing placed on sensitized solution
3. Drawing covered with black
4. Negative produced
5. Negative covered with shellac solution
6. Positive produced
7. Positive covered with black

Any substance whose surface, under the selective action of light, may be transformed from a water-receptive to a water-repellent, ink-receptive surface, meets the fundamental requirement of photolithography. Such a substance, provided it possesses the necessary elasticity, strength and chemical inertness, may be employed to make printing plates. For example, cellulose ester may be processed in the following way to yield a lithographic surface.[43] A foil of acetylcellulose is sensitized by soaking with

[43] U. Ostwald, U. S. P. 1,943,486, Jan. 16, 1934, to Kalle & Co. A.-G.; *Chem. Abs.*, 1934, **28**, 2139.

a saturated solution of ammonium bichromate in methyl alcohol. After the sheet has dried it is exposed under a negative. Following exposure, it is treated with a strong caustic soda solution. After rinsing and drying, the foil is ready for printing. In these operations, it is stated, the exposed portions of cellulose ester have been rendered unsaponifiable and remain, therefore, ink-retaining and water-repellent; the unexposed portions are saponified and the cellulose so obtained forms the moisture-retaining, ink-repellent surface.

A printing plate, in which the ink-retaining and ink-repellent surfaces consist of gelatin and Celluloid, respectively, also has been proposed.[44] A sheet of Celluloid is coated on one side with a film of light-sensitive silver gelatin. (The time of exposure is said to be greatly reduced by the use of a silver salt.) The gelatin surface is exposed under a negative (unreversed), through the transparent Celluloid backing so that the colloid contiguous to the backing is affected by the light. The plate is developed in tanning solution which renders insoluble the light-affected, image-printing portion. Following this the surface is inked to make the image-printing portion receptive to ink and repellent to moisture and the soluble gelatin then is washed away, exposing the moisture-receptive, ink-repellent Celluloid surface.

Baker[45] has proposed a process employing a smooth surface and a spongy, irregular surface of tanned colloid as water-repellent and water-receptive surfaces, respectively.

Photo-offset Printing. In offset printing, the transfer of an image from the printing plate to the impression sheet is brought about through the agency of an elastic medium. The ink is deposited from the printing plate to a resilient surface and from this is "offset" onto the impression surface. The chief advantage of the offset method is that it enables smooth prints to be obtained on rough-surfaced papers, cards or metals. If the plate were to print directly on a rough or rigid surface, contact ordinarily would not be established at every point unless impracticably high pressures were employed. The ink, therefore, would not be transferred completely. Although intaglio[46] and collotype plates are sometimes printed by offset, this method generally is associated with the printing of lithographic plates, and in this it is very largely replacing the older direct method.[47]

The offset press[48] consists essentially of three rollers in contact, arranged vertically and revolving in opposite directions. From top to bottom these rolls are termed the "plate," the "blanket," and the "impression" cylinder, respectively. The "plate" cylinder bears the printing

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[44] D. V. Gerking, U. S. P. 1,961,927, June 5, 1934; *Chem. Abs.*, 1934, **28**, 4672.

[45] E. N. Baker, U. S. P. 2,058,396, Oct. 27, 1936; *Chem. Abs.*, 1937, **31**, 58.

[46] See, for example, C. P. Shaw (U. S. P. 2,060,640, Nov. 10, 1936, to Detroit Moulding Corp.; *Chem. Abs.*, 1937, **31**, 331) for a method of producing wood grain effects by offset printing of intaglio plates.

[47] J. F. Jones, *J. Oil & Colour Chem. Assoc.*, 1933, **16**, 149; *Chem. Abs.*, 1933, **27**, 3625.

[48] See H. L. Dennis, *Am. Ink Maker*, 1937, **15** (12), 16; *Rev. Paint, Colour, Varnish*, 1938, **11**, 24.

plate. In contact with it are two rollers—the dampening roller and the inking cylinders. The plate passes first under the dampening roller which moistens the grained metal surface. From here the plate passes immediately under the inking roller where a coat of ink is picked up by the image and rejected by the moistened portion of the plate. The ink then is deposited on the surface of the blanket cylinder (which consists of a roller covered with a rubber blanket about an eighth of an inch thick) and is then offset onto the sheet being printed.

In most routine photo-offset printing, ordinary lithographic plates are used. When long runs are to be made, however, "deep-etched" plates find frequent application. The latter are prepared by illuminating the sensitized metal surface through a diapositive. Development exposes the metal in the image (or work) areas of the plate. The latter are etched to the proper depth and then covered with a greasy, ink-receptive substance. The non-work areas of the plate are desensitized and "gummed up" to enable them better to hold the mildly acid damping solution used on the offset presses.

Other methods for producing deep-etched plates are also in use. The sketches (Figure 64A) illustrate one such procedure:[49] The design is printed[50] with a greasy ink upon a grained and cleaned metal plate (Figure 64A). Dusting powder such as rosin, asphaltum, starch, flour, or talc is applied to the ink (Figure 64A) to increase the wetting action of a succeeding bichromated colloid. The excess powder is removed with water. While still wet, the entire plate is coated with a colloid mixture comprising the following composition: 2 parts photoengravers' glue (50 per cent solids), 1 part albumin (flakes), 0.6 part ammonium bichromate, plus water to make a solution containing 20 grams total solids per 100 cubic centimeters of solution (Figure 64A). Whirling the plate serves to distribute and dry the coating. Rays from an arc lamp are employed to harden the bichromatized colloid (Figure 64A). By washing with benzene, gasoline or other ink solvent and rubbing with cotton wad, the ink and hardened colloid are removed from the design areas (Figure 64A). The plate next is treated with an etching medium which does not attack the colloid but which renders the image slightly in intaglio (Figure 64A). Such a medium consists of 5 parts of nitric, hydrochloric or sulphuric acids in 95 parts of anhydrous ethyl alcohol. After the residue is dislodged from the etched areas by washing with anhydrous ethyl alcohol, benzene or gasoline, a solution of asphaltum is applied to render the surface grease-receptive. Lithographic ink subsequently is applied (Figure 64A). The ink and hardened colloid may be removed from the non-image

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[49] R. F. Reed, W. Dorst and A. George, U. S. P. 1,992,771, Feb. 26, 1935, to Lithographic Technical Foundation, Inc.: *Chem. Abs.*, 1935, 29, 2632; *Brit. Chem. Abs.* B, 1936, 172.

[50] The design may be produced by the so-called transfer method. A sheet of paper sensitized with a film of chromatized gelatin is exposed under a negative. The paper then is coated with a "transfer" ink by means of a roller. After the solvent has evaporated, the gelatin is treated with (cold) water and the unaffected colloid thus swollen. By gently rubbing the surface with cotton wool, the ink is removed from the distended gelatin but adheres to the hardened (unswollen) portions. The plate then is allowed to dry. In printing, the surface is moistened, rolled up with ink and the print made (see collotype below).

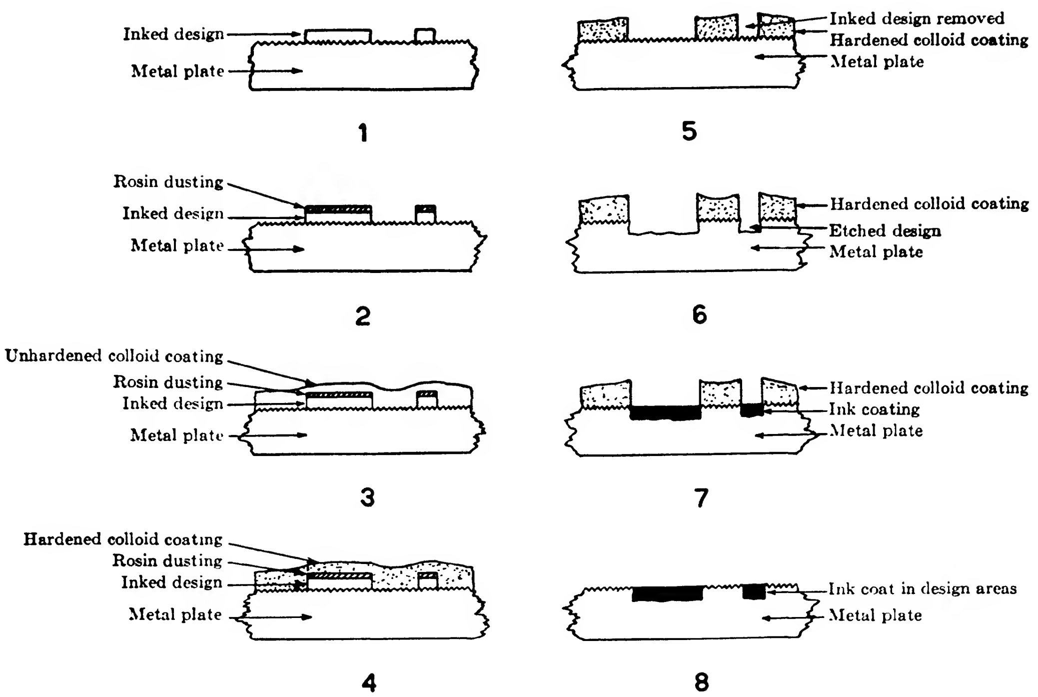

FIGURE 64A. Diagrammatic Sketch of Preparation of Deep-Etched Lithographic Plate (R. F. Reed, W. Dorst, and A. George).

1. Design produced in greasy ink or crayon
2. Plate dusted with rosin
3. Plate coated with a solution of bichromated colloid
4. Bichromated colloid hardened by exposure to light
5. Bichromated colloid and greasy ink removed from image areas
6. Printing areas etched slightly intaglio
7. Ink-receptive substance deposited on design areas
8. Bichromated colloid or etching resist removed

areas with an aqueous solution of an alkali (Figure 64A). For this purpose an aqueous solution of an alkaline-earth metal chloride with a small amount of dissolved caustic has been advocated.[51] Strong alkalies alone are said to remove the fatty ink from the design, but are stated to cause dermatitis of the operators' skins. The ink which remains in the deeply etched design areas is offset to the rubber blanket and printed in a manner similar to other offset processes.

Another procedure for obtaining deep-etched plates has been proposed by Rendall.[52] A colloid, initially insoluble, but rendered soluble by the action of light, is employed. A zinc or aluminum plate is sensitized with a layer of gelatin and bathed in a solution of ferric tartrate. The latter is absorbed and renders the gelatin water-insoluble. The plate then is exposed under a negative and developed with water. (Glycerin or calcium chloride may be added to the latter to restrain its solvent action.) The plate next is etched with aqueous or alcoholic ferric chloride. The etched areas then are rendered ink-receptive, after which the gelatin is removed as already described, to produce the finished plate. The development of the deep-etch process has given considerable impetus to the growth of offset printing.

Dot-Etching. The unadorned procedure in obtaining a lithographic broken-tone negative, namely, obtaining a simple negative, preparing from this a screen positive and from the latter in turn the negative, results in considerable flattening of tonal values. The process of modifying the screen positive, known as "dot-etching," provides photolithography with a method of accentuating and correcting tone scales.[53] The process is analogous to fine-etching of half-tone plates. The screen positive, after developing and fixing, is treated with a reagent (*e.g.*, Farmer's reducer or iodine-cyanide reducer) which has the effect of decreasing the size and sharpening the outline of the silver dots.

In what has come to be known as the "Peridak" process,[54] Farmer's reducer, consisting of an aqueous solution of potassium ferricyanide and sodium thiosulphate, is employed. A film of gelatin sensitized with silver halide is exposed through a screen to the negative to produce, after developing and fixing, the screen positive. The latter consists of dots of silver of various sizes in gelatin. The positive preferably is overexposed somewhat so that the shadow dots are slightly fogged; this tone effect is used for the solid portion of the reproduction. The film then is tanned to obviate the need for excessive care in subsequent handling. The portions of the positive which are not to be reduced are coated with a resist such as shellac and the positive submitted to the thiosulphate-

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[51] R. F. Reed, P. W. Dorst and A. George, U. S. P. 2,062.273, Nov. 24, 1937, to Lithographic Technical Foundation, Inc.; *Chem. Abs.*, 1937, 31, 788.

[52] A. G. Rendall, British P. 449,772, 1936, to Morland and Impey, Ltd.; *Chem. Abs.*, 1937, 31, 58.

[53] See R. F. Reed and P. W. Dorst (Bulletin No. 11 of the Lith. Tech. Found., Inc., 1937) for a review of the processes and a bibliography.

[54] A. Murray, U. S. P. 1,950,903, March 13, 1934, to Eastman Kodak Co.; *Chem. Abs.*, 1934, 28, 3323.

ferricyanide solution. The silver is attacked as the solvent penetrates the gelatin and is dissolved. The reaction may be represented as:

$$4Ag+4K_3Fe(CN)_6=Ag_4Fe(CN)_6\ \text{(insoluble)}+3K_4Fe(CN)_6$$
$$3Ag_4Fe(CN)_6+16Na_2S_2O_3=4Na_5Ag_3(S_2O_3)_4\ \text{(soluble)}+3Na_4Fe(CN)_6$$

Murray[55] points out that the reducing agent apparently is unable to penetrate into the interior of the silver deposit and that solution of silver occurs only at the boundary of the silver dot. The silver consequently is removed progressively at the face and sides of the dot so that both its depth and lateral area are reduced (Figure 65.) It was also found that the action of the reducing agent is more effective along the horizontal (lateral) radius. It is suggested that this may be due to a greater concentration gradient of silver salt away from the sides of the dot. As a consequence of this the reacted silver diffuses away more rapidly from the interface and allows a more rapid rate of dissolution. In any case, whatever the reason, the end effect is to produce a sharply defined silver

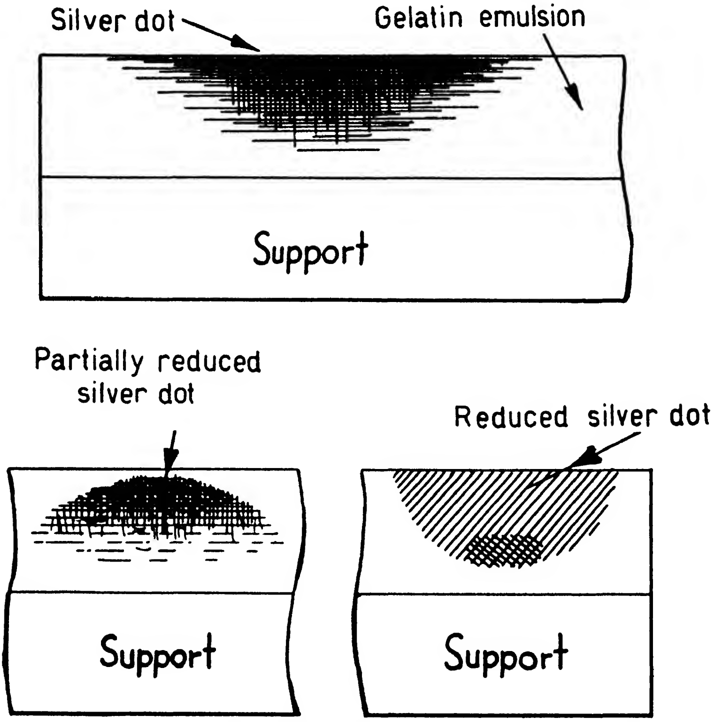

FIGURE 65. Sketch of "Peridak" Process of Dot-Etching (A. Murray).

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[55] A. Murray, *loc. cit.*

dot located at the center of the original deposit. By progressively blocking out portions of the positive and submitting the remainder to reducing solution, desired accentuation of tone is secured.

COLLOTYPE

In collotype, the printing surface consists of gelatin variably hardened by light transmitted through a negative and thus rendered ink-receptive to different degrees. A glass plate, approximately one-half inch thick, is finely grained on one side, and flowed over with a solution consisting of 5 parts of egg albumin and 2 parts of sodium silicate solution in 10 parts of water.[56] The water is evaporated, the plate heated to 60° C., cooled, washed and dried. These operations yield a surface to which the subsequently applied film of gelatin adheres strongly. An even coat of gelatin-chromate solution (18 parts of gelatin and 2 parts of potassium dichromate in 175 parts of water) is applied to the carefully leveled plate and dried at 40 to 60° C. Exposure is made under a continuous (unscreened) negative. The progress of the tanning may be observed by noting the darkening of the gel through the glass support. Exposure completed, the plate is flooded with water until all unreacted dichromate has been removed. After drying the film, it is swollen with what in the parlance of the trade is referred to as the "etching" solution. The latter consists of a hygroscopic substance and an agent for softening the film in aqueous solution (*e.g.*, equal parts of water and glycerin plus 2 per cent sodium chloride). After removal of excess solution, the plate is ready for printing. In surroundings of the proper humidity and temperature, as many as a thousand impressions may be taken without remoistening.[57]

An examination of the effects on the gelatin of the operations described above will show how printing results are obtained by collotype. When the film is exposed under a continuous (unscreened) negative, the gelatin is tanned to different depths and to somewhat different degrees, depending on the intensity of illumination. When the gelatin is treated with water, the unhardened colloid expands and ruptures the layer of hardened gel. As a result the surface consists of a large number of tanned gelatin particles on the soft gelatin base. Because of the variation in amount of untanned gel, the density of the particles will vary, being least in the highlights of the image and merging to an unbroken surface at the black portions. The crepe-like appearance of the surface is referred to as grain or "reticulation." The cracking of the gelatin layer is due to the strain existing in it as a result of the high temperature at which the film was dried.[58] The nature and degree of grain may be regu-

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[56] The proportions of this and other compositions mentioned below are those suggested by J. S. Mertle, *Graphic Arts Monthly*, 1938, 10 (6), 34; *Rev. Paint, Colour, Varnish*, 1938, 11, 280.

[57] See R. E. Fehse (*Graphic Arts Monthly*, 1938, 10 (5), 36) for some aspects of the collotype process.

[58] In the copy-relief process, the gelatin does not rupture on being swollen with water.

lated to some extent by varying the temperature of drying. When ink is applied to the moistened layer, two factors govern the quantity and distribution of ink retained. First, the ink tends to be taken up by all tanned particles and rejected by the soft moist gelatin. Secondly, the more deeply tanned portions tend to retain more ink. In the highlight portions of the surface not only is the density of the spots of ink less, but also the amount of ink on each of these spots of tanned colloid is smaller. Either of these effects would be sufficient to produce some gradation of tone. As a matter of fact, images of low contrast (in tone) may be produced from plates which have no noticeable grain.

Color Printing

The theory of color printing is based on the fact that any color including black may be obtained by mixing the three basic colors, yellow, red and blue, in the correct proportion. Thus, it should be possible to print reproductions in all colors to match the originals by means of three printing plates, one to print yellow, another to print red and another to print blue. In the three-color method, three exposures are made with panchromatic dry plates through a yellow, red and blue filter and from each of these films a printing plate is prepared as for a simple monochrome reproduction. With the corresponding plates the yellow, red and blue colors are successively printed on the impression surface so that the superimposing of the colors produces the various shades of the original. In general, because of the limitations of the processes, a black printing plate is added, in which case we have the four-color process.[59]

In preparing the yellow printing plate, for example, a so-called yellow "separation negative" is first made. The original is photographed through a purple or violet filter, *i.e.*, the color complementary to yellow. This filter permits the passage of the red and blue color value of the original and absorbs the yellow component so that this color is shut off from the negative. The yellow portion of the image in the positive which is prepared from this negative therefore will be present as dark areas, whereas the red and blue values will be light on this positive. Inasmuch as the plate which is to do the actual printing is a positive, the dark portion on the positive represents the printing surface which will be used for printing with yellow ink. The red separation negative is similarly made through a green filter which transmits only the yellow and blue color components, and the blue separation negative through an orange filter, which transmits yellow and red. The black separation negative may be made by exposure through one or more of the filters, depending on the results desired. If a screened positive is required (as in the intaglio processes), a screen is interposed during the exposure to the negative. Otherwise a continuous-tone positive (which may be retouched) is secured, and from this the broken-tone negative made.

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[59] In lithographic printing eight or nine color plates are often used to obtain effective reproduction.

The above procedure must be supplemented by considerable handwork to produce a satisfactory printing plate. Such handwork, which must be done by experts, is necessary largely because of the inherent defects of the filters. Thus, ideal color resolution—in which two colors are completely transmitted and the other fully absorbed—is not realizable and more or less of the color which is being filtered is transmitted. Since a mixture of the three component colors tends to yield black, a dulling or darkening of the shades is the result of incomplete filtering.

A means of obtaining more effective color separation is described by Wilkinson.[60] The method proposed consists of obtaining the usual three-color negatives and from these the corresponding positives; the positives and negatives being then combined to produce the "corrected" negatives. In preparing a corrected yellow negative, for example, a yellow and a blue negative are obtained by the usual method, and from the blue negative a positive is made. The density of the positive, which is called a positive overlay, is varied by the operator in accordance with the conditions encountered. The blue overlay is placed in register over the yellow negative and a corrected positive secured by photographing through the overlay and negative. Inasmuch as the blue negative was made through an orange filter, which transmits yellow and red rays, the yellow values will be dark in the blue negative and therefore light or transparent in the blue positive overlay. The light readily passes through the areas which represent strong yellow values in the yellow separation negative and blue positive overlay to record the yellow values dark in the corrected positive. Since the blue values are dark in the blue positive overlay, this will lighten the blue values in the yellow corrected positive. It is found that the red values also are reduced sufficiently in the yellow corrected positive. Thus, in the latter the yellow has been retained dark and at full strength to represent the printing surface in the final metal printing plate to be made, whereas the red and blue values have been eliminated or lightened to the extent desired. In a similar way, a red corrected positive is made from the red separation negative placed in register with the blue positive overlay; and a blue corrected positive is made from the blue separation negative and yellow positive overlay. If a screened positive is wanted, a screen is used with the negative and overlay.

Color separation achieved by means of filters may, in the reproduction of simple subjects, be done manually. The number of color components (generally more than three) which, when superimposed on one another will reproduce the original, is decided upon. This is done with the aid of a key drawing. The latter is an outline drawing of the subject on which the areas occupied by each of the color components is mapped out. By successively filling in these areas with the corresponding colors, a reproduction of the subject, in the ideal case, should be obtained. The areas

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[60] W. J. Wilkinson, U. S. P. 2,004,144, June 11, 1934, to The Miehle Printing Press & Mfg. Co.

representing each color component in the key drawing then are sketched on separate sheets and are filled in with black ink. The color sketches thus obtained are used to produce the printing plates (generally lithographic). The plates are printed successively with the proper color to yield the print. The production of the lithographic plates involves the use of a screen to produce the broken-tone negative. The necessity for the screen is eliminated by making the color sketches with black crayon on a grained zinc surface. The color areas then comprise an aggregation of black dots on the bright zinc surface. The broken-tone negative is obtained directly by photographing the grained plate.[61] By varying the pressure of the crayon the size of the dots may be varied and different depths of color secured.

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[61] The employment of enlarged color sketches reduces the size of the dots in the negative and therefore the print. W. H. Hackett and P. W. Pryke (U. S. P. 2,044,429, June 16, 1936) state that this expediency renders possible the use of fewer color components.

Chapter 12

Transfer Inks

Printing directly on materials other than paper by typographic, planographic or intaglio processes is somewhat difficult. In many cases it would be impractical to set fabrics or leather, because of area or thickness, in printing presses. In the case of lithographic stones or of objects made with glass, wood, metals or ceramics, particularly those which do not possess flat surfaces or which are relatively large, the task of direct printing from presses seems tremendous if not impossible of achievement. To avoid these obstacles, the transfer process of printing, or, as it often is termed, decalcomania, has been developed. This comprises printing or painting designs, patterns, pictures or textual matter upon a temporary base, and later transferring the printed material from the temporary to a permanent base.

Temporary bases may be prepared from paper, fabric or other substances that have flat surfaces and are of convenient size for printing, storing, transportation or other handling. However, paper apparently is employed in a larger number of instances than are other materials.

For printing transfer designs upon temporary bases, typographic, planographic, or intaglio processes may be employed. The choice of a particular method will depend to some extent upon the desired depth and sharpness of design. Typographic printing can be utilized to give patterns of considerable depth and sharpness on the temporary base, but often there is a tendency for ink to be concentrated around the edges of the lines and letters, and for indentation of the printed design on the back of the sheet to occur. Designs produced by planographic processes usually have fine, sharp lines, but the depth of impression is not great. By use of intaglio printing considerable depth of ink can be secured on the temporary base without adversely affecting the sharpness of impression. Also, where special designs are employed which do not justify a press-printing operations, the pattern may be painted or printed upon the temporary base by hand.

Transference of designs from temporary to permanent bases has been effected in some instances through heat, pressure, or a combination of these two, or by action of solvents. One method comprises setting of the temporary base in register with the permanent base so that the design is in contact with the final backing, and then pressing (with a warm or hot iron) on the back of the temporary base. If the latter had been coated with a water-soluble gum before the design was placed thereon, a damp cloth can be placed on the temporary backing beneath the iron.[1] In one procedure for transferring designs from temporary Cellophane backing, the latter was placed in contact with the permanent base, and heated to 200-230° F. under pressures between 250 and 1000 pounds per square inch.[2] On the other hand, it has been reported that temperatures in the range 120 to 160° F. are sufficient to cause transfer of designs printed in gold, silver or aluminum from temporary paper backings to permanent pottery or glass bases.[3] Afterwards, the paper may be removed by soaking with water, and the design fixed by heating at 1000-1100° F.

Imprinting of designs upon pottery or lithographic stones may be accomplished by pressure alone. For example, it was proposed that a transfer ink containing mercuric oxide be transferred from paper to pottery by pressure, the resulting imprint dusted with colors, and the whole heated to fix the design on the pottery.[4] Preparation of lithographic stones by transposing designs from paper to the stone by pressure has been described.[5] Before transference, the inked design was immersed in a dilute aqueous solution of potassium dichromate, and then exposed to light for several minutes. In this way the ink was made water-insoluble, so that no bleeding would occur when the design-bearing stone was dampened prior to application of ink.[6]

Transference of pictures from paper backings to transparent permanent bases such as glass may be accomplished by pressure.[7] In one instance, a picture on a paper backing was coated with mixture of 4 parts glycerol and 5 parts gelatin in 100 parts water. Subsequently this coating was hardened by addition of formalin (aqueous solution of formaldehyde). The hardened transparent coat was covered with a layer of glue prepared from 12.5 parts joiner's glue, 4 parts glycerol and 100 parts water. The whole was treated again with formalin. A layer of glue was placed on the permanent glass backing, and the glue layer of the picture firmly pressed to the coated glass base. The paper or backing was stated to be removed by soaking with oil and rubbing with a mixture of powdered pumice in water.

Solvents may be used to effect transposition of textual matter or patterns from temporary to permanent bases. Water has been proposed as a transference agent for temporary backing coated with water-soluble gums.[8] Also, water may be used as softening agent when the paper base

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[1] S. J. Cox, U. S. P. 1,820,559, August 25, 1931, to Colorfuse, Ltd.; *Chem. Abs.*, 1931, **25**, 5776. British P. 328,909, 1928; *Brit. Chem. Abs.* **B**, 1930, 657; *Chem. Abs.*, 1930, **24**, 5510. *Cf.* L. V. Casto, British P. 308,788, 1928, to Oxford Varnish Corp.; *Brit. Chem. Abs.* **B**, 1930, 264; *Chem. Abs.*, 1930, **24**, 305.

[2] R. L. Atkinson, U. S. P. 1,966,942, July 17, 1934, to A. D. Little, Inc.; *Chem. Abs.*, 1934, **28**, 5943. *Cf.* H. Cournont, British P. 317,970, 1928; *Chem. Abs.*, 1930, **24**, 2258.

[3] L. Allen and E. C. Deering, British P. 317,411, 1928; *Brit. Chem. Abs.* **B**, 1929, 852; *Chem. Abs.*, 1930, **24**, 2258. *Cf.* E. Rolffs, German P. 280,074, 1914; *Chem. Abs.*, 1915, **9**, 2318.

[4] J. C. Bailey, British P. 14,875, 1894; *J. S. C. I.*, 1895, **14**, 751. *Cf.* H. Doulton and J. Slater, British P. 15,041, 1894; *J. S. C. I.*, 1895, **14**, 752. M. L. Fosdick, *Bull. Am. Ceram. Soc.*, 1928, **7**, 171; *Chem. Abs.*, 1928, **22**, 3271.

[5] C. de Santeul, *Bull. soc. franc. phot.*, 1913, **4**, 364; *Chem. Abs.*, 1914, **8**, 1243.

[6] For a description of lithographic printing, see Chapter 9.

[7] A. L. de Rooij, British P. 485,260, 1938; *Chem. Abs.*, 1938, **32**, 8636.

[8] C. F. Morse, U. S. P. 979,542, Dec. 27, 1910; *J. S. C. I.*, 1911, **30**, 141; *Chem. Abs.*, 1911, **5**. 1000.

is covered with collodion.[9] Hydrocarbon distillates have been suggested in some instances. Thus, a rhodamine lake dye was suspended in a vehicle containing paraffin wax and linseed oil, and the design printed on a paper base with this mixture.[10] To effect transference, the print was placed in contact with the permanent base, and a hydrocarbon solvent for the dye (*e.g.*, benzine) employed to wet the paper. Conveyance of designs from wall paper to cotton, wool or silk fabrics with solvents has been reported.[11] One such composition contained water, castile soap, turpentine, cedarwood oil, ammonium hydroxide, sodium bicarbonate, borax, methyl alcohol, and dibromohydroxy-mercury-fluorescein. The paper was dipped in this mixture for 30-40 seconds, then dried in air. On placing the treated backing in contact with a textile material and applying pressure, the design was said to be transposed completely to the textile. Also, a blend of olive, palm, or cottonseed oil with sodium or potassium hydroxide was stated to be effective as a transfer solvent for the same materials.[12] In some instances where the temporary backing has been coated successively with wax and Celluloid, and the design printed upon the latter, transference may be effected with a solvent.[13] One proposed blend contained gelatin, sugar and acetic acid in water. By dipping the temporary base in this mixture, separation of the print from the backing was reported to take place between the wax and Celluloid. The latter containing the printed design, then was floated upon the permanent base.

A method of transposing prints through chemical reaction has been suggested.[14] Pasteboard was coated with starch, and then dipped in a solution of citric or tartaric acid. Designs were printed in reverse with a transfer ink on the treated pasteboard. Transference was stated to be obtained by placing the temporary base in contact with the permanent backing and immersing the whole in aqueous sodium carbonate solution. Reaction between the citric or tartaric acid and sodium carbonate results in evolution of carbon dioxide. The latter was said to lift the print from the pasteboard.

Molten sulphur has been proposed as a transfer agent for pictures printed on paper backing.[15] The picture was coated with molten sulphur, cooled, then soaked in water to remove the paper backing. In this way the picture was said to adhere to the sulphur slab. The back of the picture then was treated successively with oil and an aqueous solution of 7 parts gelatin and 1 part glycerol. The whole was heated to separate the sulphur slab from the gelatin-glycerol film. The latter, which was

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[9] J. F. McNutt, U. S. P. 1,996,549, April 2, 1935, to American Decal Corp.; *Chem. Abs.*, 1935, 29, 3481. U. S. Reissue 19,839, Jan 28, 1936; *Chem. Abs.*, 1936, 30, 1907. See also British P. 354,266, 1929, to Masa Ges. zur Herstellung Künstlicher Oberflächen; *Chem. Abs.*, 1932, 26, 4190.

[10] A. Schubert, U. S. P. 1,843,737, Feb. 2, 1932, to Barrett and Co.; *Chem. Abs.*, 1932, 26, 1802. See also C. Glaser, British P. 283,571, 1927; *Chem. Abs.*, 1928, 22, 4214.

[11] W. V. MacGilvra and I. M. MacGilvra, U. S. P. 1,652,949, Dec. 13, 1927; *Chem. Abs.*, 1928, 22, 875.

[12] H. J. Hurt, U. S. P. 1,629,165, May 17, 1927; *Chem. Abs.*, 1927, 21, 2174.

[13] J. Frachebourg, British P. 2,318, 1914; *Chem. Abs.*, 1915, 9, 2001. *Cf.* L. Eriksen, British P. 420,132, 1934; *Chem. Abs.*, 1935, 29, 3429.

[14] T. Sogawa, Japanese P. 31,451, 1917; *Chem. Abs.*, 1918, 12, 86.

[15] A. L. de Rooij, U. S. P. 960,707, June 7, 1910; *Chem. Abs.*, 1910, 4, 2550. The process also is described in *Diamant*, 1912, 34, 509; *Chem. Abs.*, 1912, 6, 2302.

stated to carry with it the picture, was pressed upon a permanent base which had been coated with an aqueous gelatin-glycerol solution.

PREPARATION OF TRANSFER PAPERS

Temporary bases on which transfer designs are to be placed usually are treated with modifying agents before imprinting the designs. In this way, efficient transposition of the design to a permanent base can be brought about. Thus, in general, to minimize ink absorption, temporary transfer bases should be impermeable to the inks employed. Also, if transference is to be carried out with solvents (with or without external heating), a somewhat greater degree of contact between ink and solvent will be secured when the backing is wetted thoroughly by the solvent. Materials proposed for treating temporary transfer bases prior to printing include, among others, starch, gums, natural and synthetic resins, waxes and glycerol.

A suggested method for preparing paper backing sheets involved coating the latter with a starch solution, followed by addition of dextrin thereon.[16] The whole was covered, before it had set, with a sheet of preformed cellulosic material such as Cellophane, which received the print. It was stated that any tendency toward lumpiness on the part of the printed marking was thus precluded. Stacking of such transfer sheets often results in offsetting from a base to the back of the one beneath it. Embossing of the back of starch-dextrin treated sheets has been proposed to overcome this difficulty.[17] Also, chalk mixtures bonded to the back of the transfer base by adhesives were stated to be effective in obviating offsetting.[18] In some instances a solution of citric or tartaric acid has been added to a starch-treated transfer base.[19] After the latter had dried, the design was printed directly upon this surface. When lithographic processes are to be employed in printing transfer bases, it was stated that markings might be placed upon unsized paper that previously had been coated with starch and dextrin.[20] Subsequently the whole was covered over with an alcoholic solution of sandarac, lac (shellac) and elemi gums. Because of the tendency of unsized paper to be affected by changes in temperature and humidity, sized paper has been utilized in making transfers.[21] The paper, after application of a "releasing liquid," [22] was overspread with successive layers of starch, dextrin and lacquer, the latter receiving the ink. The releasing liquid consisted of a blend of an aqueous solution of sulphonated castor oil (10 per cent) and sodium lauryl, myristyl or stearyl sulphate (0.5-2.0 per cent).[23]

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[16] J. MacLaurin, U. S. P. 2,047,700, July 14, 1936; *Chem. Abs.*, 1936, **30**, 6096.

[17] H. Atwater, U. S. P. 2,007,630, July 9, 1935, to McLaurin-Jones Co.; *Chem. Abs.*, 1935, **29**, 5956.

[18] J. MacLaurin, U. S. P. 2,007,404, July 9, 1935; *Chem. Abs.*, 1935, **29**, 5956.

[19] T. Sogawa, Japanese P. 31,451, 1917; *Chem. Abs.*, 1918, **12**, 86.

[20] H. Courmont, British P. 317,970, 1928; *Chem. Abs.*, 1930, **24**, 2258.

[21] J. MacLaurin, U. S. P. 2,038,118, April 21, 1936; *Chem. Abs.*, 1936, **30**, 3914.

[22] "Releasing liquid" is a term employed to designate a base for receiving printed matter, which base later can be removed by treatment with a solvent, *e. g.*, water.

[23] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," Vol. **II**, New York, Reinhold Publishing Corp., 1937.

A blend reported to prevent penetration of transfer inks into paper bases has been suggested.[24] A mixture of 12 parts dextrin and 2 parts starch, incorporated in boiling water, was combined with a composite of 400 parts sodium carbonate and an equal amount of colophony in water. Two hundred parts egg albumin in water, 200 parts sulphur, 400 parts gum arabic, and 2000 parts glycerol were then added. Employment of gum arabic as a foundation for transfer inks has been stated to yield a compound suitable for carbon papers.[25] When sized paper is utilized as base, the transfer ink may be printed directly upon the former, and the design then coated with gum tragacanth or gum karaya.[26] The latter substances were reported to increase the fastness of colors on fabrics on transference. Gum-coated transfer bases printed with inks containing cellulose esters or ethers together with alcohol-soluble resins have been proposed.[27] Such inks were suggested for transferring designs to glass, wood or metal surfaces. Ingress of color blends containing amyl acetate, rosin, linseed oil, nitrocellulose and bronze powder into paper bases was said to be obviated by covering the surface of the paper with dextrin.[28] Also, mixtures of dextrin and glycerol have been utilized in overspreading paper bases intended for transfer prints.[29] On the other hand, the glycerol-dextrin mixture may be applied, together with pigment and a small proportion of gum, to the temporary base.[30] In this manner, an alcohol-soluble ink that would not penetrate paper bases was stated to have been secured.

In some instances bases for marking compounds have a tendency to curl on being stored. A method to overcome this disadvantage has been proposed.[31] The paper was coated with a mixture of 25 parts animal glue, 75 parts dextrin, 2 parts glucose and 1 part glycerol in water. When the paper had dried, the adhesive was broken into segments by curling the paper. The latter was then covered with lacquer to fill up the cracks and to prevent closing up of the adhesive. In this way, a non-curling paper base was said to have been obtained. One lacquer employed was composed of nitrocellulose, dibutyl phthalate, gum dammar, ethyl and butyl acetate, ethyl alcohol and toluene.

A surface film of gum arabic placed on unsized paper has been used as foundation for water-soluble marking blends.[32] The base was stated

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[24] G. Muzzioli, British P. 312,220, 1928; *Chem. Abs.*, 1930, **24**, 932. See also C. Eckert, German P. 271,746, 1913; *Chem. Abs.*, 1914, **8**, 2466.

[25] H. W. A. Dixon and R. S. Moore, U. S. P. 2,022,276, Nov. 26, 1935, to Columbia Ribbon and Carbon Mfg. Co.; *Chem. Abs.*, 1936, **30**, 792.

[26] H. S. Sadtler, U. S. P. 1,797,997, March 24, 1931; *Chem. Abs.*, 1931, **25**, 2825. British P. 284,676, 1927; *Brit. Chem. Abs.* **B**, 1929, 280; *Chem. Abs.*, 1928, **22**, 4742.

[27] British P. 317,871, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, **24**, 2258; *Brit. Chem. Abs.* **B**, 1929, 863.

[28] A. L. Clapp, U. S. P. 1,280,399, Oct. 1, 1918; *Chem. Abs.*, 1918, **12**, 2687.

[29] C. G. Schmidt, German P. 255,192, 1912; *Chem. Abs.*, 1913, **7**, 1972.

[30] P. Yohns, U. S. P. 1,849,996, March 15, 1932, to Butterick Publishing Co.; *Brit. Chem. Abs.* **B**, 1933, 188; *Chem. Abs.*, 1932, **26**, 2876.

[31] F. W. Humphner, U. S. P. 1,965,289, July 3, 1934, to Mid-States Gummed Paper Co.; *Chem. Abs.*, 1934, **28**, 5614.

[32] W. S. Lawrence, U. S. P. 1,799,754, April 7, 1931, to Kaumagraph Co.; *Chem. Abs.*, 1931, **25**, 3139. *Cf.* J. S. Tidmus, British P. 414,205, 1934, to International Latex Processes Ltd.; *Chem. Abs.*, 1935, **29**, 258; *Brit. Chem. Abs.* **B**, 1934, 933.

to be permeable to steam utilized as transference agent. Printing on such bases may be effected by silk-screen or lithographic processes, using a lithographic ink admixed with a hard gum varnish and benzine (thinner).[33] A small proportion of kaolin or bauxite is sprinkled on the printed surface while the latter is still tacky. A coating of gum arabic then is placed over the whole print. The kaolin or bauxite was stated to aid in securing the outer coating of gum arabic to the print. It has been pointed out that the gum film may be applied during paper-manufacturing.[34] Thus, gum may be spread on one side of the paper while the latter is on drying rolls, and before the calendering operation has been started. On the other hand gum may be incorporated with the ink before the transfer is placed on the temporary base.[35] Gum dammar, paraffin and spermaceti waxes were admixed with ink before printing. After application to the transfer paper, the design was coated with an alcoholic solution of pine resin.

In transference operations involving employment of heat and steam, fusible water-soluble transfers may be utilized.[36] For example, sized paper was coated with a mixture of albumin, gum mastic, dextrin, starch, rosin and sodium hydroxide in water. The composite was reported to be fusible and soluble under combined action of heat and steam, and to form emulsions with certain types of marking compounds. A suggested ink for printing on such bases comprises a lithographic ink [37] which has been admixed with carnauba wax, tallow and gum elemi.

Dopes containing carbon black, carnauba wax and petroleum jelly have been employed for carbon paper. However, it was stated that this blend caused transfer bases to become somewhat hard and brittle, resulting in cracking of the base.[38] Treatment of the latter (prior to inking) with a solution of gutta percha in carbon tetrachloride was said to bring about increased flexibility and longer effective life.

Because of the warping action of water upon veneer wood, transfers for the latter are usually prepared from water-insoluble materials.[39] For example, backing paper was overspread with three coatings of water-resistant material and the center film, which was insoluble in solvents for the outer coverings, carried the transfer design. The ink-carrying lacquer comprised gum sandarac and rosin in alcohol, and the outer and inner films were a blend of Cumar and dibutyl phthalate in ethyl acetate, ethylene glycol, butyl ether, and a petroleum distillate boiling in the range 99-116° C.

Cellulose derivatives are used as paper-backing films for some types

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[33] A. G. Matthews, S. C. Prior and N. V. Gray, British P. 487,789, 1938; *Chem. Abs.*, 1939, 33, 288; *Brit. Chem. Abs.* B, 1939, 178.

[34] J. MacLaurin, U. S. P. 2,036,422, April 7, 1936; *Chem. Abs.*, 1936, 30, 3644.

[35] A. G. Chapela, British P. 386,583, 1933; *Chem. Abs.*, 1933, 27, 5994.

[36] S. J. Cox, U. S. P. 1,820,559, Aug. 25, 1931, to Colorfuse Ltd.; *Chem. Abs.*, 1931, 25, 5776.

[37] See Chapter 9.

[38] S. A. Neidich, U. S. P. 1,800,560, April 14, 1931, to Neidich Process Co.; *Chem. Abs.*, 1931, 25, 3449. *Cf.* J. A. L. Möller, U. S. P. 1,544,675, July 7, 1925; *Chem. Abs.*, 1925, 19, 2745.

[39] L. Davis, U. S. P. 2,023,803, Dec. 10, 1935, to McLaurin-Jones Co.; *Chem. Abs.*, 1936, 30, 792; *Brit. Chem. Abs.* B, 1936, 982.

of transfers. With ceramic transfers, when the ware is fired after the transference operation, plastic materials that will burn away have been proposed.[40] In this manner the transfer can be placed upon the final backing without removing the temporary base, since the latter will burn away during firing of the ware. In one instance paper was coated with collodion on which the design was printed with partially fused pigments. Or the marking may be placed upon a collodion film, with a clear varnish, and a charge of dry colors then blown or brushed on the outlined figures.[41] Also, nitrocellulose films may form a permanent part of the transfer. Thus, gummed paper was overspread with a nitrocellulose film, and the transfer printed thereon.[42] The whole was covered with a composite of varnish, linseed oil, zinc oxide and lithopone. This coating mixture was stated to be inert toward the nitrocellulose film and ink, and to furnish an opaque background for the design on transference. Cellulose-base lacquers were reported to be applicable as supporting films for inks containing aluminum.[43] A stated advantage of such films was that they afforded protection to the transfer against weathering effects, and at the same time were clear enough to completely expose the transfer design to view. When aluminum or bronze powders were employed in transfers, it was suggested the design be placed upon a nitrocellulose film with varnish, and the powder blown or brushed on the latter.[44] The whole was coated with a second layer of nitrocellulose lacquer on which the design was printed in ink. To furnish an opaque background for the marking, white ink was placed over the second film. A third nitrocellulose film was added, and a gummed adhesive incorporated in the outside film.

To increase drying rates of transfer inks printed by intaglio processes, incorporation of a drier in the film which receives the print has been proposed.[45] The paper first was covered with a water-soluble coating containing gelatin, gum arabic and glycerol. Subsequently a film of water-insoluble material was incorporated, consisting of nitrocellulose, tricresyl phosphate, linseed oil, cobalt linoleate, talc and gum elemi, the whole being dispersed in a blend of toluene, butyl and ethyl acetates. The latter film was reported to receive ink readily, so that high-speed offset printing could be employed in preparing transfers.[46] Also, the cobalt drier contained in the water-insoluble film was stated to aid in drying of the ink and thus to minimize sticking of the transfers when stacked.

[40] L. Allen, British P. 399,922, 1933, to Johnson, Matthey & Co., Ltd.; *Chem. Abs.*, 1934, **28**, 1831; *Brit. Chem. Abs.* **B**, 1934, 97. *Cf.* E. R. Box and F. E. Kerridge, British P. 471,219, 1936, to Johnson, Matthey & Co., Ltd.; *Brit. Chem. Abs.* **B**, 1938, 411.

[41] J. F. McNutt, U. S. P. 1,996,549, April 2, 1935, to American Decal Corp.; *Chem. Abs.*, 1935, **29**, 3481. U. S. Reissue 19, 839, Jan. 28, 1936; *Chem. Abs.*, 1936, **30**, 1907.

[42] A. J. Laws, U. S. P. 1,780,021, Oct. 28, 1930; *Chem. Abs.*, 1931, **25**, 178.

[43] F. A. Edghill, U. S. P. 1,900,048, March 7, 1933, to Rayner Decalcomania Co.; *Chem. Abs.*, 1933, **27**, 3048.

[44] W. Hepp, U. S. P. 1,968,394, July 31, 1934, to Palm Bros. Decalcomania Co.; *Chem. Abs.*, 1934, **28**, 5943; *Rev. Paint, Colour, Varnish*, 1934, **7**, 426.

[45] A. B. Poschel, U. S. P. 1,811,804, June 23, 1931, to Decorative Development, Inc.; *Chem. Abs.*, 1931, **25**, 5027.

[46] Offset printing processes are described in Chapter 1 and Chapter 9.

In some instances, cellulose ester films are applied to transfer bases together with the printing ink and not as a separate operation.[47] For example, a transfer ink was admixed with a solution of nitrocellulose and castor oil in ethyl and butyl acetate, benzol and ethyl alcohol. The design was printed with this material on gummed paper, and the whole covered with a water-insoluble adhesive. Employment of cellulose esters as coatings for transfer markings has been proposed. When designs are to be pressed finally on glass bases, cellulose lacquers have been utilized as adhesives.[48] To secure a sticky adhesive, some castor oil plasticizer may be added to the lacquer. A ratio of oil to nitrocellulose of 2-2.5:1 has been proposed.

Application of cellulose films to the reverse side of transfer bases was said to avoid the possibility of offsetting on stacking of the latter.[49] Also, addition of a small proportion of aluminum powder to the inked portion of the print was stated to aid in prevention of offsetting from one temporary base to the one beneath it.

Certain types of waxes have been employed in treating temporary transfer bases prior to printing of the design. In the preparation of a pressure-transfer a sheet of transparent paper was coated with paraffin wax, and the pattern placed on the wax with ink containing a non-drying oil.[50] Also, foundation materials may include rosin together with wax.[51] The latter were reported to be applicable with marking blends of bronze and nitrocellulose in a volatile solvent. After printing, the ink and base may be overspread with a layer of wax and rosin in which a gum or glue sizing has been admixed. The rosin may be substituted by paracoumarone.[52] For example, a composite of Chinese insect wax and paracoumarone was used to coat glassine paper, and a design placed thereon with a nitrocellulose-metallic powder marking compound. Shellac sizing subsequently was added to the print. Instead of printing the design on a wax coating, the pattern may be stamped out from a cellulose ester film, attached to the wax surface, and a coating of gum dammar applied as adhesive.[53]

Albumin and similar substances have been suggested as components of transfer prints. Thus, paper backing intended as a temporary base for inks was impregnated with an admixture of albumin, a water-soluble gum, calcium chloride and glycerol.[54] The admixture was reported to be efficient in preventing penetration of soap- and wax-containing inks

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[47] T. S. Reese, U. S. P. 1,627,407, May 3, 1927, to Di-Noc Manufacturing Co.; *Chem. Abs.*, 1927, 21, 2174.

[48] O. W. Pendergast, U. S. P. 2,046,924, July 7, 1936; *Chem. Abs.*, 1936, 30, 6096. U. S. P. 2,046,925, July 7, 1936; *Brit. Chem. Abs.* B, 1937, 1248; *Chem. Abs.*, 1936, 30, 6096.

[49] L. C. Antrim, U. S. P. 1,975,057, Sept. 25, 1934, to Autographic Register Co.; *Chem. Abs.*, 1934, 28, 7534. Canadian P. 354,229, 1935; *Chem. Abs.*, 1936, 30, 1907; *Rev. Paint, Colour, Varnish*, 1936, 9, 170.

[50] S. E. Wade, British P. 312,004, 1928, to Wade Transfer Co. Proprietary, Ltd.; *Chem. Abs.*, 1930, 24, 933.

[51] W. F. Grupe, U. S. P. 1,627,088, May 3, 1927; *Chem. Abs.*, 1927, 21, 2174.

[52] C. P. Olson, U. S. P. 1,578,203, March 23, 1926, to K. E. Olson & Son, Inc.; *Chem. Abs.*, 1926, 20, 1697.

[53] E. Hentschel, British P. 331,761, 1928; *Brit. Chem. Abs.* B, 1930, 1047; *Chem. Abs.*, 1931, 25, 178.

[54] R. Homburg, German P. 282,953, 1918; *Chem. Abs.*, 1915, 9, 2439.

into the paper base. Addition of ammonium or sodium alginate[55] to starch and dextrin was stated to furnish a product applicable for treating glassine paper prior to printing.[56] Such coatings were said to aid in securing smooth ink impressions on the transfer base.

Impregnation of paper backings with gelatin has been advocated. For example, a temporary paper base was coated with gelatin, and a layer of paraffin wax then added.[57] Such procedures were said to close the pores and smooth over the uneven portions of the paper. The whole then was covered with a film of nitrocellulose on which the design was placed. On the other hand, the wax may be omitted, and the pattern printed directly on the gelatin layer, which subsequently is treated with a cellulose lacquer.[58] Other materials may be included in gelatin coatings. Thus, an aqueous solution of gelatin, potassium alum, potassium dichromate and glycerin has been proposed.[59] Application of this composite to paper was reported to make the base impermeable to wax. The latter was utilized, together with gum thus and shellac, in preparation of a film to carry the inked design.

In addition to the substances previously described, materials such as glycerin, phenol, drying oils and sodium silicate have been used in treating temporary bases.[60] When transfer inks comprising rosin, shellac and bronze powder were employed, the paper was treated with glycerol prior to printing.[61] With this method a smooth paper, impervious to the marking compound, was stated to have been secured. A composition said to minimize ink absorption has been synthesized from phenol, neat's foot oil, toluene and kerosene. Phenol also was said to accelerate transference of the superposed ink upon application of heat and pressure. Temporary backings that were smooth and flexible at 240° F. have been reported.[62] In one instance, rag paper was impregnated with China Wood oil, and the whole overspread with beeswax. The design was placed on the wax with metallic particles, and sizing placed over the pattern.

In some instances carbon papers are desired that will transfer impressions from certain portions of the paper, the remainder of the sheet being non-transferable.[63] It was pointed out that this effect could be accomplished by coating the entire sheet with a transfer ink, and then covering with non-transferable ink the areas where transference was not wanted.

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[55] Alginic acid is obtained from algin, a nitrogenous substance present in seaweed. Algin is somewhat similar in composition to albumin.

[56] J. MacLaurin, U. S. P. 2,047,978, July 21, 1936; *Brit. Chem. Abs.* **B**, 1937, 1324; *Chem. Abs.*, 1936, **30**, 6096.

[57] J. Frachebourg, British P. 2,318, 1914; *Chem. Abs.*, 1915, **9**, 2001. *Cf.* R. Tull, U. S. P. 1,618,612, Feb. 22, 1927, to Western Lithographic Co.; *Chem. Abs.*, 1927, **21**, 1169.

[58] French P. 790,352, 1935, to Transflex Ltd.; *Chem. Zentr.*, 1936, **107** (1), 2225; *Rev. Paint, Colour, Varnish*, 1936, **9**, 93.

[59] C. A. McKerrow, U. S. P. 1,030,908, July 2, 1912, to J. H. Gillett & Sons, Ltd.; *Chem. Abs.*, 1912, **6**, 2676.

[60] For use of sodium silicate, see W. F. Clark, U. S. P. 894,815, Aug. 4, 1908; *Chem. Abs.*, 1908, **2**, 3290.

[61] A. L. Clapp, U. S. P. 1,398,770, Nov. 29, 1921; *Chem. Abs.*, 1922, **16**, 831.

[62] W. F. Grupe, U. S. P. 1,710,309, April 23, 1929, to Peerless Roll Leaf Co., Inc.; *Chem. Abs.*, 1929, **23**, 2794. See also C. Campbell, U. S. P. 1,578,952, March 30, 1926; *Chem. Abs.*, 1926, **20**, 1697;

[63] A. W. Metzner and J. E. Frey, U. S. P. 2,035,768, March 31, 1936, to J. Q. Sherman; *Chem. Abs.*, 1936, **30**, 3645.

The tendency of inks (used in making multicolored transfers) to run into one another was stated to have been prevented by coating each print with a layer of transparent varnish.[64] Admixtures of shellac, sandarac and zapon lac have been proposed for this purpose.

PREPARATION OF PERMANENT BACKINGS

Transposition of transfer prints from temporary bases to permanent backings of cotton, linen, wool or silk fabrics and of leather usually is carried out without special prior treatment of the final base. In some instances, when wood, metal, glass or cellulose ester surfaces are intended as permanent bases, these materials undergo a predisposing process.

Wood surfaces on which transfers are to be placed, with the aid of heat and pressure, may be coated with a cellulose ester lacquer.[65] Transfers blended from oil-free pigments in cellulose esters then may be applied at temperatures between 40 and 200° C. and a pressure of 200 kilograms per square centimeter. When heat is not necessary in transposing designs from temporary to permanent wood bases, it is suggested that the latter be smoothed by compression under heat.[66] Subsequently a thin layer of paste containing zinc oxide, a gum and turpentine is placed on the surface of the wood and allowed to dry. Pressure-transfers then are applied. By coating wood surfaces with an enamel whose color was complementary to those of the design, one less pigment was said to have been required in the ink.[67] The enamel was permitted to dry until it became tacky, and the design was then transposed from the temporary base.

Ammonia has been reported as an aid in obtaining permanent transfers on glass.[68] In one instance, the glass was overspread with an aqueous solution of ammonium sulphocyanide, ammonium sulphate, glycerol and hydrogen chloride. The temporary transfer contained a small proportion of sodium hydroxide. The latter was said to interact with the ammonium salts to form ammonia.

Cellulose acetate compositions have been suggested as permanent bases for transfer designs.[69] The bases were overspread with a pigmented cellulose ester lacquer before transposition was effected. The latter process was carried out with heat and pressure.

HEAT TRANSFER INKS

Indelible Inks. In marking fabrics, such as cotton, wool and silks, with transfer patterns, the properties of the inks employed must often

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[64] F. Schmid, British P. 257,940, 1925; *Brit. Chem. Abs.* **B**, 1927, 461; *Chem. Abs.*, 1927, **21**, 3110.

[65] J. Werner, U. S. P. 1,897,875, Feb. 14, 1933; *Brit. Chem. Abs.* **B**, 1933, 1020; *Chem. Abs.*, 1933, **27**, 2830.

[66] J. Werner, British P. 303,836, 1929, to F. Schlobach, G. m. b. H.; *Chem. Abs.*, 1929, **23**, 4543; *Brit. Chem. Abs.* **B**, 1930, 61.

[67] T. S. Reese, U. S. P. 1,998,638, April 23, 1935; *Brit. Chem. Abs.* **B**, 1936, 589; *Chem. Abs.*, 1935, **29**, 3754. *Cf.* A. Nefgen, British P. 29,889, 1913; *Chem. Abs.*, 1915, **9**, 1696.

[68] H. Reinknecht, U. S. P. 1,583,997, May 11, 1926, to M. Deghenghi; *Chem. Abs.*, 1926, **20**, 2052.

[69] British P. 408,485, 1934, to Romo Société d'inventions dans les arts plastiques; *Chem. Abs.*, 1934, **28**, 5667.

be such that they will not be affected by subsequent treatment of the fabric with water or alkaline washing fluids. The coloring matter, and vehicle, if the latter is to remain in the fabric after the transference operation, therefore should be water- and alkali-resistant.

In the preparation of fusible vehicles for inks, materials which are solid at temperatures below 100° F. but flowable at somewhat higher temperatures, *e.g.*, under a warm or hot iron, are commonly employed. Included in this class are some natural and synthetic resins, waxes, asphalts, pitches and gums.

Shellac, a natural resin, has been suggested as a fusible vehicle for transfer inks.[70] In one instance 16 parts of shellac were warmed and admixed with 3 parts of powdered bronze, aluminum or silver.[71] When the composite was homogeneous, it was allowed to cool and then ground into a powder. The latter was incorporated into copying inks (such as those formed from glycerol, dextrin, and aniline dyes) to furnish a material for marking fabrics. Instead of shellac, mixtures of this substance with rosin have been proposed.[72] Equal parts of shellac and rosin were heated with 5 per cent by weight of tritolyl phosphate plasticizer and a small proportion of a heavy lithographic varnish.[73] Titanium dioxide was added as pigment, the quantity of the latter being approximately 10 per cent by weight of the total mixture. Substitution of butyl tartrate as plasticizing agent for shellac-rosin vehicles was reported to provide an ink carrier which could be employed in marking leather articles.[74] Inks prepared in this way were stated to be unaffected by the stuffing greases in leather and, hence, non-smeary.[75] By changing the shellac-rosin ratio, the properties of the resulting inks have been varied somewhat. For example, marking compounds prepared from 5 parts rosin, 1 part shellac and 5 parts powdered bronze were said to furnish smooth impressions with low ink consumption when printed on glycerol-treated transfer paper.[76] When final transposition to porous bases is desired, transfers comprising equal parts of tallow and rosin have been employed.[77] Small proportions of wax and glucose were incorporated, and the whole admixed with a pigment. In place of glucose, castor or linseed oil and benzyl alcohol have been proposed.[78] After adjunction of pigment, a drier of manganese and lead acetates was added to the marking compound. In

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[70] For a discussion of the properties of shellac, see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[71] H. S. Sadtler, U. S. P. 1,590,648, June 29, 1926; *Chem. Abs.*, 1926, **20**, 3091.

[72] F. Solomon, U. S. P. 2,029,204, Jan. 28, 1936, to B. Brier; *Chem. Abs.*, 1936, **30**, 2028; *Brit. Chem. Abs.* **B**, 1937, 159; *Rev. Paint, Colour, Varnish*, 1936, **9**, 194.

[73] For properties of lithographic varnishes see Chapter 3.

[74] W. S. Lawrence and F. W. Barker, Jr., U. S. P. 1,545,836, July 14, 1925, to Kaumagraph Co.; *Chem. Abs.*, 1925, **19**, 2881.

[75] The process of adding oils and greases to leather to increase the softness, pliability and tensile strength of the latter is known as stuffing. See J. A. Wilson, "The Chemistry of Leather Manufacture," New York, The Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1923.

[76] A. L. Clapp, U. S. P. 1,398,770, Nov. 29, 1921; *Chem. Abs.*, 1922, **16**, 831.

[77] C. A. Colombo, U. S. P. 1,900,635, March 7, 1933; *Chem. Abs.*, 1933, **27**, 3048. A. Steffenini, British P. 369,762, 1932; *Chem. Abs.*, 1933, **27**, 3627. Both patents assigned to Società italiana transfers Albini, S. I. T. A.

[78] H. E. Peace, British P. 430,861, 1935; *Chem. Abs.*, 1935, **29**, 7678. See also A. G. Chapela, British P. 386,583, 1933; *Chem. Abs.*, 1933, **27**, 5994.

Table 31.—Wax-Natural Resin Mixtures.

Resin	Beeswax Comb. Temp. (° C.)	Beeswax Loss in Weight on Combining (%)	Beeswax M. P. of Mixture (° C.)	Carnauba Wax Comb. Temp. (° C.)	Carnauba Wax Loss in Weight on Combining (%)	Carnauba Wax M. P. of Mixture (° C.)	Japan Wax Comb. Temp. (° C.)	Japan Wax Loss in Weight on Combining (%)	Japan Wax M. P. of Mixture (° C.)
Batavia Dammar B	90-100	0.4	59.5	90-100	1.0	66	90-100	0	47
Bold black scraped East India	130-140	0.6	65	130-140	2.0	82.5	130-140	1.2	75
Pale East India Macassar Bold	120-130	0.4	62.5	120-130	1.4	75	120-130	1.0	65.5
Pale East India Singapore Bold	120-130	1.2	62	120-130	1.8	76	120-130	0.2	80
Elemi	98-100		56.5	100	1.0	57	98-100	1.0	45.5
Batu scraped	130-140	0	65	150-200	2.2	85	150-200	2.6	75
Singapore Dammar No. 2	100-110	2.6	60	110-120	0.8	79.5	90-100	0	42
Loba C	300-325	26.3	68	300-325	17	79			
Congo No. 4	300-325	18.5	66						
Congo No. 11	300-325	17 6	68	300-325	21.8	75.5			
Kauri pale No. 1	300-325	14.3	67	300-325	10	81.5			

Resin	Montan Wax Comb. Temp. (° C.)	Montan Wax Loss in Weight on Combining (%)	Montan Wax M. P. of Mixture (° C.)	Ozokerite Comb. Temp. (° C.)	Ozokerite Loss in Weight on Combining (%)	Ozokerite M. P. of Mixture (° C.)	Paraffin Wax Comb. Temp. (° C.)	Paraffin Wax Loss in Weight on Combining (%)	Paraffin Wax M. P. of Mixture (° C.)
Batavia Dammar B	90-100	0.4	76	90-100	0	64	140-150	0.5	49
Bold black scraped East India	130-140	0.4	99	130-140	0	73	130-140	—	62
Pale East India Macassar Bold	120-130	0.8	83	120-130	0.2	77	150-200	—	55
Pale East India Singapore Bold	120-130	0.6	95	120-130	0	86	150-200	—	64
Elemi	100	1.2	60.5	100	1.0	70			
Batu scraped	150-200	2.0	127	150-200	2.8	74	150-200	—	69.5
Singapore Dammar No. 2	90-100	0	75	130-140	0	67	140-150	0.5	50
Run brown kauri No. 2							300-325		54

some instances turpentine has been utilized as vehicle for rosin-wax inks.[79] Thus, the pigment may be dispersed in a vehicle of 350 parts wax and 400 parts rosin in 1000 parts of turpentine. Transfer inks blended from rosin, linseed oil, nitrocellulose, amyl acetate and bronze powder have been stated to be applicable where embossed effects are desired.[80]

Utilization of mixtures of waxes and natural resins is limited to some extent by the melting point of the mixture. If the latter flows too easily at relatively low temperatures, bleeding may result during storage of the temporary transfer or on transposition to the permanent base. On the other hand, too high a melting point may make necessary the application of excessive heat to effect transference. In some instances the final backing, particularly one of fabric, may be scorched.

The effect of a number of natural resins upon the melting points of various waxes has been studied.[81] The melting points of the individual waxes and resins were determined, and the combining temperatures, loss in weight on mixing,[82] and melting points of 1:1 blends of the two components were secured. The data obtained, as indicated in Tables 31 and 32, show that most of the resins employed caused an increase in melting point of the wax. An apparent exception to this generalization was elemi, which was stated to lower the melting point of some of the waxes used. Also, this resin was said to act as a plasticizer for the wax.

Table 32.—Melting Points of Natural Resins and Waxes.

Resin	Melting Point (° C.)
Batavia dammar A	99–102
Batavia dammar B	96–100
Singapore dammar No. 2	114
Bold black scraped East India	160–164
Batu scraped	169
Pale East India Macassar Bold	127–156
Pale East India Singapore Bold	147–156
Manila MA	121
Loba C	114–123
Congo No. 4	178
Congo No. 11	193–200
Kauri pale No. 1	128
Run brown kauri No. 2	120–130
Elemi	Plastic
Wax	
Beeswax (pure crude)	61.5
Carnauba (No. 1 yellow)	80
Japan (Chickusan)	43
Montan	68
Ozokerite (natural yellow)	49
Paraffin	49

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[79] G. B. Bottino, U. S. P. 1,530,926, March 24, 1925; *Chem. Abs.*, 1925, **19**, 1784. *Cf.* A. W. Hanington, A. Rosenstein and R. A. Southward, U. S. P. 1,063,791, June 3, 1913; *Chem. Abs.*, 1913, **7**, 2486.

[80] A. L. Clapp, U. S. P. 1,280,399, Oct. 1, 1918; *Chem. Abs.*, 1918, **12**, 2687. *Cf.* K. Wolf, German P. 252,998, 1911; *Chem. Abs.*, 1913, **7**, 1591.

[81] R. W. Allen, *Chem. Industries*, 1938, **42**, 507; *Chem. Abs.*, 1938, **32**, 6082.

[82] Because of the relatively high mixing temperatures required to achieve homogeneity, apparently a portion of the components was volatilized.

Synthetic resins from which fusible transfer compositions have been prepared include coumarone, indene, urea-formaldehyde and phenol-formaldehyde resins.[83] These substances have been used alone or in conjunction with drying or non-drying oils in the formulation of pigment vehicles. Coumarone resin, linseed oil and carbon black has been suggested as an indelible admixture for marking fabrics.[84] The ink was reported to be non-fusible below 100° C. and non-saponifiable, so that it would not be affected by boiling water or alkaline washing fluids. In some cases, the linseed oil may be omitted and the pigment incorporated directly into the melted resin. Plasticizing agents may also be incorporated. Thus, compositions containing 100 parts of paracoumarone, an equal quantity of a plasticizing agent, *e.g.*, dibutyl or diamyl phthalate, butyl stearate, triphenyl, tritolyl or tricresyl phosphate or triacetin (glycerol triacetate), and 2.5 parts of cobalt linoleate were suggested as carriers for a pigment.[85] When powdered bronze is used as pigment, a modifying agent consisting of a mixture of drying oil (boiled linseed oil) and non-drying oil (mineral oil) together with a small proportion (2.5 per cent by weight) of a metal drier may be added to the coumarone resin.[86] The mineral oil was stated to increase the fluidity of the ink during transference operations. After the latter operation was completed, oxidation of the drying oil was said to furnish a skin over the pigment, thereby retarding tarnishing of the bronze. In place of linseed oil, a mixture of a non-drying and semi-drying oil has been suggested.[87] Mixtures of blown castor oil with blown rapeseed oil were stated to furnish a composition that was light yellow in color, and about as viscous as molasses. In preparing ink for marking cotton, silk or wool fabrics, 65 parts of the combined oils were stirred into 100 parts of melted paracoumarone together with pigment and a small proportion of mineral oil. The finished ink was said to be sufficiently fluid to permit securing smooth impressions on transfer paper. After several weeks, slow oxidation of the semi-drying oil caused setting of the ink to a solid, flexible composition reported to be transferable by fusion. In some instances cellulose derivatives were employed instead of drying or semi-drying oils.[88] Thus, ethyl or benzyl cellulose was admixed, in solution, with a plasticizing agent (*e.g.*, tritolyl phosphate), paracoumarone, blown castor oil and pigment. The composition then was printed upon a base, and the solvent allowed to evaporate. In this way a solid, fusible pattern was said to be secured. Also, cellulose

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[83] See Carleton Ellis, "The Chemistry of Synthetic Resins," New York, Reinhold Publishing Corp., 1935.

[84] H. S. Sadtler, U. S. P. 1,542,965, June 23, 1925; *Chem. Abs.*, 1925, 19, 2419.

[85] A. Schneider, U. S. P. 1,922,016, Feb. 19, 1935; *Brit. Chem. Abs.* **B**, 1936, 109; *Chem. Abs.*, 1935, 29, 2375; *Rev. Paint, Colour, Varnish*, 1935, 8, 209.

[86] T. Marston and W. S. Lawrence, U. S. P. 1,511,816, Oct. 14, 1924, to Kaumagraph Co.; *Chem. Abs.*, 1925, 19, 185.

[87] W. S. Lawrence, U. S. P. 1,545,837, July 14, 1925, to Kaumagraph Co.; *Chem. Abs.*, 1925, 19, 2881.

[88] W. S. Lawrence, U. S. P. 1,899,420, Feb. 28, 1933, to Kaumagraph Co.; *Chem. Abs.*, 1933, 27, 3048; *Brit. Chem. Abs.* **B**, 1933, 1051. British P. 338,611, 1929; *Brit. Chem. Abs.* **B**, 1931, 127; *Chem. Abs.*, 1931, 25, 2532. *Cf.* German P. 623,698, 1935, to Chemische Fabrik Halle-Ammendorf Gebr. Hartmann; *Chem. Zentr.*, 1936, 107 (1), 5023; *Rev. Paint, Colour, Varnish*, 1936, 9, 242.

acetate has been utilized in fusible transfer inks.[89] The cellulose derivative is stirred into a vehicle of acid butyl tartrate. Small proportions of paracoumarone resin and Venice turpentine may be added to the mixture to form a solid fusible ink.

Molding compositions of the urea-formaldehyde type have been incorporated into aliphatic or aromatic alcohols to furnish vehicles for transfer inks.[90] Blown castor oil and pigment may be added to the resin solution before the pattern is placed upon a paper base.

In imprinting upon fabrics designs intended to be permanent, efforts have been made to include in the pigment vehicles substances that will penetrate the pores of the fabric so that the color may be distributed through the marked material. Waxes such as beeswax, carnauba, ozokerite, paraffin, ceresin and montan are said to be particularly efficient for this purpose. The waxes may be employed alone or in conjunction with natural or synthetic resins.

One proposed ink included a natural resin such as rosin together with beeswax.[91] For marking designs, 9-15 parts of the resin and 1-7 parts of beeswax were admixed, and 3-10 parts of pigment, 0.25-0.75 part of turpentine, 0.25-2 parts of lithographic varnish and 1 part of gum elemi were incorporated. The gum and turpentine acted as plasticizing agents for the ink, preventing flaking of the latter after transference. Addition of soap to a mixture of drying oil, paraffin wax, and a resin has been utilized.[92] Such vehicles are described as being resistant to water but not to alkali solutions. Paraffin wax and spermaceti have been suggested as components of pigment vehicles.[93] In this instance rosin and a plasticizing agent such as gum dammar may be added. In other instances, inclusion of turpentine in such blends has been proposed.[94] To achieve an embossed effect upon the marked fabric, a vehicle containing 16 parts of Cumar gum, 4 parts of rosin and 4 parts of carnauba wax has been utilized.[95] To prevent the finished ink from flaking, adjunction of 2 parts of stearic acid to the vehicle was recommended. The pigment consisted of ultramarine blue ink and a paste of Titanox[96] in lithographic varnish. As vehicle for pigments, cetyl alcohol has been proposed.[97] A mixture of carnauba wax and sesame oil was blended with the pigment and alcohol before printing.

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[89] W. S. Lawrence, U. S. P. 1 596,545, Aug. 17, 1926, to Kaumagraph Co.; *Chem. Abs.*, 1926, **20**, 3349.

[90] French P. 774,431, 1934, to British Cyanides Co. Ltd. and H. E. Peace & Co. Ltd.; *Chem. Abs.*, 1935, **29**, 2266; *Rev. Paint, Colour, Varnish*, 1935, **8**, 208.

[91] T. Marston and I. F. B. Hutton, U. S. P. 1,524,874, Feb. 3, 1925, to Kaumagraph Co.; *Chem. Abs.*, 1925, **19**, 1061. G. Muzzioli, British P. 312,220, 1928; *Chem. Abs.*, 1930, **24**, 932.

[92] S. Sakairi and M. Uchiyama, Japanese P. 111.522, 1935, to Nisshin Seihun K. K.; *Chem. Abs.*, 1936, **30**, 2411; *Rev. Paint, Colour, Varnish*, 1936, **9**, 170.

[93] J. R. Barreras, French P. 738,921, 1932; *Chem. Abs.*, 1933, **27**, 2050; *Rev. Paint, Colour, Varnish*, 1933, **6**, 198. *Cf.* H. Barth, German P. 293.251, 1915; *Chem. Abs.*, 1917, **11**, 2605.

[94] British P. 212,945, 1923, to Società anon. arti grafiche e decorative; *Chem. Abs.*, 1924, **18**, 2258.

[95] O. L. Davis, U. S. P. 1,688,117, Oct. 16, 1928, to Joseph Walker Co.; *Chem. Abs.*, 1929, **23**, 249.

[96] Titanox designates pigments containing titanium dioxide admixed with precipitated barium or calcium sulphate.

[97] German P. 600,233, 1934, to Unichem Chemikalien Handels A.-G.; *Chem. Abs.*, 1934, **28**, 6538. French P. 744,832, 1933; *Chem. Abs.*, 1933, **27**, 4360.

Embossed effects may be produced if a drying oil is present in the pigment carrier. When the transfer is placed on a paper base, the outside portion of the ink will be oxidized, forming a skin; on transference, the latter prevents the ink from penetrating the fabric. One such composition comprises 100 parts paracoumarone, 12 parts ozokerite wax, 20 parts blown rapeseed oil, 12 parts No. 6 lithographic varnish, 5 parts butyl ether of diethylene glycol and 2 parts cobalt drier.[98] The paracoumarone may be replaced by a product resulting from the condensation of phenol and formaldehyde in the presence of rosin. The latter was melted at 100° C. and 30 per cent by weight of beeswax incorporated. Blown rapeseed or linseed oil (20 per cent by weight) was stirred in and pigment added.[99] On printing on a transfer base, the ink was said to be sufficiently hardened and cooled by oxidation so that the base could be rolled into spiral form immediately after printing without danger of bleeding. When a smooth rather than an embossed surface was desired, a non-drying oil such as castor was substituted for linseed oil.[100] Resin-wax vehicles were stated to become somewhat more fluid when petroleum jelly equal to the combined resin-wax content and a small proportion (6 per cent by weight) of sesame oil were used.[101]

An ink which can be applied in the form of an emulsion to the transfer base has been suggested.[102] A composite of ozokerite, carnauba wax, stearic acid, and a paraffin wax resin was melted at 65° C. and admixed with turpentine. To this was added a warmed aqueous solution of gum tragacanth and triethanolamine. The product, a suspension of wax in an aqueous solution of gum tragacanth, was incorporated in an aqueous solution of dye at the above temperature to furnish a marking blend.

Materials such as asphalt and stearin pitch have been employed in the preparation of transfer inks. Among the reported advantages of these substances are low pigment consumption and a low gradient of viscosity change on heating.[103] The latter property permits a transference to be made at high temperatures so that deep penetration of the ink into the fabric is secured. In one instance 200 parts of an aqueous emulsion of bentonite and asphalt (containing 120 parts of the latter), and 20 parts each of paracoumarone, ozokerite and carbon black were heated, with stirring, until most of the water was removed. The resulting ink

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[98] W. S. Lawrence, U. S. P. 1,954,450, April 10, 1934, to Kaumagraph Co.; *Chem. Abs.*, 1934, **28**, 3911; *Rev. Paint, Colour, Varnish*, 1935, **8**, 109; *Brit. Chem. Abs.* **B**, 1935, 110.

[99] W. S. Lawrence, U. S. P 1,977,680, Oct. 23, 1934, to Kaumagraph Co.; *Brit. Chem. Abs.* **B**, 1935, 944; *Chem. Abs.*, 1935, **29**, 258. British P. 331,135, 1929; *Chem. Abs.*, 1930, **24**, 6040; *Brit. Chem. Abs.* **B**, 1930, 827.

[100] W. S. Lawrence, U. S. P. 1,941,697, Jan. 2, 1934, to Kaumagraph Co.; *Brit. Chem. Abs.* **B**, 1934, 924; *Chem. Abs.*, 1934, **28**, 1826; *Rev. Paint, Colour, Varnish*, 1934, **7**, 457. *Cf.* W. S. Lawrence and T. H. Miller, U. S. P. 2,008,763, July 23, 1935, to Kaumagraph Co.; *Brit. Chem. Abs.* **B**, 1936, 560; *Chem. Abs.*, 1935, **29**, 5956.

[101] German P. 611,389, 1935, to Caribonum Ltd.; *Chem. Abs.*, 1935, **29**, 6060; *Rev. Paint, Colour, Varnish*, 1935, **8**, 517.

[102] W. S. Lawrence, U. S. P. 1,954,451, April 10, 1934, to Kaumagraph Co.; *Brit. Chem. Abs.* **B**, 1935, 110; *Chem. Abs.*, 1934, **28**, 3911; *Rev. Paint, Colour, Varnish*, 1935, **8**, 109 *Cf.* E. Gorcy, U. S. P. 1,564,234, Dec. 8, 1925; *Chem. Abs.*, 1926, **20**, 513.

[103] Viscosity change of inks on heating is comparable to the viscosity index of petroleum hydrocarbons. See Carleton Ellis, "The Chemistry of Petroleum Derivatives," Vol. II, New York, Reinhold Publishing Corp., 1937.

was said to be efficient as an indelible transfer composition for marking fabrics, being little affected by water. Also, an ink containing stearin pitch, mineral oil, paraffin wax and carbon black has been proposed.[104] The latter was reported to be extremely flexible on drying, showing no tendency to flake.

A combination of transfer vehicles of somewhat different properties has been suggested to secure deep penetration of ink into the fabric and at the same time to produce an embossed effect on the surface of the marked material.[105] In the preparation of the transfer base the design was printed with an ink containing a vehicle of ethyl or benzyl cellulose, a phenol-formaldehyde-rosin condensation product, and a plasticizing agent, *e.g.*, tritolyl phosphate. This mixture, which was said to fuse slowly under the influence of heat, was overprinted with a composition of rosin, beeswax and ultramarine. On transference, the overprinting was reported to be transmitted first and to penetrate the fabric. The slowly fusible portion of the vehicle could not creep into the fabric but remained on the surface. The blended ink was proposed particularly for marking fabrics having a complicated weave.

Transfer of a design by fusion and subsequent fixing of the pattern by washing with alkaline solution has been employed in some instances.[106] An emulsifying agent was incorporated in the pigment vehicle so that washing of the fabric (after transference) with alkaline solutions caused emulsification of the pigment, resulting in deeper penetration of the latter into the marked material. One such ink comprised lanolin, Turkey red oil,[107] boiled linseed oil, paracoumarone, and induline base dye.[108] With the above vehicles it was stated to be difficult to use direct dyes, that is, dyes which do not require the use of a mordant for forming a marking on cotton. When a direct dye was desired, the latter was dissolved in glycerol before admixture with the vehicle.

When an ink has been transferred to the fabric to be marked, often steaming is employed to fix the dye. If the dye vehicle is decomposable under the action of steam, the carrier may be removed at the same time. For example, a vehicle was prepared from the reaction product of 15 parts of resorcinol and 2-2.5 parts of paraformaldehyde.[109] Heating of the reactants at 120° C. for 0.5 hour was reported to lead to formation of a water-soluble, fusible resin. The latter was dissolved in water at 100° C. together with gum arabic, methylene blue, cornstarch and tannic acid. The solution was cooled to 16-20° C. and zinc chloride incorporated.

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[104] H. Kruse, U. S. P. 1,393,142, Oct. 11, 1921; *Chem. Abs.*, 1922, **16**, 505.

[105] W. S. Lawrence, U. S. P. 1,939,821, Dec. 19, 1933, to Kaumagraph Co.; *Chem. Abs.*, 1934, **28**, 1486. British P. 333,768, 1929; *Chem. Abs.*, 1931, **25**, 605.

[106] T. Marston and W. S. Lawrence, U. S. P. 1,487,873, March 25, 1924, to Kaumagraph Co.; *Chem. Abs.*, 1924, **18**, 1758. British P. 230,275, 1924; *J. S. C. I.*, 1925, **44**, 366B; *Chem. Abs.*, 1925, **19**, 3384. W. S. Lawrence, U. S. P. 1,573,976, Feb. 26, 1926, to Kaumagraph Co.; *Chem. Abs.*, 1926, **20**, 1530.

[107] Turkey-red oil is the reaction product of sulphuric acid and castor oil. It consists mainly of ricinoleic sulphate, together with some free ricinoleic acid.

[108] Induline bases are prepared from amidoazobenzene, aniline and aniline hydrochloride. They are insoluble in water, soluble in organic solvents (alcohol, acetic acid, etc.).

[109] W. S. Lawrence, U. S. P. 1,827,591, Oct. 13, 1931, to Kaumagraph Co.; *Chem. Abs.*, 1932, **26**, 605.

Because of the presence of zinc tannate and dye in the ink, a lake was formed in the vehicle, and the need for a mordant in the fabric was said to be obviated.[110]

Inks intended for transference to glass may contain a somewhat different type of vehicle from those employed for fabric marking. One such material proposed was blended from an opaque varnish, pigment and finely pulverized glass.[111] The fusing point of the latter was slightly lower than that of the object to be marked.

Marking compounds for ceramic materials may be compounded with vehicles of the drying-oil type.[112] Boiled linseed oil was boiled with an equal quantity of lead oxide until most of the latter had dissolved. On cooling, the mixture was described as being resinous in appearance. Thinning agents such as oil of cloves, lavender or aniseed oil (10-20 per cent by weight) were added together with pigment to the drying-oil composition. The high lead content of the ink was said to remove the necessity for a flux on transference and to aid formation of sharp lines.

Soluble Inks. When a number of cutting and sewing operations are required in finishing a garment, often the positions of buttonholes, lapels, hems, pleats and embroidery designs are placed upon the fabric with transfer patterns. Upon completion of the finishing operations the patterns usually are removed by washing the fabric in hot water or soap solution. Hence, for this type of pattern an ink which is water-soluble is necessary. A marking compound reported to be permanently soluble in hot water was prepared by incorporating turpentine and gum shellac in triacetin (glycerol triacetate) at 250° F. The temperature was then raised to 270-340° F. and a basic dye stirred into the mixture.[113] Suggested dyes include Methylene Yellow, Rhodamine, Crystal Violet, and Victoria Blue. Also, compositions containing rosin and shellac soaps have been proposed.[114] Thus, 30 parts of soap flakes and 10 parts of glycerol in 50 parts of water were boiled to a gel, and 70 parts rosin, 65 parts shellac and 7 parts caustic soda added. The whole was heated to remove water and the pigment and 10 parts of β-naphthol embodied. Transferred embroidery designs with fine, distinct lines were stated to have been secured with beeswax.[115] The latter was blended with boiled linseed oil, turpentine and pigment. Also, mixtures of beeswax and carnauba wax may be used.[116] For example, a mixture of beeswax and carnauba wax, boiled linseed oil, sodium hydroxide, triethanolamine, granulated sugar

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[110] In employing basic dyes such as methylene blue, a mordant in the form of an insoluble salt of tannic acid is usually put in the fabric, when the latter is not an animal fiber. The color base of the dye reacts with the tannate to give an insoluble or sparingly soluble lake, which forms the dye.

[111] J. F. McNutt, U. S. P. 1,996,549, April 2, 1935, to American Decal Corp.; *Chem. Abs.*, 1935, 29, 3481. U. S. Reissue 19,839, June 28, 1936; *Chem. Abs.*, 1936, 30, 1907.

[112] J. Kasseker, U. S. P. 971,280, Sept. 27, 1910, to Schmidt, Kasseker & Co.; *Chem. Abs.*, 1910, 4, 3289. British P. 23,852, 1909; *Chem. Abs.*, 1911, 5, 181; *J. S. C. I.*, 1910, 29, 278.

[113] P. Yohns, U. S. P. 1,870,082, Aug. 2, 1932, to Butterick Publishing Co.; *Brit. Chem. Abs.* B, 1933, 514; *Chem. Abs.*, 1932, 26, 5439; *Rev. Paint, Colour, Varnish*, 1933, 6, 199.

[114] W. S. Lawrence, U. S. P. 1,718,966, July 2, 1929, to Kaumagraph Co.; *Chem. Abs.*, 1929, 23, 4089.

[115] J. Mossman, U. S. P. 1,159,857, Nov. 9, 1915, to M. J. Cunning Co.; *Chem. Abs.*, 1916, 10, 283.

[116] O. F. Lohmann, U. S. P. 1,990,193, Feb. 5, 1935, to Superior Trademark Mfg. Co.; *Brit. Chem. Abs.* B, 1936, 30; *Chem. Abs.*, 1935, 29, 2005.

and magnesium oxide was utilized as carrier for a water-soluble pigment. When the fabric was washed, the ink was said to be dissolved completely from the garment. Acetic acid and albumin have been reported applicable in water-soluble transfers.[117] A basic dye was added to the acid and albumin together with gum arabic, molasses and triethanolamine.

PRESSURE TRANSFER INKS

Inks which are to be transferred by pressure rather than heat usually do not contain materials that harden rapidly on exposure to air. For this reason employment of drying and semi-drying oils in formulation of vehicles is precluded. One proposed marking compound embodied tallow, paraffin wax, oxidized lead carbonate, and benzine.[118] The whole was warmed together and applied to a transfer base. On transference, the designs secured were reported to be clear and firm but easily removed by hot water or alkaline washing fluids. A composition stated to be applicable for imprinting shadings on line drawings was prepared by admixing carbon black with glycerol or lard and a non-drying oil such as castor or mineral oil.[119] The blend was placed upon a base which had been impregnated with wax, whereby penetration of ink into the base was said to have been prevented.

Unvulcanized rubber articles may be marked with designs fashioned from rubber, and the pattern and surface bearing it subsequently vulcanized together.[120] For example, a relief printing stamp was coated on the raised areas with an aqueous solution of aluminum chloride which acted as a coagulant. An aqueous dispersion of rubber was applied to the coagulant, and the design then transferred to a base which had been coated with adhesive material.

SOLVENT TRANSFER INKS

The effect of heat or pressure on certain fabrics, woods or metals may be injurious. For this reason, among others, transference is sometimes carried out with solvents for the pigment vehicles. A proposed water-soluble vehicle comprised 1 part glucose and 2 parts corn syrup.[121] Pigment was incorporated together with glycerol, the latter as a thinning agent. When alcohol is used to effect transference, an ink composed of a water-insoluble but alcohol-soluble dye, a non-drying oil, *e.g.*, castor oil, and a small proportion of rosin may be utilized.[122]

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[117] A. B. Pöschel, British P. 393,132, 1933; *Chem. Abs.*, 1933, **27**, 5553. German P. 609.404, 1935; *Chem. Abs.*, 1935, **29**, 3175.

[118] E. C. Pawla and E. W. Pawla, U. S. P. 1.606,662, Nov. 9, 1926; *Chem. Abs.*, 1927, **21**, 161.

[119] S. E. Wade, British P. 312,004, 1928, to Wade Transfer Co. Proprietary, Ltd.; *Chem. Abs.*, 1930, **24**, 933.

[120] J. S. Tidmus, British P. 414,205, 1934, to International Latex Processes Ltd.; *Brit. Chem. Abs.* **B**, 1934, 933; *Chem. Abs.*, 1935, **29**, 258.

[121] C. F. Morse, U. S. P. 979,542. Dec. 27, 1910; *J. S. C. I.*, 1911. **30**, 141; *Chem. Abs.*, 1911, **5**, 1000.

[122] A. Schubert, U. S. P. 2,013,291, Sept. 3, 1935, to Barrett & Co.; *Brit. Chem. Abs.* **B**, 1936, 943; *Chem. Abs.*, 1935, **29**, 7101; *Rev. Paint, Colour, Varnish*, 1935, **8**, 517.

Chapter 13

Emulsion Inks

CONSIDERATIONS INVOLVING PHYSICAL CHEMISTRY

An emulsion ink is one comprising pigments, modifying agents, and an emulsion of two immiscible liquids. The stability of such a composition is the prime concern of any manufacturer engaged in the production of such inks. The considerations involving physical chemistry in a study of emulsions and their stability are beyond the scope of this text, and reference must be made to literature on colloid chemistry for a complete discussion of these phenomena.[1] An attempt has been made here to indicate the more important factors which may apply in the manufacture of emulsoid inks.

The manufacture of inks is primarily a mixing problem. Mixing processes are said to result in a simple physical mixture, a physical change, a dispersion, or a chemical reaction.[2] Emulsoid inks are dispersions. In some instances, which will be noted later, chemical reactions are important features of the manufacture of such inks.[3] With reference to emulsions, it is desired to produce permanent, rather than temporary, types of dispersions.

To prevent segregation in mixtures, it is suggested that phases of nearly equal specific gravities be employed, that the pigment particles be ground to colloidal dimensions (.001 to 0.1 micron), or that the external phase have a sufficiently high viscosity to prevent settling.[4] Another necessary condition is that the particles of the internal phase be protected from touching one another by employment of a third material, such as a finely divided solid, protective colloid, or wetting agent.

In many emulsion-type inks, water is employed as the external phase. The internal, or oily phase, of emulsion inks may vary in specific gravity for different inks. In general, it may be said that most of the oily substances utilized have a specific gravity of approximately one, which is the value for water.

Carbon black (from gas burners) is said to have almost no particles

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[1] See, for example, J. Alexander, "Colloid Chemistry," New York, The Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1926. W. Ostwald, "Practical Colloid Chemistry," New York, E. P. Dutton & Co., Inc., 1924. A. Kulen, "Kolloidchemisches Taschenbuch," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1935. E. A. Hauser, "Colloidal Phenomena,' New York, McGraw-Hill Book Co., Inc., 1939.

[2] J. H. Perry, "Chemical Engineers' Handbook," New York, McGraw-Hill Book Co., Inc., 1934, pp. 1267 to 1279.

[3] A. J. Hailwood, A. Shepherdson and A. Stewart, British P. 326,516, 1930, to Imperial Chemical Industries Ltd.; *Brit. Chem. Abs.* **B,** 1930, 571.

[4] J. H. Perry, *loc. cit.*

larger than 0.2 micron. The size of particles in colloidal dispersions ranges from .001 to 0.1 micron. Therefore it is necessary to grind a carbon black to this degree of fineness. Another condition for stability is that the carbon black particles exhibit Brownian movement.[5]

Modifiers such as wetting and emulsifying agents, stabilizers, binders or protective colloids generally are used in preparation of emulsion inks, since these substances aid in dispersing two immiscible liquid materials so that one liquid comprises the disperse and the other the dispersed phase of an emulsion. Also, these modifiers apparently help in stabilizing emulsions after the latter have been formed.

Wetting or emulsifying agents are surface-active substances which depend upon the polarity of their molecules to produce orientation of the molecular configuration at an interface.[6] The tendency of the above substances to orient themselves depends upon the characteristics of the phases in contact at the interface.

Employment of a surface-active agent in creating an emulsion may be illustrated by considering the function of mahogany sodium sulphonate in an emulsoid ink.[7] In the process of manufacture, pigment, mahogany sulphonates, lithographic varnish and binders are ground together, and water is emulsified with the resulting mixture. The sodium sulphonate groups are said to be oriented toward the water while the hydrocarbon groups tend to contact the organic constituents surrounding the pigment. The water and the oil phases are said to wet each other with the aid of the mahogany sulphonates and greater stability of the emulsion may be expected.

In the investigation of two liquids, to determine whether wetting agents are required for emulsification, interfacial tension may be used as a criterion. Interfacial tension depends upon the surface energy between the two liquids.[8] In measuring the surface energy of two immiscible liquids, a capillary [9] or drop-weight method may be used.[10] Table 33 gives values for the interfacial tension of water with certain liquids. A low interfacial tension is said to favor the stability of an emulsion.[12] A wetting agent generally lowers the interfacial tension. According to Gibbs' Law, substances which decrease the interfacial energy or tension are concentrated at the interface.[13] Wetting agents are usually concentrated in that region.

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[5] Carleton Ellis in "Science of Petroleum." New York. Oxford University Press, 1938, Vol. **4**, 2853.

[6] F. E. Bartell, *Ind. Eng. Chem.*, 1939, **31**, 31.

[7] H. Heckel, U. S. P. 1,906,962. May 2, 1933, to Twitchell Process Corp.; *Brit. Chem. Abs.* **B**, 1934, 157; *Rev. Paint, Colour, Varnish*, 1934, **7**, 103; *Chem. Abs.*, 1933, **27**, 3627. German P. 618,284, 1935, to Twitchell Process Corp.; *Chem. Abs.*, 1936, **30**, 309. Mahogany sulphonates are oil-soluble sulphonates obtained in refining certain petroleum distillates with sulphuric acid. For the preparation and properties of such substances see, Carleton Ellis, "The Chemistry of Petroleum Derivatives." New York, Reinhold Publishing Corp., Vol. **I,** 1934, and Vol. **II,** 1937.

[8] E. A. Hauser, J. M. Andreas and W. B. Tucker, *Ind. Eng. Chem.*, 1939, **31**, 32.

[9] For details of determining interfacial tension by capillary methods, see W. C. Reynolds, *J. C. S.*, 1921, **119**, 460; *Chem. Abs.*, 1921, **15**, 2759.

[10] W. D. Harkins and F. E. Brown, *J. A. C. S.*, 1919, **41**, 499; *Chem. Abs.*, 1919, **13**, 3418.

[11] W. C. Reynolds, *J. C. S.*, 1921, **119**, 466; *Chem. Abs.*, 1921, **15**, 2759.

[12] E. A. Hauser, J. M. Andreas and W. B. Tucker, *Ind. Eng. Chem.*, 1939, **31**, 32.

[13] E. S. Hedges, "Colloids," London, Longmans, Green and Co., 1931, 127.

Table 33.—Observed Interfacial Tension (Capillary Method) with Water.[11]

	Interfacial Tension (Dynes per cm.)
Ethyl ether	10.6
Amyl alcohol	4.8
Benzene	34.4
Nitrobenzene	24.7
Chloroform	33.3
Carbon tetrachloride	43.8
Aniline	4.8
Cresylic acid	3.9
Petrol (gasoline)	37.1 to 46.4
Paraffin oil	43.1 to 48.7
Liquid paraffin wax	15.1 to 41
Turpentine	28.8 to 34.2
Gum acacia sol (10 per cent gum)	25.9

Emulsions may be of either the oil-in-water or water-in-oil type. "Oil" is a general term signifying that the liquid is immiscible in water. As a test for determining the type of emulsion for a given dispersion, it is suggested [14] that a small amount of oil-soluble dye (insoluble in water) be added to the system. If the emulsion is of the oil-in-water type, it will not be colored by the dye because the dye cannot reach the oily or internal phase; if a water-in-oil type of dispersion is present, coloration will take place.

Also, electrical conductivity may be used to indicate the type of dispersion. When water is the disperse (external) phase, the conductivity will be relatively large in magnitude because of the presence of small quantities of electrolyte. The conductivity is very much diminished if the external phase is oil.

It is possible to control the type of disperse system by employment of the correct emulsifier. Further, it appears that surface-active materials must be used in almost all emulsion inks, because of the relatively high interfacial tensions indicated in Table 33. An emulsifying agent which is wetted more readily by oil than by water is said to form stable water-in-oil emulsions. An emulsifier which is wetted by water to greater extent than by oil stabilizes an oil-in-water system.[15] As an illustration of this phenomenon, it is stated that alkaline earth, zinc, aluminum, and iron soaps favor the production of water-in-oil emulsions. Alkali soaps are said to produce oil-in-water systems.

Solids may be employed as emulsifying agents. The finely ground particles are said to arrange themselves at the interface between the two emulsified liquids.[16] It is necessary that the particles be wetted to some extent by each liquid, if the solid is to serve as an emulsifying agent. An indication of the wettability of a solid by a liquid is the "contact angle." The latter is the angle between the surface of the liquid and the solid

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[14] E. S. Hedges, "Colloids," London, Longmans, Green and Co., 1931, 149.

[15] E. S. Hedges, "Colloids," London, Longmans, Green and Co., 1931, 153.

[16] J. M. Fain and F. D. Snell, *Ind. Eng. Chem.*, 1939, 31, 48.

at the place where liquid and solid phases join the gaseous phase of the air. If the solid is completely wetted by the liquid, the contact angle is zero. The type of emulsion resulting from a system in which the solid is in contact with two liquids will depend on the relative magnitudes of the contact angles of the solid with each liquid. The liquid with the smaller angle is said to form the disperse phase.

Marion and Marion[17] have suggested utilization of a solid emulsifier. Colored pigments are emulsified with binders with the aid of colloidal clays, such as bentonite, Silvinite, or Vulcanite. Schlaepfer[18] reported emulsification of 33 parts of water with 67 parts of kerosene by using one part of carbon black. The latter example indicates the possible employment of pigments themselves as emulsifiers.

The mechanism of emulsification has been studied by Stamm and Kraemer.[19] The production of emulsions is said to be a two-stage process. In the first stage, shaking and mixing produces a pulverization of each phase into droplets. The second stage comprises the reunion of the droplets of one or both phases. The degree of dispersion is dependent on the magnitude of these two opposing tendencies. An emulsifying agent is said to protect the droplets of one phase from coagulating while the drops of the other phase join one another to form the external phase.

Aluminum, calcium, magnesium and zinc soaps of palmitic, stearic and oleic acids have been employed to prevent settling of pigments.[20] These soaps are non-drying, whereas lead, manganese and cobalt soaps are driers. The aluminum, zinc and magnesium soaps become oriented so that the metallic part is in contact with the pigment and the hydrocarbon chain is in contact with oil or varnish. Of these soaps, aluminum stearate is said to be the most satisfactory, because of its tendency to form alumina gels in the ink. The gel acts as a protective colloid.

A number of wetting agents for ink pigments have been indicated by Burton.[21] In addition to the soaps described above, it is suggested that saponification products containing iron, titanium and copper be employed (*e.g.*, iron oleate). Also lecithin, esters of sulphonated dibasic acids (*e.g.*, "Alphasol"), dipentene, pine oil, octyl alcohol and tributyl phosphate are recommended. These substances are said to act as wetting agents for the pigment-oil interfaces.[22]

Naphthenates, blown linseed oil and blown rapeseed oil have been proposed as wetting agents for pigments.[23] It is stated that these substances will produce inks which have a low liquefying stress[24] (even

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[17] L. Marion and S. Marion, French P. 823,422, 1938; *Chem. Abs.*, 1938, 32, 5648.

[18] A. U. M. Schlaepfer, *J. C. S.*, 1918, **113**, 522; *Kolloid Z.*, 1918, **22**, 113; *Chem. Abs.*, 1918, **12**, 2273.

[19] A. J. Stamm and E. O. Kraemer, *J. Phys. Chem.*, 1926, **30**, 992; *Chem. Abs.*, 1926, **20**, 2771.

[20] *Am. Ink Maker*, 1936, **14** (8), 25.

[21] J. L. Burton, *Am. Ink Maker*, 1937, **15** (3), 21; *Chem. Abs.*, 1937, **31**, 4141.

[22] A test for the applicability of surface-active agents to printing inks is described in Chapter 17.

[23] *Am. Ink Maker*, 1938, **16** (5), 27.

[24] Liquefying stress refers to the ease with which concentrated inks can be liquefied by remilling after storage. A low liquefying stress indicates that the ink can be reliquefied easily.

though stored for a long time) and a high degree of pigmentation. Many wetting agents are said to produce inks with high liquefying shears on storage. The quantity of wetting agent employed is stated to be important. In some instances, one per cent of wetting agent gives the maximum shearing effect, while a tenth of a per cent of the substance increases the rigidity of the ink. Therefore it would appear that the surface-active agent acts as a lubricant as well as a wetting agent.

Protective colloids and binders are employed in inks. Casein [25] and other colloids were reported to maintain the pigment in suspension and to act as an adhesive for ink and paper. According to Wu and Wu [26] these colloidal substances adsorb the pigment. In some instances the pigment apparently adsorbs the colloid. Other protective colloids suggested [27] for inks include tannins, pectins, gum, salts of alkylated fatty acid amides and amines, phenols and alcohols of high-molecular weight. Also, albumin, starch and soaps have been recommended.[28]

Adhesive substances such as casein, glue, and gelatin have been incorporated in inks to the extent of 25 per cent.[29] An illustrative composition consisted of 70 parts casein, 70 parts formamide, 150 parts water and 370 parts aluminum dust.

Protective colloids are hydrophilic colloids when present in an emulsion in amount greater than hydrophobic colloids (*e.g.*, pigment). The latter do not precipitate in presence of substances which ordinarily cause coagulation of the hydrophobic material. Addition of electrolytes and temperature changes may cause such precipitation, and the protective colloid renders the hydrophobic colloid less liable to such coagulation.

Zsigmondy [30] developed a method of measurement of the protective ability of hydrophilic colloids. The measure employed is known as the "gold number." The latter is the number of milligrams which, when added to a standard gold sol, is just insufficient to prevent a change in color, from red to blue, when 1 cc. of a 10-per cent solution of sodium chloride is added. The standard gold hydrosols must be prepared by the formaldehyde method and the particles must range in size from 20 to 30 microns. To produce such a standard gold sol 120 cc. of distilled water are heated to the boiling point and 2.5 cc. of a 0.6-per cent aqueous solution of chlorauric acid ($HAuCl \cdot 4H_2O$) and 3.5 cc. of a $0.18N$ solution of potassium carbonate added to the water. Heating is continued, and when boiling occurs again, 3 to 5 cc. of a 0.12-per cent solution of formaldehyde are added and the whole stirred vigorously. Some values of gold numbers are included in Table 34.[31] It is to be noted that small gold

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[25] M. S. Hopkins and N. Underwood, U. S. P. 1,621,541, March 31, 1927; *Chem. Abs.*, 1927, 21, 1555.

[26] H. Wu and Y. Wu in J. Alexander, "Colloid Chemistry," New York, The Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1926, Vol. 1, 380.

[27] W. Denzler, British P. 396,618, 1933; *Chem. Abs.*, 1934, 28, 1206.

[28] V. Kubelka, *Chem. Listy*, 1930, 24, 325; *Chem. Abs.*, 1930, 24, 5393; *Rev. Paint, Colour, Varnish*, 1930, 3, 275.

[29] P. La F. Magill and C. Dangelmajer, U. S. P. 2,130,807, Sept. 20, 1938, to E. I. du Pont de Nemours & Co.

[30] R. Zsigmondy, *Zeitschrift für Analytische Chemie*, 1901, 40, 697.

[31] R. Zsigmondy, *loc. cit.*

Table 34.—Gold Number of Colloids.

Colloid	Gold Number	Colloid	Gold Number
Gelatin	.005–.01	Gum tragacanth	0.5–2
Russian glue	.005–.01	Dextrin	6–20
Bone glue	.005–.01	Wheat starch	4–6
Casein	0.01	Sodium stearate	.001–10
Gum arabic	0.1–0.5	Sodium oleate	0.4–1.0
Albumin	.03–0.25	Potato starch	25

numbers are characteristic of protective colloids. Protective values expressed as gold numbers have reference to gold sols only, and the protective effect of the same colloids may be somewhat different when applied to the sol of a different substance.

Traube and Rackwitz[32] have presented a theory of protection in which they maintain that there are three adhesion intensities: the first is the adhesion intensity of the protecting colloid for water; the second is that of the protected colloid for water; the third embodies the adhesion intensity of the two colloids for each other. Surface-active substances (*e.g.*, saponin or soap) have low adhesion intensity for water and should exert less protective action than surface-inactive substances (*e.g.*, gelatin, albumin, or dextrin), which have high adhesion intensities for water. Hence wetting agents were stated not to act as protective colloids. It was reported that surface-active colloids usually do not provide protection for hydrophobic colloids (*e.g.*, gold, silver and carbon sols with surface-active colloids). However, with other colloids (*e.g.*, sulphur and arsenious sulphide sols), possessing less adhesion intensity for water, there is stated to be no difference in protective action between surface-active and surface-inactive colloids. The conclusion was drawn that wetting agents do not protect carbon particles. The effect of some substances upon sols has been summarized in Table 35 in the form of numbers, similar to gold numbers. Substances having a low number protect the sol from coagulation to a greater extent than those possessing a higher number.

Table 35.—Effect of Surface-Active and -Inactive Agents upon Sols.[33]

	Gold No.	Silver No. (I)	Silver No. (II)	Colloidal Carbon No.	Iron Hydroxide No.	Prussian (Berlin) Blue No.	Sulphur No.	Arsenic Sulphide No.
Gelatin	.002	.007	.02	.03	1	0.01	.000025	15
Gum arabic	0.1	0.25	.04	.3	5	1	.005	4
Albumin	0.5	.3	.5	0.1	3	5	.005	20
Dextrin	4	20	10	4	4	50	.025	20
Soap	1	1			25	0.4	.006	25
Sodium stearate	2	3			23	0.25	.005	
Saponin	23	7			23	0.5	.003	2

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[32] I. Traube and E. Rackwitz, *Kolloid Zeit.*, 1925, 37, 133; *Chem. Abs.*, 1926, 20, 135.

[33] I. Traube and E. Rackwitz, *Kolloid Zeit.*, 1925, 37, 133; *Chem. Abs.*, 1926, 20, 135.

The colloidal carbon sol data are applicable in choosing protective colloids for printing inks. It is evident from the above table that gelatin, gum arabic and albumin apparently afford good protection. Dextrin was said to give fair results.[34] The method of determining the numbers was similar to that employed for gold numbers described previously.[35]

Caution should be observed in adding to printing inks substances which will cause "salting out" of the colloids. Electrolytes generally tend to accelerate such precipitation. Hofmeister [36] reported that all electrolytes do not have the same precipitating power. Some of his data, which indicate the concentration (in gram mols per liter) of sodium salts required to salt out a sol of albumin, are contained in Table 36. The values represent the effectiveness of anions in causing precipitation. It was stated that citrate, tartrates, sulphates, acetates and chlorides should not be employed in preparing printing inks. Also, nitrates and chlorates should be used in limited quantities.

Table 36.—Effect of Electrolytes upon Albumin Sols.

Sodium Salt	Gram Mols of Salt Required to Precipitate a Sol of Albumin
Citrate	.56
Tartrate	.78
Sulphate	.80
Acetate	1.69
Chloride	3.62
Nitrate	5.42
Chlorate	5.52
Iodide thiocyanate	Saturated solutions do not salt out

It has been found [37] that cations cause salting out. The effectiveness of positive ions in bringing about precipiattion increased in the following order: sodium, potassium, lithium, barium, strontium, magnesium, calcium. The sol employed was prepared from wheat flour. This would indicate that sodium, potassium, lithium, barium and strontium salts should be added in small proportions to printing inks.

The hydrogen ion concentration, or pH, is important in the maintenance of stable emulsions of hydrophilic colloids since the latter substances are electrically charged. Protein substances are amphoteric in nature and as the pH is changed the electric charge of protein colloids changes from positive to negative. A neutral point is observed where the colloid will not migrate in the electric field. The hydrogen ion concentration at which the colloid is uncharged is called the isoelectric point.

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[34] The colloidal carbon was prepared by the method of P. C. L. Thorne, *J. C. S.*, 1916, **109**, 1916; *Chem. Abs.*, 1916, **10**, 1461. The reader is referred to that source for further details.

[35] For methods of preparing some of the sols described see, R. Zsigmondy, *Z. anal. Chem.*, 1901, **40**, 711 (gold sol); E. Abderhalden, "Handbuch fur biochemischen Arbeitsmethoden," Urban and Schwarzenburg, Berlin, 1910 (silver sols); W. Ostwald, "Practical Colloid Chemistry," New York, E. P. Dutton & Company, Inc., 1924 (Berlin Blue, sulphur, arsenic sulphide and iron hydroxide sols).

[36] Hofmeister, *Archiv fur Path. Pharmakol.*, 1899, **24**, 247; **25**, 1.

[37] R. A. Gortner, W. F. Hoffman and W. B. Sinclair, *Kolloid Z.*, 1928, **44**, 97; *Chem. Abs.*, 1928, **22**, 1513.

At this pH the stability of the colloid is least. In the case of proteins, the molecular configuration is said to be as follows: [38]

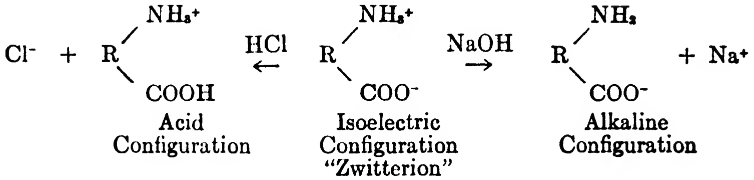

Table 37.—Isoelectric Points of Protein Colloids.

	Isoelectric Point pH
Egg albumin	4.6–5.0
Milk albumin	4.6
Gelatin	4.0–5.6
Casein	4.6–4.7
Lecithin	2.6–4.7

Table 37 represents the isoelectric points of some colloids.[39] To avoid precipitation of protective colloids such as albumin or casein, the pH of the printing inks in which these substances are used generally is maintained at a value greater or less than 4.6 to 5.0. In practice borax, ammonia or alkalies are employed to keep the pH of the ink above the isoelectric point.

INTAGLIO EMULSION INKS

As binders and protective colloids for intaglio emulsion inks, rubber, albumin, acaroid, casein, asphalt, rosins, synthetic resins, gum dammar, dextrin, or glue have been suggested. Casein, albumin, dextrin and glue generally are dissolved in water. Alkalies are required to keep casein and albumin in solution. Among bases proposed are borax, potash lye, sodium carbonate and ammonia.

Asphalt, rubber, synthetic resins, cellulose esters, gum dammar, acaroid and rosins usually are dissolved in organic solvents. The latter include xylene, petroleum fractions (boiling from 130 to 180° C.), kerosene, turpentine, acetone, alcohol, benzene and dipentene.

Turpentine is said to be an efficient solvent for dammar and resins.[40] This solvent is reported to oxidize on exposure to air, oxygen or ozone, forming a resinous body resembling a peroxide.

Dipentene is a terpene with a sweet odor, and is produced from turpentine by treatment with alcoholic solutions of sulphuric acid. It is stated to be a good solvent for gums and resins and to retard skinning of ink.[41]

Isopropyl, amyl, octyl and ethyl alcohols are suggested [42] as solvents

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[38] L. J. Harris, *Biochem. J.*, 1930, **24**, 1080; *Chem. Abs.*, 1931, **25**, 15.

[39] A. W. Thomas, *J. Am. Leather Chem. Assoc.*, 1934, **29**, 3; *Chem. Abs.*, 1934, **28**, 1371.

[40] M. Phillips, *Am. Ink Maker*, 1937, **15** (6), 18.

[41] M. Phillips, *loc. cit.*

[42] M. Phillips, *loc. cit.*

for synthetic resins and gums. Amyl and octyl alcohol, in combination with solvents for nitrocellulose, are said to increase the solvent power of any true solvents. This is known as "coupling action" and is a property of many alcohol-type solvents.

Benzene, xylene and petroleum hydrocarbons dissolve certain synthetic resins, cellulose esters and asphalt.[43] They may be used as diluents for inks.

Emulsifying agents employed for intaglio inks include sulphonated oils (*e.g.*, Turkey-red oil), saponified resins and condensation products of oleic acid and ethylene oxide. These agents are reported to produce oil-in-water systems.

Some intaglio inks contain sulphonated hydrocarbons[44] as wetting agents. Emulsions employed in the preparation of printing compositions usually are composed of oil and water. Sulphonate radicals in the wetting agent apparently dissolve in the water layer, while the hydrocarbon radical is oriented toward the oil phase. One intaglio composition containing sulphonated hydrocarbons was prepared by admixture of 500 parts of a varnish, consisting of naphtha drying oils, varnish gums and driers, with 25 parts of mahogany sodium sulphonate. Then 200 parts of fire-red pigment were ground in the blend. 500 grams of water were added to form an emulsion with the pigment-sulphonate-varnish mixture.[45]

Solutions of asphalt or resins in petroleum hydrocarbons, which are emulsified with water, have been suggested[46] as vehicles for intaglio inks. It was stated that the petroleum solvents utilized should have a boiling point of 130 to 180° C. and a flash point above 30° C. Proposed emulsifying agents comprised the condensation products of alkylene oxides or polyglycols with aliphatic carboxylic acids, alcohols, amines, carboxylic acid amides, or mineral oil sulphonates. Also, reaction products of aliphatic or cycloaliphatic carboxylic acids and aminosulphonic acids were advocated.

An intaglio ink containing asphalt was prepared by dissolving 15 parts of gilsonite in 40 parts of petroleum hydrocarbon and emulsifying the solution with an aqueous dyestuff paste. The latter was composed of 4.5 parts of aluminum hydroxide lake of Vesuvin, 38 parts of water, and 2.5 parts of an ethylene oxide-oleic acid reaction product. The resulting ink was said to be incombustible, nearly odorless, non-settling and waterproof.

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[43] M. Phillips, *loc. cit.*

[44] Carleton Ellis, "The Chemistry of Petroleum Derivatives," New York, Reinhold Publishing Corp., 1935, 1074.

[45] H. Heckel, U. S. P. 1,906,962, May 2, 1933, to Twitchell Process Corp.; *Brit. Chem. Abs.* B, 1934, 157; *Rev. Paint, Colour, Varnish*, 1934, 7, 103; *Chem. Abs.*, 1933, 27, 3627. German P. 618,284, 1935, to Twitchell Process Corp.; *Chem. Abs.*, 1936, 30, 309.

[46] British P. 414,801, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1269; *Rev. Paint, Colour, Varnish*, 1934, 7, 457. British P. 439,524, 1935; *Chem. Abs.*, 1936, 30, 3667; *Rev. Paint, Colour, Varnish*, 1936, 9, 93.

It has been suggested[47] that asphalt may be used both as coloring matter and as a binder for intaglio compositions. One ink comprised asphalt dissolved in xylene to which was added an aqueous solution of sodium sulphoricinoleate (wetting agent). An aqueous solution of casein solubilized with soda then was incorporated. Subsequently carbon black was ground into the mixture. Also, the aqueous portion may contain soaps, saponins, Turkey-red oil (sulphonated castor oil), alkylated salts of amines, tannins, or gums to stabilize the emulsion. Instead of asphalt, cellulose esters, linseed oil, or rubber may be employed.

Rapidly drying inks which contain asphalt are reported to be employed for intaglio printing. One composition[48] of this type contained 22 per cent gilsonite (asphalt), 51 per cent of a hydrocarbon solvent for gilsonite, 22 per cent water, and 5 per cent glue. Also, the hydrocarbon solution of asphalt was mixed with ⅓ its volume of an aqueous syrup of dextrin and pigment. It is stated that the ink has high fluidity and sufficient homogeneity to enable it to enter and to be retained in the depressions of hard metal intaglio printing forms. Also, the ink is said not to penetrate into paper.

Hopkins and Underwood[49] advocated utilization of an emulsion ink in which pigment is dispersed in any oil medium. An aqueous solution containing casein, borax, ammonia and sodium fluoride then was added.

Emulsified intaglio inks may contain casein and asphalt.[50] The employment of these substances depends upon the requirements of the particular situation. Intaglio inks must be stable in physical properties and should not deteriorate before use by the printer. Compositions with volatile solvents, such as xylene, are said to be somewhat inflammable and must be modified to depress this characteristic.

In rotogravure intaglio printing, high-speed rotary presses are employed. Rapid drying of the inks is a necessity in such work. It is essential that the ink fill the engraved portions of the printing plate and that the composition be readily wiped from the smooth surface.

Asphalt may be employed to give the flow and binding properties required in intaglio printing. As vehicle for such inks kerosene has been suggested. The latter is inflammable, but is not as volatile as xylene, and inflammability was said to be lessened. An example of asphalt coloring compound was prepared from 2 parts of gilsonite (solid asphalt) in 2 parts of kerosene. To the kerosene solution, 1 part of liquid asphaltum was added. The resulting mixture was ground with 2 parts of Van Dyke brown. The asphalt was stated to act as a protective colloid for the pig-

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[47] W. Denzler, British P. 396,618, 1933; *Chem. Abs.*, 1934, **28**, 1206. French P. 748,759, 1933; *Chem. Abs.*, 1933, **27**, 5559.

[48] E. Winship, French P. 680,881, 1929; *Chem. Abs.*, 1930, **24**, 4176. G. D. Knight, Canadian P. 304,857, 1930, to E. Winship; *Chem. Abs.*, 1931, **25**, 833. U. S. P. 1,858,449, May 17, 1932; *Chem. Abs.*, 1932, **26**, 2942. U. S. P. 1,725,649, Aug. 20, 1929; *Chem. Abs.*, 1929, **23**, 4836; *Rev. Paint, Colour, Varnish*, 1929, **2**, 332.

[49] M. H. Hopkins and N. Underwood, U. S. P. 1,621,541, 1,621,542, 1,621,543, March 21, 1927, to Charles Eneu Johnson & Co.; *Chem. Abs.*, 1927, **21**, 1555.

[50] M. H. Hopkins and N. Underwood, *loc. cit.*

ment, to serve as a pigment itself, and to aid in making a firm bond with the paper. Also, casein was proposed by Hopkins and Underwood[51] as a binding material for intaglio inks. Ammonia, borax, and sodium fluoride were utilized to maintain the casein in aqueous solution. Casein is reported to be an excellent protective colloid for pigment and to produce a stable solution. In the process of drying, this protein is said to bind the ink to the paper. Also, albumin has been proposed for intaglio emulsion inks. Posse[52] suggests that 1.4 parts of albumin (or casein), 0.18 part of borax, 2.8 parts of sulphonated castor oil, 5.4 parts of a laked color, 3.5 parts of turpentine, 2.2 parts of carbon black, and 14 parts of water be stirred together to give such an ink.

An intaglio ink, containing albumin, has been advocated by Schutze.[53] An aqueous mixture of albumin, pigment and alkaline salt was emulsified by the aid of oil-sulphonic acids with turpentine or rosin oil.

A casein composition in which ammonia and potash lye were utilized to make the protein soluble has been reported. One such vehicle consisted of 2.0 parts of rosin, 0.1 part of casein, 1.6 parts of 10-per cent potash lye, 0.24 part of ammonia solution (sp. gr. 0.91), 4.0 parts of water and 0.2 part of turpentine.[54] Pigment then was ground into the vehicle.

Resinous condensation products of polyhydric alcohols (*e.g.*, glycerol) with polybasic organic acids (*e.g.*, phthalic anhydride) and unsaturated fatty acids may be incorporated into aqueous suspensions.[54a] An aqueous solution of casein, ammonia and a small amount of a magnesium or lead salt of a high-molecular weight organic acid is advocated as the emulsifying medium. Coloring matter, (*e.g.*, carbon black or chromic oxide) is added and the resulting mixture diluted with water to obtain the desired consistency.

An intaglio ink[55] which is said to comprise a stable, aqueous, non-skinning emulsion was prepared from rosin, a volatile petroleum distillate, caustic soda, a drying oil and water. It was reported that the composition dries quickly upon application to paper, through evaporation of the hydrocarbon solvent and absorption of water by the paper. Also, the ink was said not to adhere to the embossing rollers.

"Safety inks" are reported[56] to have been prepared by mixing a drying-oil ink with an aqueous solution of water-soluble color. Approximately

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[51] M. H. Hopkins and N. Underwood, *loc. cit.*

[52] G. E. Posse, U. S. P. 1,142,365, June 8, 1915; *Chem. Abs.*, 1915, 9, 2000.

[53] L. Schutze, U. S. P. 1,096,198, May 12, 1914; *Chem. Abs.*, 1914, 8, 2228; *J. S. C. I.*, 1914, 33, 642. L. Schutze and R. Fischer, British P. 12,567, 1913; *Chem. Abs.*, 1914, 8, 3723; *J. S. C. I.*, 1913, 32, 1007. German P. 265,902, 1912; *Chem. Abs.*, 1914, 8, 579.

[54] H. Kurz and K. Albert, U. S. P. 1,890,996, Dec. 13, 1933; *Chem. Abs.*, 1933, 27, 2050. U. S. P. 1,962,823, June 12, 1934; *Chem. Abs.*, 1934, 28, 4923. French P. 43,145, 1934; *Chem. Abs.*, 1934, 28, 5262. French P. 746,863, 1933; *Chem. Abs.*, 1933, 27, 4698. French P. 711,613, 1931; *Chem. Abs.*, 1932, 26, 1810. British P. 390,780, 1933; *Chem. Abs.*, 1933, 27, 5995; *Brit. Chem. Abs.* B, 1933, 478. British P. 396,654, 1933; *Brit. Chem. Abs.* B, 1933, 879; *Chem. Abs.*, 1934, 28, 1206. British P. 371,527, 1931; *Brit. Chem. Abs.* B, 1932, 687. Austrian P. 124,742, 1931; *Chem. Abs.*, 1932, 26, 860.

[54a] German P. 522,776, 1933, to I. G. Farbenind. A.-G.; *Rev. Paint, Colour, Varnish*, 1933, 6, 99.

[55] E. H. McLeod, U. S. P. 2,005,945, June 25, 1935, to International Printing Ink Corp.; *Chem. Abs.*, 1935, 29, 5682.

[56] A. A. Wittnebel, U. S. P. 2,116,374, May 3, 1938; *Chem. Abs.*, 1938, 32, 5237. British P. 469,232, 1937; *Chem. Abs.*, 1938, 32, 814.

90 parts of drying-oil ink and 10 parts of water ink are the proportions used. The quantity of water-soluble pigment in the final product will be about 7 per cent by weight of the water-insoluble pigment. The water-soluble ink is said to smudge if the stamps or other documents printed with this ink are tampered with, *e.g.*, if ink-eradicator is employed to remove cancellation marks.

For copper-plate printing it has been suggested that an ink[57] be prepared by admixing 500 parts of copper-plate printing lacquer with 50 parts of water. The whole then was ground with 100 parts Lake Red C. The product may be thinned with 50 parts of toluene.

Typographic Emulsion Inks

These may be either oil-in-water or water-in-oil emulsions. Most typographic emulsion inks are of the oil-in-water type. The pigment, in the latter class of inks, is usually in the oil phase, and modifiers are admixed with the latter to maintain the coloring agent in a stable dispersed condition.

Water-in-oil compositions are said to have the pigment in the aqueous phase. Stabilizing agents usually are not added to the oily phase as in oil-in-water emulsions. Specific wetting agents generally are utilized for individual pigments to maintain the latter in stable water suspensions.

Materials such as sulphite liquor from paper manufacturing, spindle oil, fish oil, petroleum fractions, turpentine, castor oil, rubber solutions or asphalt solutions are utilized as vehicles in typographic emulsoid inks. Also, halogenated tung oil sometimes is used to promote rapid drying.

Binders and protective colloids employed in the manufacture of inks of this type include asphalt, bird lime distillate, chlorobenzene, casein, albumin, gum tragacanth, paracoumarone, and zinc hydroxide. Some of these substances are susceptible to bacterial decay. It was suggested that a preservative, such as formalin, be employed in conjunction with such agents.

As wetting agents for pigment and oil used in typographic inks, sodium silicate, benzoic acid, xylenol and guaiacol have been suggested. Caustic soda is frequently employed with some of these substances. Also, high-molecular weight alcohol sulphates, polymerized alkyl aryl sulphonates and monobutylphenyl sodium monosulphates are suggested as being satisfactory wetting agents for pigment-water systems. In some instances aluminum, magnesium and calcium soaps, wool grease and oleic acid are advocated.

Generally emulsion inks consist of emulsions in which the pigment is in the inner phase of oil or hydrocarbon. However, Curado[58] has reversed the above arrangement by dispersing the pigment in water, with

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[57] K. Gross, U. S. P. 2,038,839, April 28, 1936; *Chem. Abs.*, 1936, **30**, 4344; *Rev. Paint, Colour, Varnish*, 1936, **9**, 242. French P. 755,755, 1933; *Chem. Abs.*, 1934, **28**, 2203; *Rev. Paint, Colour, Varnish*, 1934, **7**, 196.

[58] J. G. Curado, U. S. P. 2,120,588, June 14, 1938, to General Printing Ink Corp.; *Chem. Abs.*, 1938, **32**, 6083.

the aid of a wetting agent. The dispersion subsequently was emulsified with linseed oil or other water-immiscible vehicle.

The advantage, said to result from using the pigment as the inner phase of the water layer, is that the same vehicle may be used with any pigment. Lithographic varnishes usually must be modified for use with specific pigments. If the pigment particles are completely surrounded by water, the non-aqueous vehicle does not come into contact with them and no special modification of the oil is necessary. For example, it was stated that No. 2 linseed oil varnish gives satisfactory tack, setting rate, drying properties, and viscosity if ground with a phloxine toner. This same vehicle ground with Milori Blue was said to give an ink that was too tacky and rapid-drying for typographic purposes.

An example of a water-wetted pigment and oil emulsion composition consists of 25 per cent of Red Lake C toner, 25 per cent of water, 5 per cent of wetting agent, 15 per cent of linseed varnish, 16 per cent of blown linseed oil, 12 per cent of petrolatum, and 2 per cent of lead naphthenate (drier). The wetting agent [58a] was dissolved in water at 140° F. and the pigment added to the solution. The pulp produced from the water, wetting agent and pigment mixture was digested for several hours to effect dispersion of the pigment in the water. A blend of linseed varnish, blown linseed oil, petrolatum and drier then was agitated with the pulp to disperse the water-wet pigment in the oil vehicle. Other wetting agents recommended were sulphated high-molecular weight alcohols, organic salts of polymerized aralkyl sulphonic acids and monobutylphenylphenol sodium sulphonate.

A typographic ink employing aluminum, calcium, and magnesium soaps as emulsifying agents was advocated.[59] Thus, an ink was prepared from 100 parts of aluminum soap, 30 to 45 parts of calcium soap, 10 to 20 parts of magnesium soap, 45 to 80 parts of distillation products of bird lime, 75 to 100 parts of mineral oil, 45 to 75 parts of water and 45 parts of carbon black. In place of the distillation products of bird lime, whale wax or Chinese wax may be employed. Bird lime [60] is a waxy substance, prepared by macerating and pounding the inner bark of holly (*Ilex Integra*). It is said to consist principally of mochyl and ilicyl palmitates and some caoutchouc. On distillation, palmitic acid and a hydrocarbon with the formula $C_{26}H_{44}$ are obtained.

A typographic emulsion ink consisting of lampblack, mineral oil, rosin, catechu, formalin, sodium silicate, sodium carbonate, gum arabic, aluminum resinate, coloring agent and water was suggested by Ishida.[61]

[58a] The wetting agents employed by Curado were said to be those commercially designated as "Gardinol," "Darvan," "Erkalin," and "Areskap." Although the exact formula for each was unknown, they are believed to be derived from the sulphonated condensation product of hydroxydiphenyl alcohol (described in British P. No. 409,773, to Rubber Service Laboratories Co., May 10, 1934) or from the condensation of naphthalene with sulphonic acid (as described in U. S. P. 1,336,759, April 30, 1920, to Otto Schmidt).

[59] S. Horii, Japanese P. 39,066, 1921; *Chem. Abs.*, 1922, 16, 2234.

[60] E. Divers and M. Kawakita, *J. C. S.*, 1888, 53, 268.

[61] K. Ishida, U. S. P. 1,410,572, Mar. 28, 1922; *Chem. Abs.*, 1922, 16, 1875. British P. 194,156, 1922; *Chem. Abs.*, 1923, 17, 3615.

The mineral oil and rosin were boiled together and carbon black added to the boiled mixture. The remaining ingredients then were ground in the pigment-rosin-oil blend.

Instead of adding wetting agents, the latter may be produced *in situ* during the preparation of the ink. For example, a portion of the oil vehicle may be saponified to give a soap[62] which serves as wetting agent or protective colloid. One such ink was blended by admixing barium lake of Victoria Blue in linseed oil varnish, and agitating the dispersion with aqueous caustic soda. A portion of the varnish was stated to be saponified, forming a soap. An aqueous solution of a coal-tar dye then was incorporated, together with carbon black.

A rapidly drying typographic ink is reported[63] to contain a vehicle consisting of a chlorinated drying oil (*e.g.*, chlorinated tung oil) and an activator (zinc and aluminum paste). Bromine or iodine may be used in place of chlorine in the halogenation, and oiticica, linseed, perilla or fish oil substituted for tung oil. The speed of drying was stated to be in proportion to the extent of halogenation. To aid the drying process, the ink was heated directly after printing.

A composition, comprising an emulsion of water in oils, fats, resins or pitches is proposed as a vehicle for typographic ink.[64] Alkali (*e.g.*, sodium hydroxide, potassium hydroxide) and aromatic hydrocarbons or aromatic hydrocarbon salts (*e.g.*, sodium salicylate, or *o*-, *m*- or *p*-cresol) were incorporated in the water as emulsifying agents.

For example, to 100 parts of water were added 15 parts of sodium hydroxide and 1.5 parts of benzoic acid, sodium salicylate, *o*-, *m*-, or *p*-cresols, xylenol or guaiacol. The oily phase consisted of 100 parts of asphalt dissolved in 900 parts of linseed oil varnish. The latter mixture then was emulsified with 25 per cent by volume of the aqueous solution described above, and 9 parts of nigrosine (pigment) ground into the whole.

Inks for use with rubber forms are made by dispersing a water- and alcohol-insoluble pigment or lake in an alkaline solution of shellac in alcohol or acetone.[64a]

Another typographic ink[65] contains 20 per cent asphaltic base petroleum residuum oil, 68 per cent water, and 12 per cent of an oil-insoluble coloring medium, such as carbon black. The composition is said to be satisfactory for newspaper printing.

Dispersions of rubber have been suggested[66] as a vehicle for printing ink. Aqueous emulsions of natural rubber latex or of rubber itself with drying oils have been proposed. Casein and ammonia, or resins, are

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[62] H. Zimmer, British P. 357,150, 1929; *Chem. Abs.*, 1933, **27**, 1773.

[63] W. J. Koenig, U. S. P. 2,136,108, Nov. 8, 1938, to Sloane-Blabon Corp.; *Chem. Abs.*, 1939, **33**, 1525.

[64] R. O. Bratke, British P. 431,642, 1935; *Brit. Chem. Abs.* **B**, 1935, 860; *Chem. Abs.*, 1936, **30**, 193.

[64a] German P. 669,052, 1939, to Kast & Ehinger G. m. b. H.; *Rev. Paint, Colour, Varnish*, 1939, **5**, 181.

[65] E. H. McLeod and W. W. Mock, U. S. P. 1,524.872, Feb. 3, 1925; *Chem. Abs.*, 1925, **19**, 1061.

[66] British P. 409,009, 1934, to I. G. Farbenind. A.-G.; *Rev. Paint, Colour, Varnish*, 1934, **7**, 407.

stated to act as stabilizers for these emulsions. Thus, an ink was prepared by homogenizing 262 parts of chlorinated rubber (chlorine content about 60 to 68 per cent) with 131 parts of linseed oil, and 131 parts of tung oil, at a temperature of 100 to 140° C. Subsequently, 9 parts of an aqueous solution (containing 6.8 per cent lead and 1.4 per cent manganese), 162 parts of iron oxide pigment, and 48 parts of castor oil were ground with the chlorinated rubber dispersion. The resulting mixture was treated with 26 parts of alkaline aqueous solution of casein, 5 parts of ammonia solution, 5 parts of borax and 400 parts of water.

Salts of deacetylated chitin or chondroitin have been employed in aqueous mixtures containing wetting agents, (*e.g.*, Saponin), aldehydic compounds (*e.g.*, formaldehyde), and resins, oils, or waxes.[66a] When nonreactive, water-insoluble substances which remain in solid form in dispersion (*e.g.*, carbon black or Milori Blue) are added, printing mediums are obtained.

Printing ink may be prepared by mixing the colors[67] with an aqueous emulsion of albuminous substances. Thus, sodium carbonate was dissolved in water and albumin incorporated. To the resulting solution were added sodium ricinoleosulphonate and oil of turpentine. Barium lake of naphthol black subsequently was ground into the emulsion.

An emulsoid printing ink[68] in which the vehicle comprises a water-in-oil emulsion has been advocated. The emulsion may be prepared from mineral oil, water and wool grease.

For newspaper printing it was recommended[69] that inks utilizing waste sulphite liquors obtained in the manufacture of paper be employed. One such ink was produced by treating concentrated sulphite waste lye with nitric acid in the presence of copper or zinc. The black product secured was admixed with concentrated sulphuric acid. In this manner a dark black, syrupy product was obtained which could be used as ink in typographic printing.

In another procedure, waste sulphite liquor is concentrated by evaporation and the concentrate treated with alkali, water and phosphoric acid to form sodium phosphate without saponification of any of the sulphite constituents.[70] The product obtained on addition of alkali is emulsified with mineral oil and combined with pigment. To the resulting mixture alkaline dichromate and spindle oil (diluent) are added. The purpose of the sodium phosphate is to prevent moisture from penetrating water-

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[66a] British P. 458,816, 1937, to E. I. du Pont de Nemours & Co.; *Rev. Paint, Colour, Varnish*, 1937, 10, 124. These derivatives of natural products (chitin is a horny substance found, for example, in the hard shells of crabs whereas chondroitin is an essential constituent of cartilage) were prepared as described in British P. 458,839, 1937.

[67] French P. 458,646, 1913, to Berger & Wirt; *Chem. Abs.*, 1914, 8, 3245.

[68] S. Horrobin and A. Stewart, British P. 388,072, 1933, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1933, 27, 4698; *Rev. Paint, Colour, Varnish*, 1933, 6, 198.

[69] K. J. Smidt and R. Jaeger, British P. 187,537, 1922; *Chem. Abs.*, 1923, 17, 1157.

[70] M. Ludwigsen, Danish P. 46,482; *Rev. Paint, Colour, Varnish*, 1934, 7, 103; *Chem. Zentr.*, 1934, 105 (1), 1891. British P. 268,966, 1926; *Chem. Abs.*, 1928, 22, 1486; *Brit. Chem. Abs.* B, 1927, 452. Danish P. 37,548, 1927; *Chem. Abs.*, 1928, 22, 3056; *Rev. Paint, Colour, Varnish*, 1928, 1, 178. Swedish P. 68,241, 1929; *Chem. Abs.*, 1930, 24, 1528.

absorbent rolls (*e.g.*, rolls made of stearin, glycerol and glue) and to provide better covering power. Rapid drying, by oxidation of sulphite in air, is said to take place as soon as the ink is printed and good adhesion of the composition to the paper is reported.

Cross and Engelstad[71] also recommend the use of waste sulphite liquor in inks. For example, 130 parts of lignone extract (concentrated waste sulphite liquor containing 37 per cent solid matter) and 6 to 8 parts of chromic acid were stirred together and enough water added to make a 20-per cent aqueous solution. Before gel formation occurred the mixture of lignone and chromic acid was incorporated in 130 parts of lubricating oil and 5 to 7 per cent (by weight) of carbon admixed with the viscous emulsion. Toners then were added.

Also, sulphite waste liquor ink[72] may contain carbon black, mineral oil and soap. The latter is dissolved in sodium salts of concentrated waste sulphite liquor and carbon black dispersed in mineral oil subsequently added to the soap-sulphite blend.

It has been proposed that a typographic printing ink be[73] formed from sulphite cellulose lye which has been neutralized with ammonia. Soap and mineral oil are added to the neutral sulphite liquor, and the mixture emulsified with albuminic acids. Pigment and linseed oil (or glycerol) are ground with the sulphite emulsion.

Neutralized sulphite liquor has been suggested[74] as an ink binder in conjunction with hygroscopic substances (*e.g.*, glycerol).

In some instances, emulsion-type inks in which emulsifying agents are absent have been proposed.[75] Thus, 5 parts of chrome yellow were ground into 3 parts of linseed oil varnish. Addition of 1.5 parts of water to the dispersion with continued grinding was stated to yield a stable emulsion applicable to book printing. Instead of water, glycerol may be employed as one liquid phase.[76] The trihydric compound was emulsified with a suspension of carbon black in lubricating oil.

PLANOGRAPHIC EMULSION INKS

Most emulsion inks for this purpose are modified to eliminate the wetting apparatus generally used in lithographic printing and to prevent "greasing." Some inks contain hygroscopic substances such as calcium chloride or glycerol to take up moisture from air. Another method is to chill the plates below the dew point so that moisture from the air will

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[71] C. F. Cross and A. Engelstad, British P. 263,520, 1925; *Chem. Abs.*, 1928, **22**, 162; ***Brit. Chem. Abs.* B**, 1927, 185.

[72] G. A. Richter and E. W. Lovering, U. S. P. 1,738,798, Oct. 12, 1929, to Brown Co.; *Chem. Abs.*, 1930, **24**, 979; ***Brit. Chem. Abs.* B**, 1930, 249; *Rev. Paint, Colour, Varnish*, 1930, **3**, 34.

[73] W. Schultz, French P. 717,079, 1931; *Chem. Abs.*, 1932, **26**, 2879. German P. 542,587, 1929; *Chem. Abs.*, 1932, **26**, 3394.

[74] F. Croner, *Zellstoff u. Papier*, 1925, **5**, 225; *Chem. Abs.*, 1925, **19**, 3025.

[75] K. Gross, French P. 755,755, 1934; *Chem. Abs.*, 1934, **28**, 2203; *Rev. Paint, Colour, Varnish*, 1934, **7**, 196. U. S. P. 2,038,830, April 28, 1936; *Chem. Abs.*, 1936, **30**, 4344; *Rev. Paint, Colour, Varnish*, 1936, **9**, 242.

[76] M. J. Leahy, *Refiner*, 1937, **16**, 88; *J. Inst. Pet. Tech.*, 1937, **23**, 204A.

condense out and provide a film of water on the non-printing surface. In the latter instance the inks must be modified so as to run easily at the low temperature employed.

Emulsion planographic inks may be composed of oil phases which are volatile (*e.g.*, xylene). This permits rapid drying, particularly of asphalt inks.

Emulsions may be employed to promote chemical reactions with leuco bases of dyes. A reaction of this sort is said to promote very fine dispersion of the coloring matter. Some inks are prepared with water solutions of casein and may contain as much as 60 per cent water. Ammonia or other alkali must be employed to stabilize these solutions. The latter are usually emulsified with linseed oil (2 per cent) and rosin soap (7 per cent). Alcohol frequently is utilized in these compositions (as a solvent for the rosin).

Constituents of the oil phase include tung oil, linseed oil, xylene, "Cellosolve," castor oil or methyl cellulose. Wetting agents employed may be wool fat, oleates, gum dammar, aluminum stearate, Turkey-red oil or Yorkshire grease. Binders of the following type generally are used: dextrin, resin, gum arabic, gum tragacanth, asphalt, aluminum hydroxide, chlorinated rubber, casein and copal resin. As drier, cobalt linoleate has been advocated.

Offset emulsion inks usually are of the water-in-oil type.[77] The consistency of an ink should not change greatly as a result of the absorption of moisture if printing is to be uniform. It is stated that inks containing 12 to 15 per cent moisture at the moment of printing are applicable in offset work.

A short offset ink tends to pile on the rollers and to distribute poorly on the plate. Emulsification of greasy ink with water is said to cause an ink to become shorter. For this reason, it is recommended that an excess of water beyond the limit mentioned above be avoided.

Lithography depends upon the grease-repelling property of water, and for the selective inking of the surfaces a dampening roller usually is employed to wet the non-printing area of the stones. The water, in contact with the stones, repels the greasy inks to the water-repelling portions of the lithograph.

Price [78] proposes to eliminate the need for special dampening apparatus by the application of a composition comprising an aqueous solution of water-soluble salts, emulsified with oil. It was stated that the salts must be capable of forming a water-in-oil type of emulsion and must be deliquescent so that the ink will not lose water while in use. For example, an emulsion said to be applicable for lithographic ink was prepared by admixing 14 parts of an aqueous 39 per cent solution of calcium chloride, 4 parts of linseed oil varnish ("Mid Varnish"), 4 parts of thin lin-

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[77] A. Grunder, *Am. Ink Maker,* 1936, 14 (3), 25, 27: *Chem. Abs.*, 1937, 31, 6034.

[78] W. P. Price, U. S. P. 1,817,522, Aug. 4, 1931, to Horace Cory and Co.; *Chem. Abs.*, 1931, 25, 5584.

seed oil varnish, 8 parts of petroleum jelly, and 1 part of ammonium chloride or borax. This emulsion was incorporated in a lithographic ink in the proportions of 8 parts of emulsion to 3 to 11 parts of ink. Calcium chloride is a deliquescent salt which absorbs moisture from the air. The ammonium chloride, or borax, is stated to prevent calcium chloride from attacking the plate or stone and forming thereon a surface which will not repel ink ("scumming").

An ink-repellent, for admixture to planographic inks,[79] is said to contain glycerin, gum tragacanth, ammonium acid phosphate and nickel nitrate. The above composition was emulsified with the planographic ink. On printing, the ink was stated to repel from the non-printing areas of the metallic plate.

Another ink depending upon glycerol to achieve repulsion of the ink from the non-printing surfaces of a lithographic plate is suggested by Mehl.[80] In preparing the composition, 2 parts of a saturated aqueous solution of sodium hyposulphite, 2 parts of glycerol, 2 parts of rubber cement, 2 parts of nicotine in aqueous solution, and 1 part of benzene were admixed. The blend then was emulsified with greasy lithographic ink.

As previously mentioned, it has been proposed that wetting of non-printing areas of a lithographic plate be effected by maintaining the plate below the dew point of the surrounding atmosphere. In this manner, water will condense out upon the chilled plate to serve as ink-repellent. An ink for lithographic presses or plate cylinders chilled to a temperature below the dew point was suggested by Goedike.[81] It is reported that utilization of wool fat and gum arabic as ingredients to produce greasiness and stiffness in lithographic compositions results in impressions with great color strength and soft consistency. Wool fat was advocated because of its low hardening point.

In the preparation of such an ink, 50 parts of red pigment, 45 parts of number 1 lithographic varnish, 1 part of wool fat, and 3 parts of a water-varnish emulsion containing gum arabic were used.

A rotogravure composition stated to be non-corrosive, stable and quick-drying has been suggested.[82] Thus, barium oleate was dissolved in xylene and to this solution gilsonite was added. The whole then was triturated with Para Red toner and carbon black. An aqueous solution of Bismarck brown and methylene blue was heated to 180° F. and ground into this blend.

Gum dammar has been recommended[83] as an emulsifying agent for water-in-oil emulsions. The oil phase of the emulsion may be benzene,

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[79] G. S. Rowell, U. S. P. 2,090,704, Aug. 14, 1937, to Addressograph-Multigraph Corp.; *Chem. Abs.*, 1937, **31**, 7273.

[80] J. V. Mehl, U. S. P. 1,958,311, May 8, 1934; *Chem. Abs.*, 1934, **28**, 4255.

[81] J. G. Goedike, U. S. P. 1,935,629, Nov. 21, 1933; *Chem. Abs.*, 1934, **28**, 917; *Rev. Paint, Colour, Varnish*, 1934, **7**, 102.

[82] F. G. Lasher, U. S. P. 1,822,533, Sept. 8, 1931; *Chem. Abs.*, 1931, **25**, 5999; *Rev. Paint, Colour, Varnish*, 1932, **5**, 25.

[83] H. N. Holmes and D. H. Cameron, U. S. P. 1,410,012, Mar. 21, 1922; *Chem. Abs.*, 1922, **16**, 1875. H. N. Holmes, *J. Phys. Chem.*, 1925, **29**, 1205; *Chem Abs.*, 1926, **20**, 320.

toluene, carbon tetrachloride, carbon bisulphide, petroleum fats, greases, waxes, or chloroform. It was stated that, on printing, the oil body carrying the pigment permits the water to evaporate through the dried (or drying) oil film.

Lithographic ink may be prepared [84] by emulsifying an aqueous solution of soluble dyestuff with an oil. The dyestuff then is precipitated and is said to be removed from the aqueous to the oil phase. For example, a solution of 30 parts of linseed oil in 90 parts of benzene was emulsified with 10 parts of water and 10 parts of ammonium oleate. The emulsion produced is admixed with a leuco compound. The latter is prepared from 8 parts of Caledon Brown R, 15 parts of 34-per cent caustic soda, 7.5 parts of sodium hydrosulphide and 300 parts of water. The whole was maintained at 50° C. until the dyestuff had been reduced to a water-soluble leuco compound. Air was stirred into the emulsion containing the leuco compound, to oxidize the latter to an insoluble pigment. The emulsion of oxidized leuco compound was broken by addition of hydrochloric acid, and the linseed oil, after the removal of the benzene and water, was stated to contain the dyestuff as a transparent coloring agent. The product is said to be an excellent transparent brown ink.

A vehicle for the manufacture of inks[85] for printing on wall paper was composed of a drying oil solution of a resin emulsified with water. For example, equal weights of resin (phenylphenol-formaldehyde type) and tung oil were heated together for 1 hour at 200° C. A small proportion of cobalt linoleate drier then was incorporated into the mixture, and the whole emulsified with "Cellosolve" (monethyl ether of ethylene glycol) or xylene. The product was reported to be waterproof and quick-drying.

Planographic emulsion inks prepared from Yorkshire grease (washing liquor from wool), mineral oil, nigrosine and water have been advocated.[86] Two parts of Yorkshire grease were dissolved in 1.5 parts of light mineral oil (sp. gr. 0.85; viscosity 0.19 dynes). The resulting solution then was ground with 5 parts of a 10-per cent aqueous solution of nigrosine. Instead of Yorkshire grease, aluminum stearate or Turkey-red oil was suggested. The emulsion is said to be of water-in-oil type. However, certain pigments, such as methyl violet, appear to be soluble in both the oil and water phases, and to cause separation of the emulsion.

For offset printing, quick-drying emulsoid inks have been proposed.[87] In one instance a typographic ink was admixed with a solution of a vinyl ester resin in diacetone alcohol and ethylene glycol monoacetate. The whole subsequently was emulsified with glycerol and sodium tartrate.

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[84] A. J. Hailwood, A. Shepherdson and A. Stewart, British P. 326,516, 1928, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1930, **24**, 4944; *Brit. Chem. Abs.* **B**, 1930, 571. French P. 680,695, 1929; *Chem. Abs.*, 1930, **24**, 4103.

[85] British P. 422,416, 1935, to Bakelite Ltd.; *Rev. Paint, Colour, Varnish*, 1935, **8**, 240.

[86] A. de Waele, British P. 183,513, 1922; *Chem. Abs.*, 1923, **17**, 217.

[87] German P. 609,868, 1935, to Chemische Fabrik Halle-Amendorff Gebr. Hartmann; *Rev. Paint, Colour, Varnish*, 1935, **8**, 208.

An ink, said[88] to be applicable for photogravure printing, comprised 26 parts of a 50-per cent aqueous dispersion of a synthetic resin, 20 parts of methyl cellulose in water, 12 parts of a 20-per cent water solution of casein, and 40 parts of color paste (Hansa yellow GT paste with aluminum hydroxide). Also, photogravure inks containing ammoniated casein solution have been reported.[89] Pigment and binders were added to this solution.

Hadert suggested[90] that mixtures of emulsifying agents (*e.g.*, Turkey-red oil) and water with natural or synthetic copal solutions (with added alkalies) be employed as vehicles for photogravure inks. Triethanolamine and water were admixed with the wetting agents and pigments added to this vehicle. A small proportion of tannin was incorporated before addition of the pigment, to give the ink a gloss on printing.

In some instances aqueous mixtures of pigment pastes containing calcium or barium hydroxide have been ground into stand oil to furnish colored emulsoid inks.[91]

A composition reported[92] to be applicable for lithographic or offset printing contains dextrin, drying oils, aluminum or bronze powder, fillers and driers. Thus, 10 parts of rosin ester, 60 parts of linseed oil, 40 parts of tung oil, 5 parts of an alkali naphthalenesulphonate, 5 parts of dextrin, 1 part of lead manganese resin and 100 parts of aluminum powder were ground together.

An oil color may be obtained from a water-wet pigment by forming an emulsion of the pigment, water, oil and an emulsifying agent such as a soluble soap. The emulsion is broken by adding a salt of an alkaline earth metal, magnesium, aluminum or lead to precipitate the soap. In this manner it is possible to separate water from the oil and pigment.[92a]

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[88] German P. 585 167, 1933, to I. G. Farbenind. A.-G.; *Rev. Paint, Colour, Varnish*, 1934, **7**, 103; *Chem.-tech. Übersicht*, 1934, **58** (1, 2), 4.

[89] G. Pepe, Italian P. 341,703, 1937; *Chem. Zentr.*, 1937, **108** (2), 3967; *Rev. Paint, Colour, Varnish*, 1938, **11**, 25.

[90] H. Hadert, Dutch P. 56,423, 1936; *Chem. Zentr.*, 1936, **107** (2), 877; *Rev. Paint, Colour, Varnish*, 1936, **9**, 316. See also U. S. P. 2,170,198, Aug. 22, 1939.

[91] N. Kozlov, Russian P. 46,700, 1936; *Chimie et industrie*, 1937, **37**, 1153; *Rev. Paint, Colour, Varnish*, 1937, **10**, 342.

[92] Auerbach, Weissberger and Spol, Czechoslovak P. 47,430; *Chem. Zentr.*, 1934, **105**, 1851.

[92a] British P. 452,556, 1936, to International Printing Ink Corp.; *Rev. Paint, Colour, Varnish*, 1936, **9**, 373.

Chapter 14

Special Types of Printing Inks

ANILINE INKS

Simultaneously with the growth of dyestuff manufacture in the United States occurred the development of aniline printing inks which may be employed on a great variety of materials, such as Cellophane, glassine paper, Protectoid,[1] kraft paper and machine finished paper.[1a] The bag industry quickly adopted this kind of printing, since the short drying period of these inks permits printing and folding of paper bags and containers at high speed on the same machine in one operation. For many years aniline printing was used for numbering cartons, but its wide employment appears to have been brought about by the general use of moisture-proof cellulosic wrapping material, which is now printed without offset.[2]

Aniline inks are primarily solutions of a coal-tar dyestuff in an organic solvent, *e.g.*, an alcohol, ester, ketone or ether. In some instances the solvents may be admixed with water. Such simple compositions, although drying rapidly, have disadvantages: the dyes being water-soluble, bleeding of the ink is caused by moisture; few of the dyes are light-fast enough to stand ordinary requirements in this respect, and lack of pigments makes the inks unsuitable for printing dark shades, their hiding power not being very great. By addition of modifying agents many of the properties of these inks can be improved. For example, incorporation of a resinous material or tannin often imparts to the solution the consistency required for application to a particular surface and renders the ink fast to light and waterproof. In the case of opaque inks, a pigment (generally white), is incorporated into the composition.

Aniline inks, because they dry very rapidly and obviate offset caused by ordinary quick-drying oil-base inks, may be used to advantage on cellulosic materials. Furthermore, they are not so likely to dry on the press as other varieties and no heating is required to dry them on the paper. Economy of production results from the use of one type of aniline ink which contains a special drier which penetrates the cellulosic deriva-

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[1] The term Cellophane applies to cellulose acetate films made of specially treated pulp. Glassine paper is a similar, but thinner and more transparent product (*Paper*, 1934, 33 (26), 66).

Protectoid is the trade name for a cellulose acetate plastic produced in the form of films, rods and tubes (*Chem. & Met.*, 1937, 44, 490). For a glossary of papermaking terms see *Paper*, 1924, 33 (26), 66.

[1a] For a review of such applications of aniline inks, see *Deutscher Drucker*, 1937, 44 (518), 57; *Rev. Paint, Colour, Varnish*, 1938, 11, 23.

[2] A. McNeil, *Am. Ink Maker*, 1935, 13 (10), 15; *Chem. Abs.*, 1936, 30, 306; *Rev. Paint, Colour, Varnish*, 1935, 8, 516.

tive and binds the ink to the sheet, protecting the printed material from abrasion. One of its advantages is obtained by its direct printing from a roll, thus removing the necessity of extra parts on the press.[3]

Dyestuffs in Aniline Inks. The rapid increase in the application of aniline inks has resulted in a greater usage of dyestuffs in the printing ink industry. Most of the coal-tar dyes dissolve easily in alcohol, are brilliant but not waterproof.[4] The latter property, however, can be improved by addition of glycerol or metal salts.

Coal-tar dyes are classed as either acid or basic. Acid dyes contain sulpho-, hydroxyl- or carboxyl- groups which are neutralized by an alkali or other metal. Basic dyes are those forming hydrochloric salts or a tannic lake. Generally, basic dyes are used in aniline inks as they are more intense and brilliant, although not as permanent as acid dyes. Basic dyes possess comparatively high surface tension, causing a tendency against spreading on the material to be printed. A small quantity of the solvent "Cellosolve" may be added to the dye solutions to promote spreading of the latter. To prevent bleeding and increase fastness to light, tannic acid may be added to the solution of the dye together with sufficient acetic acid to hinder the formation of a tannin lake of the dye.[5] Usually about ten parts of dyestuff are dissolved in nine parts of the solvent.[6] Basic dyes are more economical in use than acid dyes, since a smaller quantity of the former will give the same intensity in color. The advantages of both types can be secured by mixing them.[7] According to McNeil,[8] spirit-soluble acid dyes give brilliant transparent inks and are resistant to a coat of hot wax. On the other hand, basic dyes are used for softer, opaque colors, and dissolve in wax. Hadert states that spirit-soluble dyestuffs dissolve easily in paraffin wax, and that only water-color inks should be coated with it.[9]

The following dyes are often applied in aniline inks: triphenylmethane dyes such as Fuchsine, Malachite Green, Brilliant Green, and Methyl Violet; azo (acid) dyes, *e.g.*, Lake Red, Lithol Red, Permanent Red, Diamond Green, and azo (basic) dyes, *e.g.*, Chrysoidine, Victoria Blue; Safranine (red, of the azine type); Rhodamine (pink, group of xanthone dyes); Auramine (yellow, diphenylmethane dyes), and also Hansa Yellow, of the pyrazolone type. These more generally employed are Rhodamine, Safranine, Auramine, Chrysoidine, Victoria Blue and Brilliant

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[3] *Paint Manuf.*, 1932, 2 (10), 267.

[4] H. Hadert, *Farben-Chem.*, 1935, 6 (1), 11; *Chem. Abs.*, 1935, 29, 3536; *Brit. Chem. Abs.* **B**, 1935, 366; *Rev. Paint, Colour, Varnish*, 1935, 8, 25.

[5] Substitution of dyestuffs by pigments is reported to yield aniline inks more stable to light and less likely to bleed. J. J. Deeney, *Am. Ink Maker*, 1938, 16 (7), 25; *Rev. Paint, Colour, Varnish*, 1938, 11, 364.

[6] A. McNeil, *Am. Ink Maker*, 1936, 14 (8), 17; *Chem. Abs.*, 1936, 30, 6967; *Rev. Paint, Colour, Varnish*, 1937, 10, 24.

[7] R. M. Bates, *Am. Ink Maker*, 1937, 15 (6), 25; *Paper Trade J.*, 1937, 104 (13), 141; *Chem. Abs.*, 1937, 31, 5184; *Rev. Paint, Colour, Varnish*, 1937, 10, 259.

[8] A. McNeil, *Am. Ink Maker*, 1935, 13 (10), 15; *Chem. Abs.*, 1936, 30, 306; *Rev. Paint, Colour, Varnish*, 1935, 8, 516.

[9] H. Hadert, *Farben-Chem.*, 1935, 6, 11; *Chem. Abs.*, 1935, 29, 3536; *Brit. Chem. Abs.* **B**, 1935, 366; *Rev. Paint, Colour, Varnish*, 1935, 8, 25.

Green, these being alcohol-soluble although also dissolved by water.[10] Rotor Green Y is used with ethylcellulose and denatured alcohol.[11]

In some instances complex chromium compounds of the dyes are employed.[12] Such derivatives may be prepared by treatment of the dye, dissolved in an alcoholic solution of shellac, with a salt of hexavalent chromium, such as potassium dichromate. After reaction is complete, aqueous ammonia is added to the mixture to furnish a product applicable for printing on paper.

Aniline inks with small covering power, so-called transparent inks, are still used for printing transparent and white material such as glassine or Cellophane. On smooth surfaces for line engravings and designs and those affording great hiding power, however, these printing compositions are not satisfactory, and an opaque pigment must be added, thus allowing a wider field of application and also overprinting (discussed later in this chapter). The pigment is ground into a mixture of ethyl "Cellosolve" and an alcoholic solution of shellac in a closed system (to prevent evaporation of the vehicle). Afterwards the resulting composition is mixed with a concentrated solution of the dyestuff. The opaque inks, because of the presence of pigments, have a tendency to thicken, so addition of solvent can be made as needed during the printing process. It is advisable to strain the opaque inks after complete solution to remove small amounts of insoluble material usually present in dyestuffs. Examples of pigments used in aniline inks are titanium dioxide, chrome yellow and cadmium red.[13] Opaque whites are colorless pigments containing oxides of titanium, lead, zinc or tin.[14] Titanium dioxide is the pigment generally used, as it has greatest tinting strength and hiding power of all white pigments. Colored pigments are not as effective opaquing agents as the white pigment bases, with the exception of Lake Red C,[15] which is employed when a very intense red is required. White ink containing titanium white can also be used alone, but it is more frequently added to transparent inks of any color, making them opaque. The concentration of the dye may be increased to obtain the shade required; it should be kept as low as possible, however, as saturated or nearly saturated solutions are unstable and may cause trouble in use.[16] The particle size of the applied pigment should be controlled to obtain best opacity and uniformity of color. Too small particles cause loss in opacity. Smaller particles than in usual typographic printing are necessary for half-tones to avoid filling

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[10] G. Haegens, *Papier-Ztg.*, 1935, 60 (32), 606; 60 (33), 624; *Chem. Zentr.*, 1935, 106 (2), 763; *Brit. Chem. Abs.* B, 1936, 831; *Rev. Paint, Colour, Varnish*, 1935. 8, 401.

[11] French P. 776,825, 1935, to Imperial Chemical Industries, Ltd.; *Am. Ink Maker*, 1936, 14 (4), 35; *Chem. Abs.*, 1935, 29, 3863.

[12] Swiss P. 198,348, 198,349, 198,350, 1938, to J. R. Geigy, A.-G.; *Chem. Abs.*, 1939, 33, 3616.

[13] A. McNeil, *Am. Ink Maker*, 1935, 13 (10), 15; *Chem. Abs.*, 1936, 30, 306.

[14] L. M. Larsen and F. A. Weymouth. *Am. Ink Maker*, 1937, 15 (9), 44; *Paint, Oil, Chem. Rev.*, 1937, 99 (17), 20; *Chem. Abs.*, 1937, 31, 7673.

[15] Lake Red C is 2-amino-5-dichloro-*p*-toluenesulphonic acid coupled with β-naphthol. R. N. Shreve, "Dyes Classified by Intermediates," New York, The Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1922.

[16] R. M. Bates, *Am. Ink Maker*, 1937, 15 (6), 25; *Paper Trade J.*, 1937, 104 (13), 141; *Chem. Abs.*, 1937, 31, 5184; *Rev. Paint, Colour, Varnish*, 1937, 10, 259.

up of printing face.[17] Black aniline colors always show some bronze effect, which cannot be avoided entirely, owing to the fact that these blacks are mixtures of colors such as red, blue and yellow. The dispersing power of different *transparent* shades causes the bronze effect, unless the light coming from the colored paper to the eye forms a right angle with the paper.[18]

For printing on waxed surfaces certain types of pigmented inks, so-called "Fastopake" inks, may be used. These inks are insoluble in water after being printed, possess a high degree of opacity and light-fastness, and are odorless and non-inflammable. The losses owing to evaporation are small because of the relatively low volatility of the solvent. Their use is especially recommended on absorbent material.[19]

Solvents for Dyestuffs Used in Aniline Inks. The following types of solvents or combinations thereof are used for the most part in the preparation of aniline inks: alcohols, ethers, ketones, ketone-alcohols, ether-alcohols, esters of carboxylic or hydroxy-acids, such as salicylic or lactic acid, and acid amides. Methyl and ethyl alcohol are appropriate solvents for aniline inks. A solvent of simple composition and relatively low molecular weight is preferred in most instances since the solvent power of the liquid often decreases with increasing molecular weight.[20] Of the alcohol-ether solvents the (mono) methyl, ethyl and butyl ethers of ethylene glycol and diethylene glycol are of considerable importance in the manufacture of aniline inks. The ethers of ethylene glycol are specially known as methyl, ethyl and butyl "Cellosolve," respectively, while the special trade names of the respective diethylene glycol ethers are methyl, ethyl and butyl "Carbitol." These solvents are widely used in pigmented aniline inks.[21] Simple solvents, such as methyl or ethyl alcohol as well as denatured alcohol, are relatively highly volatile, so that an addition of a somewhat higher-boiling solvent is necessary for making solutions of uniform strength. Incorporation of the latter liquid is often effected during the printing process. Such agents which decrease evaporation rate are ethylene glycol monoethyl ether (ethyl "Cellosolve"), ethylene glycol monomethyl ether (methyl "Cellosolve"), or their acetates, methylcyclohexanone and methylcyclohexanol acetate. Xylol, toluol and furfural (inexpensive solvents) are reported to be unsatisfactory for the purpose.[22]

Acetic acid is used to decrease evaporation of alcohol, with an addition of glycerol to make the ink waterproof.[23] To prevent very rapid drying

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[17] L. M. Larsen and F. A. Weymouth, *Am. Ink Maker*, 1937, 15 (9), 44; *Paint, Oil, Chem. Rev.*, 1937, 99 (17), 20; *Chem. Abs.*, 1937, 31, 7673.

[18] G. Haegens, *Papier-Ztg.*, 1935, 60 (32), 606; 60 (33), 624; *Chem. Zentr.*, 1935, 106 (2), 763; *Rev. Paint, Colour, Varnish*, 1935, 8, 401. See also M. Luckiesh, "Color and Its Applications," D. Van Nostrand Co., New York, 1921.

[19] E. S. Hanes, *Brit. Printer*, 1935, 48 (285), 109; *Rev. Paint, Colour, Varnish*, 1935, 8, 516.

[20] R. M. Bates, *Am. Ink Maker*, 1937, 15 (6), 25; *Paper Trade J.*, 1937, 104 (13), 141; *Chem. Abs.*, 1937, 31, 5184; *Rev. Paint, Colour, Varnish*, 1937, 10, 259.

[21] M. Phillips, *Am. Ink Maker*, 1937, 15 (6), 20.

[22] A. McNeil, *Am. Ink Maker*, 1935, 13 (10), 15; *Rev. Paint, Colour, Varnish*, 1935, 8, 516; *Chem. Abs.*, 1936, 30, 306.

[23] T. A. F. Sexton, *Brit. Printer*, 1934, 47 (277), 9; *Rev. Paint, Colour, Varnish*, 1934, 7, 293.

and to retain moisture in the dye, glycerol may be added to the ink. A better result is obtained with glycol, which is reported to be more hygroscopic than glycerol, so that much smaller quantities are needed,[24] thereby avoiding unnecessary dilution of the dye solution. Aqueous-alcoholic solutions of a resin and alkali are employed as vehicles for inks containing water- and alcohol-insoluble, light-fast pigments or laked dyes. Often it is of advantage to use water-free solutions of alkali and resin, as inks thus prepared are reported to dry more quickly and to have a better flow and consequently eliminate smudging on the press. As an alkali, borax usually may be used. However, corresponding quantities of ammonia, ammonium carbonate or other inorganic or organic bases are applicable.[25] Aniline ink is available also in concentrated form when thinning is done by the printer, according to his own requirements. Solvents such as "Carbitol" and diacetone alcohol for the concentrated solutions must have a high solvent power for the dye. The price of these inks is about three times as much as of those ready for printing without further thinning.[26]

As already mentioned, tannin and resins have an important role in aniline inks in determining the consistency and improving waterproofness and light-fastness. Resins or tannin prevent "striking through" of the ink by filling up the pores of the paper. Tannin, being more expensive, is found only to a small extent or not at all in cheaper inks. Although tannin or resins may cause stickiness of the ink, this can be avoided by applying heated air to the printed sheets or by slower running of the press.[27] To prevent sticking, a plasticizer such as "Irgasol"[28] may be added to the solution of the dye. The plasticizer also avoids clogging of the ink in small type, and as a result a more intense impression is claimed to be possible because a greater quantity of color can be used per gallon of ink. A general formula for use on sulphite paper and similar material consists of 3 to 4 lbs. of dry aniline color, 1 to 1½ pints of "Irgasol" and 6 pints of methylated spirits.[29]

Resins improve the mechanical properties, such as toughness, elasticity, and resistance against abrasion of the dried ink film. A small percentage of nitrocellulose or cellulose ester lacquer is added to aniline inks for printing on Cellophane and other non-absorbent surfaces.[30] Shellac has a high degree of combined hardness and fair elasticity and therefore is of service as a binder in aniline inks.[31] Its disadvantages are the tendency to clog small type and line cuts, and to dry and become sticky on the roll.

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[24] German P. 309,911, 1917, to Th. Goldschmidt A.-G.; *Chem. Abs.*, 1919, 13, 1772; *J. S. C. I.*, 1919, 38, 379A.

[25] British P. 405,483, 1934, to Lövinsohn & Co.; *Chem. Abs.*, 1934, 28, 4614; *Brit. Chem. Abs.* B, 1934, 334. The exception of alkyl hydroxyamino compounds is mentioned as to alkalies to be used instead of borax.

[26] R. M. Bates, *Am. Ink Maker*, 1937, 15 (6), 25; *Paper Trade J.*, 1937, 104 (13), 141; *Rev. Paint, Colour, Varnish*, 1937, 10, 259; *Chem. Abs.*, 1937, 31, 5184.

[27] H. Hadert, *Farben-Chem.*, 1935, 6 (1), 11; *Chem. Abs.*, 1935, 29, 3536; *Rev. Paint, Colour, Varnish*, 1935, 8, 25; *Chem. Abs.*, 1935, 29, 3536.

[28] Produced by the Geigy Colour Co., Ltd.

[29] T. A. F. Sexton, *Brit. Printer*, 1934, 47 (277), 9; *Rev. Paint, Colour, Varnish*, 1934, 7, 293.

[30] A. McNeil, *Am. Ink Maker*, 1935, 13 (10), 15; *Rev. Paint, Colour, Varnish*, 1935, 8, 516; *Chem. Abs.*, 1936, 30, 306.

[31] R. M. Bates, *Am. Ink Maker*, 1937, 15 (6), 25; *Paper Trade J.*, 1937, 104 (13), 141; *Rev. Paint, Colour, Varnish*, 1937, 10, 259; *Chem. Abs.*, 1937, 31, 5184.

Various kinds of natural and synthetic resins have been suggested as substitutes for shellac. Novolak, a synthetic phenol-formaldehyde product,[32] was used without much success. Better results were obtained with sandarac resin, which is soluble in methanol, amyl alcohol and other organic solvents and shows great resistance to abrasion, the dried film of sandarac being harder than that of shellac. A mixture of shellac and sandarac can be used, increasing elasticity and toughness of the dried ink film after evaporation of the solvent.[33] Other substitutes, such as gum copal, Vinylite, Glyptal, ester gum, manila gum and manila pontianak, improve gloss and resistance to bleeding on smooth, hard, highly finished surfaces, but are not as suitable for rough, absorbent material.[34] Although some ink manufacturers do not include binders in their formula, the general composition of a simple transparent ink consists of 8 oz. of a dye, 800 cc. of alcohol and 4 lbs. of orange shellac. Variations of these amounts are, of course, permissible to conform to special requirements.[35] Improvements in the production of shellac now makes it possible to meet special requirements. Thus, the wax in these shellacs is finely and uniformly divided in order to keep it in suspension and prevent it from settling out in solution. Pigmented aniline inks require a pigment- and wax-free shellac, which is prepared by special processes which do not involve bleaching. The latter reduces the toughness and elasticity of the shellac.[36]

Some high-acid, unmodified alkyd resins are alcohol-soluble to a certain degree and can be used in this way to a limited extent.[37] However, certain alkyd resins dissolve in di-ether-alcohols and are used in inks to be coated later with hot wax.[38] A form of alcohol-soluble nitrocellulose dries to a film which is harder, more resistant against abrasion, and more adhesive to Cellophane and other cellulosic surfaces than shellac. It has no effect on the tint of aniline inks, being colorless itself.[39] Tannin or tannic acid is added to aniline inks to improve their resistance to bleeding, as the dyestuff forms an insoluble tannin lake after evaporation of the solvent. Traces of humidity must be present in the dried film, as formation of the lake occurs only in the presence of water. The moisture always present in air, and also in alcohol, is generally sufficient for this purpose.[40] Incorporation of some acetic acid in solutions containing tannin is necessary to prevent precipitation of the tannin lake.[41] The

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[32] See Carleton Ellis, "The Chemistry of Synthetic Resins," New York, Reinhold Publishing Corp., 1935.

[33] A. McNeil, *Am. Ink Maker*, 1935, **13** (10), 15; *Rev. Paint, Colour, Varnish*, 1935, **8**, 516; *Chem. Abs.*, 1936, **30**, 306.

[34] R. M. Bates, *Am. Ink Maker*, 1937, **15** (6), 25; *Paper Trade J.*, 1937, **104** (13), 141; *Rev. Paint, Colour, Varnish*, 1937, **10**, 259; *Chem. Abs.*, 1937, **31**, 5184.

[35] R. M. Bates, *Am. Ink Maker*, 1937, **15** (6), 25; *Paper Trade J.*, 1937, **104** (13), 141; *Rev. Paint, Colour, Varnish*, 1937, **10**, 259; *Chem. Abs.*, 1937, **31**, 5184.

[36] *Am. Ink Maker*, 1938, **16** (4), 41.

[37] T. McE. Sanderson, *Am. Ink Maker*, 1938, **16** (4), 23.

[38] M. Phillips, *Am. Ink Maker*, 1937, **15** (6), 18.

[39] A. McNeil, *Am. Ink Maker*, 1936, **14** (18), 18; *Rev. Paint, Colour, Varnish*, 1937, **10**, 24; *Chem. Abs.*, 1936, **30**, 6967.

[40] G. Haegens, *Papier-Ztg.*, 1935, **60**, 606, 624; *Chem. Zentr.*, 1935, **106** (2), 763; *Rev. Paint, Colour, Varnish*, 1935, **8**, 25; *Brit. Chem. Abs.* B, 1936, 831. *Cf.* T. A. F. Sexton, *Brit. Printer*, 1935, **47** (280), 177; *Rev. Paint, Colour, Varnish*, 1935, **8**, 25.

[41] Kümmol, *Farben-Ztg.*, 1937, **42** (2), 40; *Rev. Paint, Colour, Varnish*, 1937, **10**, 24.

acetic acid evaporates simultaneously with the solvent from the ink film. Gum tragacanth as well as wheat or other starch-containing thickener may be used in inks containing aqueous solutions of dyes and intended for multicolor printing. The addition of thickeners, however, must not prevent the production of composite colors.[42] The manufacture of aniline inks is carried out in a closed, glass-lined and water-jacketed kettle with the aid of a mechanical stirrer. First the solvents are brought into the vessel, then the dye is added slowly, each portion being dissolved completely before the next one is added. After all the dye has been dissolved, shellac or resins are added (if included in the formula) and dissolved. Finally, the ink is strained through fine cheesecloth or voile. However, the last operation in some instances can be omitted. According to McNeil the solvent should be heated to about 150° F. while dissolving the dyestuff.[43] Kümmel [44] does not recommend warming while the dyestuff is stirred into the solvent, for it may cause the formation of lumps. After solvent and dyestuff have been mixed to a paste and then suitably thinned, the mixture may be heated to complete solution. If heat is applied, the solution should be cooled before further addition of tannin or resins.[45] The inks, pigmented (opaque) or transparent, may be mixed by stirring them together for one minute,[46] thus making a large number of shades available.[47]

Aniline inks are widely used in printing different kinds of wrappers, bags, containers and envelopes made from paper, Cellophane, glassine or Diaphane. It is often necessary to pass freshly printed waterproof cellulosic surfaces over an electrically heated hot plate or hot-air oven to secure adhesion of the ink to the material and to prevent rubbing off. Another procedure consists of printing the reverse side of a transparent cellulosic material, such as Cellophane or glassine for bags or envelopes, giving them the appearance of a glossy overprint varnish. The printing thus is rendered scratch-proof and does not bleed when the cellulosic material is handled with wet fingers.[48]

The requirements for food-wrapper and food-container inks are very strict regarding toxicity, odor and attractiveness. It may be assumed that all organic lakes and toners containing lead salts as well as pigments having lead, cadmium, mercury, copper or arsenic as a constituent, are poisonous and therefore cannot be used in food-wrapper inks. Phosphotungstic and phosphomolybdic lakes of dyes are suitable pigments for printing on articles such as toys or food wrappers, being insoluble and therefore not toxic.

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[42] R. G. Cave, British P. 367,480, 1932; *Chem. Abs.*, 1933, 27, 3627.

[43] A. McNeil, *Am. Ink Maker*, 1936, 14 (8), 18; *Rev. Paint, Colour, Varnish*, 1937, 10, 24; *Chem. Abs.*, 1936, 30, 6967.

[44] Kümmel, *loc. cit.*

[45] R. M. Bates, *Am. Ink Maker*, 1937, 15 (6), 25; *Paper Trade J.*, 1937, 104 (13), 141; *Rev. Paint, Colour, Varnish*, 1937, 10, 259; *Chem. Abs.*, 1937, 31, 5184.

[46] *Papier-Ztg.*, 1937, 62 (75), 1282; *Rev. Paint, Colour, Varnish*, 1937, 10, 412. *Cf.* R. F. Salade, *Paper and Print*, 1938, 11 (41), Suppl. 20.

[47] See Chapter 6.

[48] A. McNeil, *Am. Ink Maker*, 1935, 13 (10), 15; *Rev. Paint, Colour, Varnish*, 1935, 8, 516; *Chem. Abs.*, 1936, 30, 306.

As a large number of bread and other food wrappings receive a protective paraffin coating to prevent drying out and penetration of odors and moisture, aniline inks are especially applicable, as it is possible to print and give a coat of wax to the rapidly drying impressions in one operation, by coupling the printing press and the appliance for waxing. On passing the fresh print through a bath of melted paraffin, the dyes are fixed to the paper and coated with wax, thus preventing bleeding while the wrapper is being used. The solvents are evaporated quickly by the heat of the melted wax.[49] A typical formula of transparent aniline ink for printing on Cellophane consists of 44 per cent methylated spirits, 10 per cent dye, 44 per cent clear white shellac and 2 per cent glacial acetic acid.[50] Aniline colors are used in printing decorations or advertisements on blotting paper.[51] For printing on wet lumber a water-soluble aniline color is dissolved in glycerol and vinegar and mixed with a paste of water and starch.[52] On paper bags for cement and lime, alkali-fast aniline inks are used.[53] A stenciling ink consists of 1 per cent of a basic aniline dye, 5 to 10 per cent of acetic acid, 0.5 per cent of tartaric acid, 5 per cent of tannin, and sufficient aqueous emulsion of gum tragacanth to give the mixture a syrupy consistency.[54]

The use of aniline printing inks is reported[55] to diminish difficulties connected with drying of the printed films, such as "offsetting"[56] and "slipsheeting" of printed sheets. These problems often are acute when printing with oil inks. The dried film of aniline ink is odorless. The wrappers (paper or Cellophane) are printed mostly by the rotary principle. The rapid drying of the inks permits printing and folding in one operation. Printing machines using aniline inks are high-speed roll or web-fed rotary presses specially designed for highly fluid and volatile spirit inks, printing usually from rubber stereotype plates. These heavy, compact machines print from one to three colors in succession without apparent sticking or offsetting, although smearing is occasionally observed. As aniline inks do not require a complex inking system, the presses are of comparatively simple construction; therefore cleaning and changing of plates can be done quickly and easily. The constant addition of solvent (during printing) to replace the evaporated quantities and the use of expensive dyestuffs make the cost of aniline printing relatively high. Covered ink ducts and distributing rolls may overcome these disadvantages.[57]

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[49] R. Rolev, *Am. Ink Maker*, 1938, 16 (6), 18.

[50] R. F. Salade, *Brit. Printer*, 1936, 49 (291), 125; *Rev. Paint, Colour, Varnish*, 1936, 9, 400.

[51] British P. 418,338, 1934, to Société anon Imprimeries E. Chambrelent, "E. T. I. O. P."; *Chem. Abs.*, 1935, 29, 2375.

[52] L. A. Mizener, U. S. P. 1,930,178, Oct. 10, 1933, to Chicago Mill and Lumber Corp.; *Chem. Abs.*, 1934, 28, 351.

[53] *Deutscher Drucker*, 1937, 44 (518), 61; *Rev. Paint, Colour, Varnish*, 1938, 10, 23.

[54] C. A. Pellew, U. S. P. 911,327, Feb. 2, 1909; *Chem. Abs.*, 1909, 3, 1097.

[55] L. M. Larsen and F. A. Weymouth, *Am. Ink Maker*, 1937, 15 (9), 44; *Paint, Oil, Chem. Rev.*, 1937, 99 (17), 20; *Chem. Abs.*, 1937, 31, 7673.

[56] **Offsetting**: smearing of freshly printed ink when the sheets are placed on top of each other. **Slipsheet**: a sheet of paper placed between freshly printed sheets to prevent offsetting.

[57] A. McNeil, *Am. Ink Maker*, 1935, 13 (10), 15; *Chem. Abs.*, 1936, 30, 306; *Rev. Paint, Colour, Varnish*, 1935, 8, 516.

Aniline inks are now used with success on nickel-faced copper-electro plates, nickel-type and nickel-plated stereotype plates, rubber stereotype and engraved (hand cut) rubber plates, on line engravings and zinc etchings. Coarse screen, deep-etched half-tones have been printed with some success. Rubber stereotype printing is reported to be useful in printing with aniline inks from type faces as small as five point. The plates are made by pressing together a cast metal mold and a thick sheet of plastic rubber by a hydraulic press, then vulcanizing the rubber plate.[58] Surveys show that 95-97 per cent of the products of the bag and envelope industries are now being printed from molded rubber plates.[59] Aniline inks printed from rubber types also are employed in veining of paper and for folding cartons. Rubber cliches (*i.e.*, stereotype plates) are reported to have been produced with extremely fine screens.[60] According to Haegens[61] their low viscosity not being advantageous for clear-cut prints, aniline inks should be printed from rubber plates only.[62] Although such inks are easily bleachable, they are not sufficiently economical for news printing.[63]

METALLIC PIGMENT INKS

Metallic inks, which include inks containing metals as pigments in the form of a powder or a paste, were not used extensively before 1927, mostly because of lack of sufficient knowledge of the properties of metallic pigments. In 1928 aluminum was manufactured in the form of a powder of great fineness and good working qualities. Since then the use of aluminum in inks has increased greatly, particularly for booklet decorating and in advertisements in magazines and trade journals printed in metallic colors.[64] The reason for the extended application of metallic, especially aluminum, inks lies in their attractiveness and suitability for modernistic designs.[65] Although these pigments have been known for a long time,[66] their use was limited mainly to printing book coverings and similar purposes. This limitation was due, at least in part, to the fact that application of such inks required three steps, *i.e.*, printing with an adhesive liquid composition, applying metal powder or foil, and removing the excess foil or powder. One development involved preparation of inks which contained metallic pigments and could be applied in a one-stage operation. An example of such a composition consists of metallic powder mixed with

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[58] A. McNeil, *loc. cit.*

[59] *Am. Ink Maker*, 1938, 16 (6), 21.

[60] H. Hadert, *Farben-Ztg.*, 1935, 6 (1), 11; *Chem. Abs.*, 1935, 29, 3536; *Rev. Paint, Colour, Varnish*, 1935, 8, 25.

[61] G. Haegens, *Papier-Ztg.*, 1935, 60, 606, 624; *Chem. Zentr.*, 1935, 106 (2), 763; *Rev. Paint, Colour, Varnish*, 1935, 8, 401; *Brit. Chem. Abs.* B, 1935, 831. *Cf.* Hartmann, *Klimchs. Druck. Anzgr.*, 1936 (52), June 30; *Rev. Paint, Colour, Varnish*, 1937, 10, 260.

[62] For a discussion of the properties required of inks for printing from rubber plates, see J. D. Cohen. *Paper and Print*, 1937, Spring, 22; *Rev. Paint, Colour, Varnish*, 1937, 10, 260.

[63] See Chapter 8.

[64] F. C. Arthur, *Am. Ink Maker*, 1936, 14 (6), 23; *Rev. Paint, Colour, Varnish*, 1936, 9, 241; *Chem. Abs.*, 1936, 30, 5818.

[65] J. H. Meyer, *Am. Ink Maker*, 1931, 9 (7), 21; *Rev. Paint, Colour, Varnish*, 1931, 4, 208: *Chem. Abs.*, 1931. 25, 5582. For descriptive history and developments of metallic inks, see *Brit. Printer*, 1938, 50 (298), 185; *Rev. Paint, Colour, Varnish*, 1938, 11 (61), 23; *Paper Making and the Printer*, 1937, Autumn, 15.

[66] For example, D. McKeller (U. S. P. 87,350, Mar. 2, 1869) suggested bronze powder as a pigment in compositions from printing designs on the toes and heels of boots.

$\frac{1}{3}$ of its weight of a grease, *e.g.*, lard, free from water. The mixture then was thickened to a stiff paste or ink (for use on rollers) with gold size and varnish.[67] Another ink containing metallic powder and applied in one operation, known as "direct-or," was made up by mixing gold or bronze powder with coconut oil, palm oil, laurel oil, copal varnish and dammar.[68]

A somewhat different use of metal powder is a method of Renault [69] for the copying of drawings. The drawing, made in a slightly sticky ink upon which a metallic powder is superimposed, is laid on a sheet of sensitized paper. By the action of the metal powder the lines of the design are developed on the sensitive layer. The copying process may be repeated several times by moistening the dried ink of the original with alcoholic vapors and renewing the metal powder.

The successful application of metallic pigments depends upon the kind of paper used and character of the design. Since almost any paper requires an ink of individual composition, it is advisable to make experimental prints to find out the treatment that produces the most satisfactory results.[70] The smoother the surface of the paper, the better the prints obtained with respect to brilliancy, uniformity and drying properties. Finely coated paper stocks will usually give excellent effects with the metallic ink, but dull-coated, cover, offset or antique papers [71] require sizing or coating with a base before applying the metal.[72]

Difficulties and subsequent investigations in printing of chocolate wrappers revealed that many types of papers are not suitable for metallic pigments. All papers to be printed with metallic colors should be tested for sizing. A properly sized paper will not pick when pressed with a wet finger, and ink lines (which may be drawn in gold size) will not penetrate the paper, but dry slowly. The surface of fancy papers and cardboards is sometimes too loose for receiving a metallic impression, and therefore seals or labels, containing the printed portion, are pasted on the paper. Gummed seals are usually unsuitable, since the amount of glue on these seals is insufficient for a very absorbent surface. Duplex folding box boards are often too low-sized; therefore it is better to print on special box tops suitable for metallic printing and fasten them on the boxes.[73] Papers containing wood or cellulose must be free from sulphur (present as sulphite) to prevent reaction with the metal when the prints are heated. Calendered paper usually requires a first print of size, varnish or lacquer (with an addition of some white pigment in the case of colored papers)

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[67] G. Priestley and E. Swann, British P. 955, 1895; *J. S. C. I.*, 1895, **14**, 373.

[68] E. Maître, British P. 30,121. 1896; *J. S. C. I.*, 1898, **17**, 55.

[69] B. Renault, *Compt. rend.*, 1872. **14**, 1412; *Chem. Zentr.*, 1872, **3**, 473.

[70] For discussions of the use of metallic inks, see J. Maff, *Am. Ink Maker*, 1931. **9** (11), 25; *Rev. Paint, Colour, Varnish*, 1931, **4**, 288; *Am. Ink Maker*, 1931, **9** (12), 13; *Rev. Paint, Colour, Varnish*, 1932, **5**, 25. H. Bloy, *Paper and Print*, 1938, **11** (44), 234; *Rev. Paint, Colour, Varnish*, 1939, **12**, 19. *Printing Equipment Engineer*, 1939, 17; *Rev. Paint, Colour, Varnish*, 1939, **12**, 180.

[71] Offset paper is a variety of printing paper especially sized for offset lithography, is non-curling and absorptive. Antique papers are obtained from a soft bulky pulp or soft rags; their finish does not involve machine calendering (*Paper*, 1924, **33** (26), 66).

[72] J. H. Meyer, *Am. Ink Maker*, 1931, **9** (7), 21; *Rev. Paint, Colour, Varnish*, 1931, **4**, 208; *Chem. Abs.*, 1931, **25**, 5582.

[73] R. Holder, *Mod. Lith. and Offset Printer*, 1933, **29** (1), 3; *Rev. Paint, Colour, Varnish*, 1933, **6**, 36.

to receive the metallic powder. Wax-coated papers of loose structure take metallic prints, but do not hold a printed metallic effect very satisfactorily.[74] Cellophane may be printed first with an adhesive such as a sizing, then the bronze (or other) powder is applied, the excess removed, and a thin, transparent coat of a waterproof lacquer applied to the print and also to the opposite side of the Cellophane. Finally the elements of the design are printed complementarily on the opposite side on top of the waterproofing composition.[75] For printing Cellophane the inks employed should be of the quick-drying type or of a composition which allows rapid resinification of the surface of the ink film.[76]

Sizing and Pre-printing of the Paper with Varnish. In early methods of applying metal powders the design is first printed in ink or size and the metal dusted upon it with a soft material such as cotton or sheepskin. The first print (a gold size) is made either with colored or with white ink, the latter avoiding the possibility of showing through the metallic film. The size is applied to glossy papers by running them through the press in the usual way. The size for colored surfaces should contain a small amount of white pigment to provide opacity. Antique papers should receive a double coat of size; the first contains white pigment and is dried thoroughly before printing the second coat, to which, when dried to sufficient tackiness, the metallic powder is applied.[77]

The pre-print for gold-bronze contains a yellow lacquer, for silver-bronze a mixture of zinc white and a blue lacquer. The use of chrome yellow is not recommended, as it contains lead which would tend to tint the finished prints black.[78] To insure an adhesive and tacky film, upon which metallic powder can be successfully applied, copal varnish and drier may be added to the lacquers.[79] The drier must be free from fats as otherwise it would penetrate the paper, causing fatty spots. Picking of the gold size can be averted by adding a few drops of unboiled linseed oil and a very small proportion of varnish consisting of boiled linseed oil admixed with wax.[80] An adhesive for bronze powder is made by incomplete fermentation of dextrin and glucose with yeast at approximately 24° C. and incorporation of hydrogen or sodium peroxide and a small amount of an aqueous castor oil emulsion. A conserving agent such as sodium benzoate may also be added.[81]

A metallic coating with a mirror-like surface may be prepared by depositing on a paper base 0.4 to 2 oz. per square yard of a composition

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[74] **H. Hadert**, "Handbuch über die Herstellung und Verwendung der Druckfarben," O. Elsner Verlagsges, Berlin, 1931; *Farben-Chem.*, 1935, 6, 87; *Chem. Abs.*, 1935, **29**, 5680; *Rev. Paint, Colour, Varnish*, **1935, 8, 109.**

[75] **F. X. Malocsay**, U. S. P. 1,969,569, Aug. 7, 1934, to Consolidated International Corp.; *Chem. Abs.*, **1934, 28, 6309.**

[76] **H. Hadert**, *loc. cit.*

[77] **D. H. Caldwell**, *Times Trade and Eng.*, 1937, 40 (877), special supplement "Aluminum and Its Applications," XLIV; *Rev. Paint, Colour, Varnish*, 1937, 10, 174. See also Krug, R., *Papier-Ztg.*, 1936, 61 (93), **1763**; *Farben-Chem.*, 1936, 7 (12), 459; *Rev. Paint, Colour, Varnish*, 1937, **10, 24.**

[78] **H. Hadert**, *loc. cit.*

[79] **H. Hadert**, *loc. cit.*

[80] **R. Holder**, *Mod. Lith. and Offset Printer*, 1933, 29 (1), 3; *Rev. Paint, Colour, Varnish*, **1933, 6, 86.**

[81] **R. Wolffram**, German P. 515,522, 1929; *Chem. Abs.*, 1931, **25**, 2531.

containing 43.8 per cent of a polyhydric alcohol-polybasic resin modified by tung oil and linseed oil, 53.5 per cent of a mixture of mineral thinner and high-flash naphtha, and the remainder a drier solution.[82] The paper is then passed through a 72-foot drying oven at about 200° F. at the rate of 5 yards per minute. A metal coating made up of a powder, the individual particles of which have light-reflecting faces, is put on the paper and the non-adhering particles dusted off. The remaining particles are oriented to bring the light-reflecting surfaces parallel to the surface of the coating. The article is then heated to harden the coating.

Metal Powders and Pastes. Aluminum powder is made of the commercial metal by a stamping procedure. The particles are polished or unpolished flakes, not granules. Instead of dusting the powder on a tacky surface, it is now usually incorporated in a printing ink as a pigment and applied by regular printing operations. The phenomenon known as "leafing" gives the metallic film its smoothness and brilliancy. Leafing is produced by the flakes which, when admixed with varnish, rise to the surface and form a continuous film resembling the arrangement of fallen leaves.[83] By later processes the number of flakes per unit of weight has been nearly doubled. The film of the fine flakes has a high hiding power. High gloss of the metal produces a striking contrast to surrounding areas, especially with red, blue or green color and also with black. Aluminum-printed solid areas show the highest effects. The brightest impressions are made with inks which have stood for one or two days after mixing.

Finer grades of aluminum bronze pigments are known as Extra Fine Lining, in paste or powder form.[84] Of the powder, 99 per cent should pass through a screen of 325 meshes per square inch and 95 per cent through one of 400 meshes.[85] Coarser grades of aluminum bronze powder are reported to be lacking in covering power, when used in printing antique-finished or colored paper.[86]

In paste form, aluminum bronze pigments are reported to eliminate some troubles experienced with inks made with powdered metal. Such difficulties are, for example, their lack of standing ability and their thickening or solidifying on printing rollers or plates. Other advantageous properties of paste pigments are good spreading, high gloss and covering power. Inks made with paste pigment give satisfactory results when printed on colored or antique papers, owing to the high opacity of this pigment. Also, fewer wash-ups of the press are necessary.[87]

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[82] D. McBurney and E. H. Nollau, Canadian P. 361,667, 1936, to Canadian Industries, Ltd.; *Rev. Paint, Colour, Varnish*, 1937, 10, 228; *Chem. Abs.*, 1937, 31, 1529.

[83] J. H. Meyer, *Am. Ink Maker*, 1931, 9 (7), 21; *Chem. Abs.*, 1931, 25, 5582; *Rev. Paint, Colour, Varnish*, 1931, 4, 208. For manufacture, properties and uses (descriptive) of aluminum paste pigment, see J. K. Parkinson, *Oil Colour Trades J.*, 1938, 93, No. 2059, 962.

[84] F. C. Arthur, *Am. Ink Maker*, 1936, 14 (6), 23; *Chem. Abs.*, 1936, 30, 5818; *Rev. Paint, Colour, Varnish*, 1936, 9, 241.

[85] J. H. Meyer, *loc. cit.*

[86] D. H. Caldwell, *Times Trade and Eng.*, 1937, 40 (877), special supplement: "Aluminum and Its Applications," p. XLIV; *Rev. Paint, Colour, Varnish*, 1937, 10, 774. See F. C. Arthur and J. B. Barnitt, U. S. P. 2,125,870, Aug. 9, 1938, to Aluminum Co. of America; *Chem. Abs.*, 1938, 32, 7399.

[87] D. H. Caldwell, *loc. cit.*

Silver or aluminum bronze consists of finely ground sheet aluminum; so-called gold bronzes are often made from copper or brass. Colored bronzes are made either by heating these metals or by coloring of the powders. Aluminum powder is said to give better results because it is softer than copper or brass. Though cheap bronzes often have a good appearance, they must be used in a greater quantity than other more costly materials. Waste metal powder can be reworked on a machine specially constructed for this purpose.[88]

According to Hadert [89] bronze powder ground into a varnish and the mixture incorporated with a thinner is applicable for printing large letters on matte papers as well as for printing on packages, cigarette boxes and chocolate wrappers. The effect of dusted bronze powder, however, is not nearly attained.

The shining of spots of a white surface (provided the spots are not too large) through aluminum flakes does not appreciably affect the gloss of the ink because white paper generally has a high power of reflection. Colored papers must be completely covered by the metal flakes, otherwise the metallic print would appear as if discolored.[90]

An ink used for label printing consists of gold bronze powder and chrome yellow in a vehicle of cresylic acid, sulphuric acid, borax, flour, varnish and water.[91]

The metallic pigment should be applied to the gold size as soon as the latter is printed. The powder used should not be too soft.[92]

Vehicles for Metallic Inks. Proper formulation of the varnish is essential to obtain good "leafing" of the ink, and its most important characteristics are consistency and drying ratio. As varnish bases, linseed oil, tung oil and (more recently) perilla oil are used. Kettle-bodied linseed oil finds wide application, but tung oil and perilla oil are now preferred because they yield a smoother film than linseed oil. Binders such as gums, natural or synthetic resins or rosin oil, and metallic driers such as lead, manganese or cobalt salts are incorporated into the drying oil to form a varnish. When the aluminum paste is mixed with a thinner, care should be taken that the thinner is compatible with the varnish, otherwise difficulties during the printing operation may arise. Kerosene, gasoline or amyl acetate, often employed as thinners, should be used only when their effect on other agents in the ink is known.[93]

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[88] Machinery for the production of bronze and other metallic powder (E. Krammer, U. S. P. 2.112,497, March 29, 1938, to Hartstoff Metall A.-G. "Hametag") is described in *Am. Ink Maker*, 1938, **16** (5), 37. An apparatus to rework waste metal powder is described by Hadert, *loc. cit.* For a discussion of pigment combinations to obtain gold, silver, and copper effects, see Lange, *Kartonnagen-u.-Papierwaren-Ztg.*, 1936, **40** (43), 461; *Farben-Chem.*, 1936, **7** (11), 420; *Rev. Paint, Colour, Varnish*, 1936, **9**, 377.

[89] H. Hadert, "Handbuch über die Herstellung und Verwendung der Druckfarben," O. Elsner Verlag, Berlin, 1931; *Farben-Chem.*, 1935, **6**, 87; *Chem. Abs.*, 1935, **29**, 5680; *Rev. Paint, Colour, Varnish*, 1935. **8**, 109. Also see Keller, *Papier-Ztg.*, 1937, **62** (94), 1632; *Rev. Paint, Colour, Varnish*, 1938, **11**, 109.

[90] H. Hadert, *loc. cit.*

[91] M. Baer, British P. 346,313, 1929; *Chem. Abs.*, 1933, **27**, 1529. U. S. P. 1,918.829, July 18, 1933; *Chem. Abs.*, 1933, **27**, 4942.

[92] R. Holder, *Mod. Lith. and Offset Printer*, 1933, **29** (1), 3; *Rev. Paint, Colour, Varnish*, 1933, **6**, 36.

[93] F. C. Arthur, *Am. Ink Maker*, 1936, **14** (6), 23; *Chem. Abs.*, 1936, **30**, 5818; *Rev. Paint, Colour, Varnish*, 1936, **9**, 241.

A thickened linseed oil varnish is applicable without adding a drier. Quickly-evaporating thinners may be incorporated. A copal-linseed oil varnish is obtained by boiling 12 parts copal resin with 25 to 30 parts of linseed oil varnish and thinning this mixture with 6 to 8 parts of oil of turpentine. Hadert [94] states that although fair smoothness of the ink may be insured by using tung oil in the varnish, the exclusive use of this oil as a varnish base is often unnecessary. When using metal powder, the particular proportion of powder and varnish is left to the choice of the printer. The ink should always run as thin as possible for uniform covering. If the ink collects on plates and rollers after running a short time, it means that too much powder is present, and varnish should be added. Only a minimum amount of ink should be made up at a time and kept stirred up in the inkwell.[95]

The use of China Wood, or tung, oil in metallic inks improves many of their qualities, such as gloss and covering power, for example. When it was found that linseed oil was not satisfactory in earlier stages of metallic ink production, asphalts dissolved in drying oils and thinned with turpentine were used to fill up the pores of the paper and so develop brilliancy of the overlying layer of bronze powder. Occasionally wax was incorporated together with Canada balsam or Venice turpentine, but neither of these varnishes had the desired covering power. A bronze ink having a tung oil vehicle is reported to have been first produced in 1928.

Wax is added to an ink to increase its covering power, though by so doing the brilliancy of the dried ink films decreases in proportion to the amount of wax. Tung oil has proved a good substitute for wax as to covering power, gloss and adhesion, and it can be boiled to almost any consistency and even gelatinized or hardened. In the latter forms it is used in varnishes as a wax substitute. It is reported that gelatinized tung oil can be dispersed in varnishes, similarly to wax. A varnish of this type includes 6 parts of tung oil which, after being heated to 270° C., is chilled with 4 parts of linseed oil. This mixture is incorporated with finely divided gelatinized tung oil and subsequently thinned with 4 parts of oil of turpentine. The gloss of an ink prepared with such a vehicle is stated to be very high.[96]

Extensive use has been made of waste rubber, especially from old automobile tires, as a fixing agent or binder for metallic inks. Enough fresh rubber is added to the waste to impart stability to the product, which is dissolved in a mixture of camphor oil and naphtha at a temperature high enough to produce a liquid state. The bodying agent thus prepared is dissolved in copal varnish, prepared metal powder is added and the whole is thoroughly mixed. This ink is used for printing cloth to be used for wall covering. Any tendency toward gumminess on the

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[94] H. Hadert, *loc. cit.*

[95] E. T. Rhodes, *Brit. Printer*, 1936, **49** (201), 109; *Rev. Paint, Colour, Varnish*, 1936, **9**, 877.

[96] C. Eckmann, *Farben-Chem.*, 1935, **6**, 295; *Chem. Abs.*, 1936, **30**, 2409.

printed fabric is obviated by running the cloth over hot metal cylinders to set the varnish.[97]

Application of ink to book coverings by means of a heated die often avoids the use of acidic vehicles and resins which might tend to corrode the metal powder. A non-corrosive, but rather expensive vehicle may be formed by thickening terpineol (80 to 90 per cent) with ester gum (10 to 20 per cent). Fine lining powder of any pigment metal may be incorporated.[98] Another non-corroding composition, also of too high cost for extensive commercial use, includes a solvent boiling at the stamping temperature of 200° C. or above, such as terpineol or benzyl alcohol, a dissolved resin and dispersed bronze powder. Ordinary rosin may be employed for thickening.[99]

A thickening agent is reported to be made up by heating together 400 grams of water and 500 grams of glue and adding 100 grams of either resorcinol or phenol and allowing the mixture to cool.[100] This composition may be included in a printing paste consisting of 250 grams of Schlenk's "Hochglanzgold," 500 grams of the thickener, 75 cc. of formaldehyde (11° Bé.) and 75 cc. of 25-per cent ammonium hydroxide.

A non-tarnishing ink consists of bronze powder, terpineol and a resin. The ink may be used in stamping book covers and the printed film afterwards coated with nitrocellulose.[101] Aromatic esters boiling between 200 and 300° C., such as terpinyl acetate, ethyl benzoate or mixtures of these, although expensive materials, may serve as solvents. Thickening agents such as colophony, dammar, copal, Burgundy pitch, Canada balsam or their mixtures can be incorporated in the solvent and the metal powder added. The resulting ink is applied to bookbindings or labels by heated stamps.[102] As a binder coumarone resin can be used with rosin oil, the latter rendering the resin more plastic. An ink composition, for example, applicable for stamping book covers and labels in metallic print, consists of 2.25 parts of bronze powder incorporated in a vehicle containing 16 per cent coumarone resin dissolved in 79.8 per cent terpineol and 4.2 per cent rosin oil. One-third by weight of this mixture is added to two-thirds of bronze powder, producing an ink of pasty or semi-liquid consistency.[103]

Another composition for a vehicle for metallic ink includes various other resins, such as paracoumarone, para-indene, and benzofurane.

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[97] G. Rice, *Rubber Age N. Y.*, 1931, 28, 611; *Chem. Abs.*, 1931, 25, 2596.

[98] W. J. McElroy and J. Clarke, U. S. P. 1,489,356 and 1,489,357, April 8, 1934, to Alchemic Gold Co., Inc.; *Chem. Abs.*, 1934, 28, 1916.

[99] H. W. Doughty, U. S. P. 1,439,695 and 1,439,696, Dec. 26, 1922; *Chem. Abs.*, 1923, 17, 1157.

[100] Martin Battegay, *Report on Sealed Letter No. 1287*, Sept. 7, 1901, *Bull. soc. ind. Mulhouse*, 83, 56; *Chem. Abs.*, 1913, 7, 2119. It is pointed out that the inventor, Joseph Stephen, has unknowingly created conditions in his procedure which produce the resin Bakelite.

[101] W. F. Smith, U. S. P. 1,752,462, Apr. 1, 1930, to Kingsport Press, Inc.; *Chem. Abs.*, 1930, 24, 2622.

[102] W. J. Mellersh-Jackson, British P. 199,923, 1922, to Alchemic Gold Co., Inc.; *Chem. Abs.*, 1924, 18, 336; *J. S. C. I.*, 1923, 42, 841A.

[103] W. J. McElroy and J. Clarke, U. S. P. 1,450,692, April 3, 1923; *Chem. Abs.*, 1923, 17, 1896; British P. 198,308, 1923; *Brit. Chem. Abs.* B, 1923, 731; *Chem. Abs.*, 1923, 17, 3737; both to Alchemic Gold Co., Inc.

The recipe calls for 70 per cent of a carrier (benzene or toluene), 20 per cent of a fixative agent (one of the above resins) and 10 per cent of a neutralizing fixative agent, for which stearic acid is employed. The proportions of the various constituents may be varied to suit special circumstances.[104]

Klein [105] suggests heating a mixture of animal fat, oil and wool wax to a temperature of about 400° C., cooling the mass, and again subjecting it to a heating operation. In this manner there is eliminated any glycerol or acrolein (resulting from decomposition of the fats), and a viscous liquid is secured which is reported to be insoluble in water or alcohol. The product then is filtered and admixed with a metallic pigment and a drier, *e.g.*, manganese borate. Such compositions are reported to be particularly applicable for printing trade-marks on cigars.

In printing tin plates with aluminum pigment the latter is stirred into a nitrocellulose lacquer the solvent of which is a mixture of alcohol, phthalic dibutyl ether and ethylene glycol monoethyl ether.[106] Metallic powder such as aluminum bronze, silver, or gold powder incorporated in camphor oil or China Wood oil containing gum dammar is used in printing upon leather or analogous material used in making shoes. For making purple impressions a solution of a purple aniline dye is added to the ink.[107]

It has been found possible to obtain various color effects by tinting aluminum inks with strong toning pigments or oil-soluble dyestuffs. The depth of tone determines the amount of pigment used, but in no case should enough pigment be incorporated to destroy the "leafing" effect of the aluminum particles. When these dyes are used, it is necessary to add a considerable amount of cobalt drier to overcome the non-drying nature of the pigments.[108]

For materials which cannot be printed with inks containing drying oils the metallic powder (aluminum, copper or brass) is suspended in glue, gelatin or similar pastes. As fixing agents for the dried prints, albumin, casein, natural or synthetic rubber, cellulose or cellulose esters may be used. The ink is applied to textiles, *e.g.*, to cotton or rayon, and after drying, the printed material is subjected to pressure by passing it between rollers.[109] In printing metallic colors from rubber cylinders, highly viscous inks are used containing, as a binder for bronze powders, ethyl alcohol solutions of polymerized products of aliphatic vinyl compounds, such as vinyl esters (*e.g.*, acetate), ethers (*e.g.*, vinyl methyl ether), esters of acrylic acid (*e.g.*, ethyl acrylate) and also condensation products of polymerized vinyl alcohol with acetaldehyde. To increase

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[104] J. G. Shilvock, U. S. P. 1,411,673, April 4, 1922; *Chem. Abs.*, 1922, **16**, 2035.

[105] E. Klein, U. S. P. 811,156, Jan. 15, 1907; *J. S. C. I.*, 1907, **26**, 421.

[106] British P. 318,567, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, **24**, 2316; *Brit. Chem. Abs.* **B**, 1929, 1047; *Rev. Paint, Colour, Varnish*, 1929, **2**, 331.

[107] F. A. Putnam, U. S. P. 1,203,779, Nov. 7, 1916; *Chem. Abs.*, 1917, **11**, 104.

[108] *Am. Ink Maker*, 1938, **16** (1), 23; *Rev. Paint, Colour, Varnish*, 1938, **11**, 107.

[109] P. Bellecour, *Industrie Textile*, 1937, **54**, 298; *J. Text. Inst.*, 1937, **28**, 556A; *Rubber Res. Abs.*, 1937, **15** (12), 795; *Rev. Paint, Colour, Varnish*, 1938, **11**, 108.

the flexibility of inks and obtain uniform prints, small amounts, according to requirements, of glycerol, tannin, ethylene glycol monoethyl ether ("Cellosolve") or its acetate are incorporated in the solution.[110]

Driers are added to the ink so that the varnish will not penetrate and be absorbed by the paper, leaving the metal pigment lying loose on the surface. The period of drying on the paper is, however, not influenced by large quantities of drier, though an excess of the latter may cause drying or "caking" on rollers and plates. The correct drying operation leaves a clean, hard film with metal particles tightly held together. Too much drier loosens the contact of particles in the film, and the softening which results makes rubbing off easily possible.[111] The drier should be added to the varnish before mixing the latter with the metallic pigment, otherwise the print will tend to offset at various spots, on account of inhomogeneity in drier concentration. Lead driers should be avoided because they may dull the color and gloss and decrease the keeping quality of the ink; commonly the linoleates of cobalt or manganese are used.[112]

When the ink, because of too great drier content, dries on the press but otherwise works satisfactorily, an addition of about $\frac{1}{2}$ oz. of glycerol per pound of ink will usually retard drying. To prevent rubbing off after setting overnight or filling up fine lines in the design, 1 oz. of a gum (for purposes of bodying) per pound of ink may be added.[113]

When printing ink of the ordinary type is superimposed upon a metallic ink film, care should be taken to include the same drying oil, for instance, tung oil, in both vehicles.[114] Large continuous areas of a metallic film do not furnish a very adhesive base for overprinting, and the second coat is easily rubbed off. When a subsequent printing is done on a metallic surface, the material of the second coat should contain only fine lines or ordinary type faces without extensive solid areas to insure better adhesion.[115] The superior effect of a design of this type due to the high reflective power of the metallic film warrants its use in spite of the long drying period required and the numerous other difficulties encountered.

If the design requires printing of fine lines and small types, the ink is apt to "creep" beyond the limits of the design. To avoid this, there should be (as a rule) a minimum space of $\frac{1}{16}$ inch between elements of the design. Also, plates should be cut away sufficiently deep at the edges to prevent filling up of areas not belonging to the design.

If the surface to be printed upon is dull-coated or an antique paper, a base is required under the metal pigment. However, one of the other

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[110] British P. 426,805, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 6082; *Brit. Chem. Abs.* B, 1935, 511. German P. 619,501, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, 30, 1595. French P. 774,851, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 2265.

[111] J. H. Meyer, *Am. Ink Maker*, 1931, 9 (7), 21; *Chem. Abs.*, 1931, 25, 5582; *Rev. Paint, Colour, Varnish*, 1931, 4, 208.

[112] F. C. Arthur, *Am. Ink Maker*, 1936, 14 (6), 23; *Chem. Abs.*, 1936, 30, 5818; *Rev. Paint, Colour, Varnish*, 1936, 9, 241.

[113] E. J. Rhodes, *Brit. Printer*, 1936, 49 (291), 109; *Rev. Paint, Colour, Varnish*, 1936, 8, 377.

[114] E. J. Rhodes, *loc. cit.*

[115] J. H. Meyer, *loc. cit.*

colors desired in the print can be applied as a base to save one impression time. For this type of operation colors of light tints are more suitable than dark ones. However, under certain conditions dark colors, even black, have been used successfully.[116] The base print should be overprinted before it is dry.[117] Very pleasing effects are obtained by printing a double coat of aluminum ink.[118]

Every ingredient of the ink must be carefully weighed before mixing. In making an ink, first a sufficient amount of varnish is added to the weighed pigment to produce a fluid paste, then the remainder of the varnish is added in small portions and mixed, with minimum stirring and without grinding the pigment. The metal flakes are wetted more easily and uniformly when this procedure is adopted than when the varnish is added in bulk. If a thinner is to be incorporated in the ink composition, the pigment should be wetted with such a liquid before admixing with the varnish.

The amount of pigment should be about 20-30 per cent of the ink by weight, but this proportion may be widely varied according to the quality of pigment, the consistency of the ink, the type of material to be printed, and the press. A single-sized paper requires an ink containing 20-25 per cent pigment, but for good coverage only 15 per cent is necessary on double-sized paper.[119] In the case of high-speed presses, the powder in the ink may be 30-40 per cent for single-sized paper and only 20 per cent by weight for double-sized paper. It is reported that, within limits, thinning the varnish increases its pigment-binding capacity.

Metallic pigment inks can be printed on flat-bed, semi-rotary or high-speed rotary presses. Care should be taken to avoid formation of ink film on the transfer rolls and filling up of impression plates.

Printing on a cylinder press requires more attention than on a job press, because the transfer of ink from fountain to plates is more complicated, and the ink has more opportunity to dry. Excess pressure on the transfer rolls and on the plates causes the vehicle to separate from the pigment and forces it to the edges of plates or types. More ink can be used and consequently brighter impressions secured on a job press.[120] The advantage of etching plates somewhat deeper than in ordinary printing was early recognized.[121] Distribution of ink should be carefully controlled and must not be pressed to capacity of the inking system.[122]

When printing by offset,[123] one of the colors can be printed over the areas where the (gold) bronze will be printed. The gold size printed on this color will hold better than if applied directly to the paper. As

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[116] J. H. Meyer, *loc. cit.*

[117] E. J. Rhodes, *loc. cit.*

[118] H. Hadert, "Handbuch über die Herstellung und Verwendung der Druckfarben," 2nd ed., Berlin, O. Elsner Verlagsgesellschaft m. b. H., 1931.

[119] F. C. Arthur, *Am. Ink Maker*, 1936, 14 (6), 23; *Chem. Abs.*, 1936, 30, 5818; *Rev. Paint, Colour, Varnish*, 1936, 9, 241.

[120] J. H. Meyer, *Am. Ink Maker*, 1931, 9 (7), 21; *Chem. Abs.*, 1931, 25, 5582; *Rev. Paint, Colour, Varnish*, 1931, 4, 208.

[121] F. C. Arthur, *loc. cit.*

[122] E. J. Rhodes, *Brit. Printer*, 1936, 49 (291), 109; *Rev. Paint, Colour, Varnish*, 1936, 9, 377.

[123] For discussion of offset printing see Chapter 9.

the metallic particles printed from rubber blankets may stick to colors printed from the same blanket, bronzing must be at the last phase of the work. For offset printing a rather soft bronze is to be used, which can be easily distributed on rubber rolls. A special offset gold size which requires no addition of linseed oil contains gold varnish and a printing tincture.[124] Troubles which may arise from offset printing can be avoided by using a platen machine instead of the former method.

Automatic bronzing machines make possible control of waste powder and dissipation into the air, thus improving hygienical conditions in bronze printing.[125]

The power of impression must be sufficiently great to press the metal powder into the gold size or the underlying coat of varnish, as otherwise the particles do not adhere firmly and rub off at the slightest touch. Calendering is generally not helpful here because the pre-print dries to a hard film usually before it reaches calendering rolls. As a consequence the particles cannot be forced deeper into the gold size.[126]

Offsetting of the finished prints can be prevented by passing the sheets over a row of gas flames which are in contact with the paper. Experiments to avoid offset have been made with ozone and ultraviolet radiation, but because of the complicated method of application and high expenses, apparently these methods as yet are not used commercially. On high-speed rotary presses a spray of wax will overcome a tendency to offset.[127]

Other precautions which can be taken to avoid offset are handling the sheets as little as possible, examination of the ink for uniform coverage, and appropriate temperature of the pressroom, which should be about 80° F. If despite these precautions offsetting cannot be prevented, the sheets are to be slip-sheeted,[128] in which case kraft slip-sheets are especially useful.[129]

Ink-transferring rolls should possess minimum tackiness to insure the deposit of a smooth, uniform film on the printing plates. The press machines in general must be cleaned frequently, not allowing ink accumulation on rollers, plates and etched parts of the plates, which causes spreading of ink around the limits of design. The latter effect gives rise to an irregular appearance of the prints and interferes with the register where the metallic print contacts other color lines and areas.[130]

OVERPRINTING VARNISHES AND PROTECTIVE COATINGS

Overprints are applied to increase attractiveness and durability of printed matter. Coverings of most magazines are overprinted, as well

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[124] R. Holder, *Mod. Lith. and Offset Printer*, 1933, 29 (1), 3; *Rev. Paint, Colour, Varnish*, 1933, 6, 36.

[125] D. H. Caldwell, *Times Trade and Eng.*, 1937, 40 (877), special supplement, "Aluminum and Its Applications," XLIV; *Rev. Paint, Colour, Varnish*, 1937, 10, 174.

[126] H. Hadert, "Handbuch über die Herstellung und Verwendung der Druckfarben," 2nd ed., Berlin, O. Elsner Verlagsgesellschaft m. b. H., 1931.

[127] F. C. Arthur, *loc. cit.*

[128] For definition of slip-sheeting see the section in this chapter on aniline inks.

[129] E. J. Rhodes, *loc. cit.*

[130] J. H. Meyer, *loc. cit.*

as wrappers for a great variety of commercial articles, to prevent soiling and damaging of the prints by scratching and smearing,[131] and to add a pleasing effect of brilliancy to the surface which is so treated.

Strictly speaking, overprinting is the application of a varnish by means of typographic or lithographic[132] printing processes to printed material, thus providing protection of the latter against damage. However, the term overprinting is widely used for indicating the application of spirit label varnishes and lacquers, which are applied not by a printing process but by brushing, spraying or roller-coating.[133]

According to another classification one type of overprint varnish is that containing a volatile liquid such as methylated spirits or turpentine, while others contain non-volatile vehicles. The latter type is very conveniently printed by regular methods and is applicable upon colors which bleed in a methylated spirit varnish.[134]

The manufacture of satisfactory overprint varnishes was made possible by the development of synthetic resins which, when present in products for overprints, impart to them desirable properties. Highly polymerized, rosin-modified phenol formaldehyde resins may be employed with very good results. By reducing drying time of oils in the varnishes, penetration into the fibers and pores of paper is decreased, and consequently a relatively high gloss of the dried film is obtainable. The varnishes made with desirable synthetic resins yield hard and tough films and should be free from excessive tack, thereby avoiding troubles often encountered during and after printing, such as drying on the press or tendency to stick or offset of the printed sheets.[135]

The practicability has been demonstrated of using gum dammar in making overprint varnishes for labels. Gum dammar has the desirable properties of being practically colorless and of causing almost negligible darkening upon drying. By an extended series of tests, it has been shown that excellent varnishes may be made if certain precautions, such as oil length, drier content, and cooking temperature are observed. Tung oil, linseed oil, and 6-per cent cobalt drier were used in the composition, the drying time of which ranged, depending upon the proportions of the ingredients used, from 2½ hours to 24 hours. The inclusion of paraffin wax and kerosene improved the quality of the varnish considerably. Absolutely no after tack develops if a good drying oil is used.[136]

On the other hand, varnishes of too little tackiness or too slight body are not desirable, being the cause of slipping or sliding of rollers, thus hindering proper distribution of the varnish. Furthermore, gloss may be destroyed by absorption of varnish by the paper to which it is applied.

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[131] F. H. Kelson, *Am. Ink Maker*, 1936, 14 (5), 51; *Chem. Abs.*, 1937, 31, 4142; *Rev. Paint, Colour, Varnish*, 1936, 9, 242.

[132] Typographic and lithographic printing are discussed in Chapter 7 and Chapter 9, respectively.

[133] F. H. Kelson, *loc. cit.* H. B. Hillman, *Inland Printer*, Feb. 1938, 64; *Rev. Paint, Colour, Varnish*, 1938, 11, 108.

[134] J. D. Cohen, *Brit. Printer*, 1934, 47 (278), 79; *Rev. Paint, Colour, Varnish*, 1934, 7, 376.

[135] F. H. Kelson, *loc. cit.*

[136] C. L. Mantell and A. Skett, *Paint, Oil, Chem. Rev.*, 1939, 101 (4), 7; *Am. Ink Maker*, 1939, 17 (3), 41.

The desired synthetic resin is dissolved in a drying oil, which is selected in accordance with the type of press and grade and weight of the stock used. The oil should be processed carefully, since upon it depend most of the working qualities of the varnish. A proper oil, being of light color, rapid drying and low penetration, can dissolve a relatively high percentage of resin without becoming too sticky, and also can prevent the dried film of varnish from becoming brittle because of its toughening effect on the resin.

A bodied oil is usually preferable, although raw oils often are employed in preparing a varnish. The material forming the boiling kettle is of importance as it must be resistant to cooking temperatures (about 600° F.) and must not discolor the varnish. Monel metal, stainless steel or copper are suitable materials; aluminum, although it produces light-colored varnishes, is quickly damaged by the required heat and must be carefully handled. Iron is unsuitable since it darkens the color of varnish. Similarly, enameled iron is not recommended, because under the influence of heat the enamel is easily broken, and darkening of the varnish, as stated, is caused by the iron.

Fast cooking of the oil is generally desirable. The correct procedure to be followed in any instance can be determined experimentally. The oil is usually cooked to a slight body; then resins are incorporated and cooking continued until the resins are properly distributed and dissolved, and hence do not settle out on cooling. Stirring of the varnish while cooking prevents discoloration caused by local overheating. Discoloration due to surface oxidation of the liquid can be prevented by heating in an atmosphere of carbon dioxide or nitrogen. Waxes or greases are added to the varnish during cooling, but while it is still warm, to prevent sticking or offsetting and to insure a smooth film.

Driers employed in overprints are mainly metallic soaps of cobalt, as small amounts are sufficient, and cobalt has a marked tendency to bleach the varnish after a storage period of several weeks. Lead compounds often render the varnish cloudy and settle out, and manganese driers have a decided darkening effect.[137]

Organic salts of metals of the alkaline earth or earth metal group, such as stearic or palmitic soaps of these metals, especially of aluminum, often are added to the varnish. These salts, being easily dispersed in the varnish, are incorporated to increase viscosity and shorten the varnish, thus reducing its tack.[138] The proportion of these ingredients required in the varnish is about 0.5 per cent. For instance, 15 g. aluminum stearate is incorporated into a varnish consisting of 200 g. linseed oil, 100 g. of a hard resin and 5 g. linoleate of cobalt, or 15 g. of aluminum palmitate in 180 g. of wood oil, 90 g. of hard resin and 0.5 g. of lead salicylate. The soaps may be formed in the varnish by adding the metallic hydroxide

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[137] F. H. Kelson, *Am. Ink Maker*, 1936, 14 (5), 51; *Chem. Abs.*, 1937, 31, 4142; *Rev. Paint, Colour, Varnish*, 1936, 9, 242.

[138] *Am. Ink Maker*, 1936, 14 (8), 25.

and acid separately, *e.g.*, finely divided aluminum hydroxide and stearic acid. These varnishes are used for high-gloss overprints, and may be colored by oil-soluble substances such as Victoria Blue base, Rhodamine base, Sudan dyes, Milori Blue, Fanal Green and Permanent Red.[139]

Incorporation of oil-soluble dyestuffs into the composition often gives unusual and striking effects. For example, the effect of a 3-impression print may be obtained by printing a colored varnish over a black or dark-colored half tone, thus coloring and overprinting in one operation. With especially good results it is possible to give warm pastel shades in overprint varnishes.[140]

Prints can be treated by rubbing with a paste to give them the appearance of engraving on matte paper. The colored or colorless paste includes besides wood oil and boiled linseed oil dry hydroxide of aluminum, borate of zinc, white potassium soap and technical ammonia.[141]

To bring the varnish to the proper tack and consistency for use on the press, reducers are incorporated. Reducers are more or less volatile compounds drying by evaporation and penetration. Especially on lithographic and offset presses, due to their elaborate distributing system, highly volatile reducers or thinners should be avoided.

For a long time overprint varnishes were not applicable by lithographic or offset presses, partly because the quantity of varnish these machines carried was not enough to produce the desired high-gloss surfaces and partly because the water employed in the dampening fountain [142] of the presses emulsified with or hydrolyzed the oil in the varnish and so destroyed its gloss-producing effects. Due to later improvements, varnishes are available which can be applied by lithographic or offset printing methods in the same thickness as by typographic printing. These varnishes have a relatively heavy consistency and high percentage of resin content.[143]

Certain anhydrous lacquers containing cellulose esters or ethers are applicable for printing colored or colorless coatings or designs on non-resilient materials such as metal, wood, synthetic compositions, *e.g.*, resins, vulcanized fiber or stone. The printed films are highly resistant to mechanical effects. Successive prints (also in different colors) can be applied without drying of each film. The lacquers can be printed on intaglio,[144] offset and lithographic presses, for example, with deeply engraved rollers or plates to prevent too rapid drying of the lacquers on the press. On top of the prints a transparent protective varnish or lacquer may be applied. If necessary, the surface of the non-resilient

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[139] British P. 434,450, 1935, to Chem. Fabr. Halle-Ammendorf Gebr. Hartmann; *Chem. Abs.*, 1936, 30, 886; *Brit. Chem. Abs.* B, 1935, 1056; *Rev. Paint, Colour, Varnish*, 1935, 8, 517. French P. 789,912 and 781,913, 1935; *Chem. Abs.*, 1935, 29, 7102; *Rev. Paint, Colour, Varnish*, 1935, 8, 517.

[140] F. H. Kelson, *loc. cit.*

[141] C. F. W. Schneemann, German P. 260,695, 1910; *Chem. Abs.*, 1913, 7, 3206.

[142] Inks for lithographic and offset printing and the function of the dampening fountain are mentioned in Chapter 9.

[143] F. H. Kelson, *loc. cit.*

[144] For intaglio printing see Chapter 10.

material, before being printed, is evened and smoothed by priming with a filling composition, lacquer or oil paint, which also prevents the printed coat from being pulled off.

A lacquer containing dry nitrocellulose dissolved in a mixture of alcohol, phthalic dibutyl ester and ethylene glycol monoethyl ether and a metallic or other pigment (*e.g.*, aluminum bronze or Prussian Blue) or dyestuffs, is printed on tin plate. Other lacquers consist of a cellulose ester, *e.g.*, acetylcellulose, in a vehicle of phthalic dimethyl ester and glycol ester and colored by a dyestuff (*e.g.*, Hansa Yellow) which is mixed with ethylene glycol monoethyl ether acetate. Also gums, resins, oils and varnishes may be incorporated in the lacquers.[145] Other coatings for non-resilient materials are produced by dissolving colored cellulose plastics in solvents. Colored masses are obtained by milling together a cellulose ester and a softening or swelling agent, *e.g.*, camphor, with an organic or inorganic coloring substance non-soluble in the mixture of cellulose ester and swelling agent.[146]

Protective Coatings. As protective coatings, varnishes or lacquers may be applied by brushing or spraying over the printed surface. The compositions of these coatings depend upon the kind of surface to which they are applied. It is also equally important that the ink be suited to the paper on which it is used.[147] A varnish for printed labels and wrappers consists of a cellulose derivative heated with an unsaturated oil and dissolved in a solvent. For example, ethylcellulose is heated with wood oil, air is blown through the mixture to promote combination of the cellulosic material and oil and the product is then dissolved in butyl lactate, butyl "Carbitol" or "Carbitol" acetate.[148] For printed posters mounted on metal, transparent cellulose is used and applied in several layers as a coating, with no solvent effect on the printing ink. The metal is thoroughly cleaned and a priming of cellulose employed.[149] Food wrappers printed with a priming of an adhesive water-color paste and an oil-base ink on the dried priming may be coated with a film of wax on the printed side of the paper.[150] To prevent lifting or other attacking of common oleograph, or drying-oil, inks, a fine spray of nitrocellulose varnish first is applied under pressure (about 4 atmospheres) over the print and then, before this can dry, a second coat of nitrocellulose is applied.[151] Lithographed metal signs may be coated with a

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[145] British P. 318,567, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, **24**, 2316; *Brit. Chem. Abs.* **B**, 1929, 1047; *Rev. Paint, Colour, Varnish*, 1929, **2**, 331.

[146] British P. 247,288, 1924, to Badische Anilin- & Soda-Fabr.; *Brit. Chem. Abs.* **B**, 1926, 315.

[147] For a review of the application of overprint varnishes, see E. St. John, *Inland Printer*, July 21, 1938; *Rev. Paint, Colour, Varnish*, 1938, **11**, 364. *Inland Printer*, April, 1937, 68; *Rev. Paint, Colour, Varnish*, 1937, **10**, 174.

[148] J. D. Murray, U. S. P. 2,099,570, Nov. 16, 1937, to Murray Liquafilm Corp.; *Am. Ink Maker*, 1938, **16** (2), 37.

[149] S. G. Pipe, *Brit. Ind. Finishing*, 1930, **1**, 233; *Rev. Paint, Colour, Varnish*, 1930, **3**, 269.

[150] R. A. Hayward, British P. 471,388, 1937; *Chem. Abs.*, 1938, **32**, 1498; *Brit. Chem. Abs.* **B**, 1938, 411.

[151] British P. 364,520, 1931, to Masa Ges. zur Herstellung künstlicher Oberflüchen; *Brit. Chem. Abs.* **B**, 1932, 272; *Rev. Paint, Colour, Varnish*, 1932, **5**, 188.

nitrocellulose varnish to prevent early chalking and fading. The varnish consists of nitrocellulose or "Rezoglaz" (a synthetic polystyrene resin) plasticized either with 25 or 50 per cent of its weight of dibutyl phthalate. Other varnishes may be formed of nitrocellulose and a high percentage of alkyd resins.[152]

To an exposed light-sensitive layer of bichromated albumin a fixing coating may be applied, consisting of a powdered earth color mixed with printer's varnish, gasoline or other readily volatile liquid. For instance, one composition consists of 10 per cent of printer's varnish, 30 per cent of gasoline, 2 per cent of oil of lavender and 58 per cent of pigment.[153] To fix lithographic and other transfers,[154] a varnish can be used which consists of heavy benzine (760-860 g.), Judaea bitumen (mineral pitch), 90-120 g., and essence of copaiva, 7-20 drops.[155]

To render prints resistant to gasoline and to heighten their effects, a composition is applied by means of sprinkling on moist impressions. The composition consists of a saccharine substance (*e.g.*, glucose), 1 part, with a pigment (*e.g.*, lampblack), 3 parts, and water, forming a plastic mass which is dried and powdered. Afterwards 5-20 per cent of an inert filling material, such as starch, is incorporated.[156]

PRINTING ON CELLULOSE ESTER PLASTICS

The manufacture of inks for printing on cellulosic materials such as celluloid, Cellophane and various kinds of highly glazed transparent papers (for example, glassine) offers special problems due to particular properties of these types of surfaces. For example, thickness and rigidity of the materials prevent them from clinging well to the printing forms. Also, density of the surface or, in other words, low porosity, renders such surfaces non-absorbent, causing problems in drying of the ink. Again, the high smoothness of the surfaces gives rise to difficulties in adhesion of inks.[157] In some instances, increased adhesion to a nitrocellulose film by the ink may be secured if the printed material is subjected to light of high intensity, *e.g.*, light from a 1,000-watt tungsten bipostal lamp.[158]

The composition of the inks must be specially adapted and mixed to overcome these difficulties. Ordinary drying-oil inks, applied by usual printing processes, would dry very slowly (in several days) and be non-resistant to mechanical or chemical action and heat. The inks generally

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[152] H. A. Gardner, *Am. Paint, Varnish Mfrs. Assoc. Tech. Sect. Circ.*, 437, 230; *Chem. Abs.*, 1933, **27**, 4425; *Brit. Chem. Abs.* **B**, 1933, 1068; *Rev. Paint, Colour, Varnish*, 1933, **6**, 176.

[153] British P. 474,404, 1937, to Primographic Co.; *Rev. Paint, Colour, Varnish*, 1938, **11**, 111.

[154] For discussion of transfer printing see Chapter 12.

[155] C. F. Rousset, British P. 606, 1886; *J. S. C. I.*, 1886, **5**, 609.

[156] S. M. McMurray and J. R. Parrish, U. S. P. 1,215,293, Feb. 6, 1917; *Chem. Abs.*, 1917, **11**, 1048; *J. S. C. I.*, 1917, **36**, 395.

[157] K. Eichstädt, *Nitrocellulose*, 1934, **5**, 221; *Chem. Abs.*, 1935, **29**, 1626. *Cf.* H. Hadert, *Am. Ink Maker*, 1933, **11** (6), 13; *Paint Manuf.*, 1933, **3** (7), 202; *Rev. Paint, Colour, Varnish*, 1933, **6**, 198; *Chem. Abs.*, 1933, **27**, 3625. J. D. Cohen, *Paper and Printing*, 1938, **11** (41), Suppl. 26; *Rev. Paint, Colour, Varnish*, 1938, **11**, 199.

[158] B. McBurney, *Bookbinding & Book Production*, 1938, **28** (5), 26; *Rev. Paint, Colour, Varnish*, 1939, **12**, 19.

used in printing fibrous cellulosic materials exert a slight solvent action on the printed surface itself, so that they penetrate the surface and solidify within the material, drying by absorption and partly also by evaporation of the solvents used. Ingredients of these inks are a plasticizable base, such as a thickener and a plasticizer, pigments or dyestuffs, and a fluid which is a solvent for both the ingredients of the ink and the surface to be printed.

The vehicle may contain a cellulose derivative or a natural or synthetic resin. Often it is of advantage to use the same cellulose derivative which forms the material to be printed.[159] Cellulose esters or ethers which may be employed include nitrocellulose, acetylcellulose, methylcellulose or cellulose butyrate. The ester should be of low viscosity (*i.e.*, about 0.1 to 0.75 of that of silk acetate) to increase penetration into the surface.[160] In inks containing such cellulosic compounds[161] a large proportion of plasticizing agent is often present, the weight of the latter material being five times or more that of the cellulose derivative.[162]

Cellulose esters often may be replaced by resins of the diphenylolpropane-formaldehyde, phenol-formaldehyde or Glyptal type (the latter being condensation products of di- or polyhydric alcohols with di- or polybasic acids),[163] by ester gum, colophony[164] or shellac.[165] Also a combination of a cellulose ester solution with resins may be employed, *e.g.*, cellulose nitrate or acetate, copal resin and ester gum.[166]

Plasticizers may be incorporated, their purpose being to produce a smoother film as well as to promote penetration of the ink into the surface by exerting a softening action upon it.[167] The plasticizers are nonvolatile liquids such as dimethyl phthalate, diethyl phthalate, dibutyl tartrate, tricresyl phosphate, diethyl carbonate, di- or triacetins, triphenyl acetins, methyl or ethyl toluenesulphonamides. The proportion of plasticizer may be varied over wide limits. A quantity of 10 to 20 times by weight of the cellulose ester in the ink is particularly useful

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[159] British P. 456,898, 1936, to British Celanese Ltd.; *Chem. Abs.*, 1937, 31, 2457; *Rev. Paint, Colour, Varnish*, 1937, 10, 25. Nitrocellulose as a vehicle in printing inks for non-absorbent surfaces is discussed by A. Kraus, *Papier-Fabr.*, 1937, 35, 373; *Brit. Chem. Abs.* **B**, 1937, 1322; *Rev. Paint, Colour, Varnish*, 1938, 11, 25. G. Pundsack, Canadian P. 343,266, 1935; *Chem. Zentr.*, 1935, 106 (2), 443; *Rev. Paint, Colour, Varnish*, 1935, 8, 307.

[160] A. F. Caprio and W. Bowker, U. S. P. 1,931,485, Oct. 24, 1933, to Celluloid Corp.; *Chem. Abs.*, 1934, 28, 662; *Brit. Chem. Abs.* **B**, 1934, 685; *Rev. Paint, Colour, Varnish*, 1934, 7, 22. W. W. Mock, U. S. P. 2,081,949, June 1, 1937, to International Printing Ink Corp.; *Chem. Abs.*, 1937, 31, 5188; *Rev. Paint, Colour, Varnish*, 1937, 10, 413. A. E. Shannon, U. S. P. 1,880,502, Oct. 4, 1932; *Chem. Abs.*, 1933, 27, 675; *Brit. Chem. Abs.* **B**, 1933, 837; *Rev. Paint, Colour, Varnish*, 1933, 6, 335. E. B. Middleton, U. S. P. 1,833,086, Nov. 24, 1931, to du Pont Film Manufacturing Corp.; *Chem. Abs.*, 1932, 26, 931. H. Wobornik, Austrian P. 125,010, 1927; *Chem. Abs.*, 1932, 26, 860; *Rev. Paint, Colour, Varnish*, 1932, 5, 107.

[161] See British P. 498,390, 1939, to Shellmar Products Co.; *Chem. Abs.*, 1939, 33, 4352.

[162] W. H. Moss, U. S. P. 2,165,499, July 4, 1939.

[163] See Carleton Ellis, "The Chemistry of Synthetic Resins," New York, Reinhold Publishing Corp., 1935.

[164] British P. 456,898, 1936, to British Celanese Ltd.; *Chem. Abs.*, 1937, 31, 2457.

[165] J. H. Clewell, U. S. P. 1,806,965, May 26, 1931, to DuPont Viscoloid Co.; *Chem. Abs.*, 1931, 25, 4138; *Brit. Chem. Abs.* **B**, 1932, 234. Canadian P. 307,397, 1931, to Canadian Industries, Ltd.; *Chem. Abs.*, 1931, 25, 1108.

[166] E. M. Davidson, U. S. P. 2,091,966, Sept. 7, 1937, to Continental Can Co., Inc.; *Paint Tech.*, 1937, 2, 320; *Chem. Abs.*, 1937, 31, 7677; *Rev. Paint, Colour, Varnish*, 1937, 10, 413.

[167] E. M. Davidson, *loc. cit.*

for intaglio printing of foils and films of organic cellulosic derivatives.[168] The plasticizer may be used alone or with a solvent.[169] However, a small amount of a volatile liquid such as alcohol, acetone or ethyl acetate accelerates solution of the cellulose derivative in the plasticizer.[170]

Various types of solvents, because of their solvent action on cellulose ester surfaces, are applicable for celluloid and Cellophane inks. Examples are acetic acid,[171] monohydric alcohols such as methyl alcohol,[172] ethyl alcohol,[173] butyl[174] and isobutyl alcohols,[175] furfuryl alcohol,[176] dihydric alcohols, *e.g.*, diethylene glycol,[177] ketones, *e.g.*, acetone,[178] or diacetone alcohol.[179] Also employed are dioxane,[180] dichlorohydrin[181] or even camphor dissolved in lavender oil.[182] As solvents, many organic esters may be used, such as ethyl acetate, butyl acetate, amyl acetate,[183] glycol acetate,[184] methylglycol acetate,[185] the acetates of ethylene glycol monoethyl ether (ethyl "Cellosolve"),[186] and ethylene glycol monomethyl ether (methyl "Cellosolve"),[187] butyl propionate,[188] ethyl lactate,[189] and cyclohexanol acetate.[190] Ethers used as solvents are ethylene glycol monoethyl ether,[191] ethylene glycol monobutyl ether,[192] diethylene monomethyl,[193] and diethylene monobutyl ethers.[194] Other solvents are hydro-

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[168] British P. 456,898, 1936, to British Celanese Ltd.; *Chem. Abs.*, 1937, 31, 2457; *Rev. Paint, Colour, Varnish*, 1937, 10, 25. A. F. Caprio and W. Bowker, U. S. P. 1,931,485, Oct. 24, 1933, to Celluloid Corp.; *Chem. Abs.*, 1934, 28, 662; *Brit. Chem. Abs.* B, 1934, 685; *Rev. Paint, Colour, Varnish*, 1934, 7, 22.

[169] W. W. Mock, U. S. P. 2,081,949, June 1, 1937, to International Printing Ink Corp.; *Chem. Abs.*, 1937, 31, 5188; *Rev. Paint, Colour, Varnish*, 1937, 10, 342.

[170] A. F. Caprio and W. Bowker, U. S. P. 1,931,485, Oct. 24, 1933, to Celluloid Corp.; *Chem. Abs.*, 1934, 28, 662; *Brit. Chem. Abs.* B, 1934, 685.

[171] P. L. Herbinet, French P. 753,365, 1933; *Chem. Abs.*, 1934, 28, 1205; *Chem. Zentr.*, 1935, 105 (I), 132; *Rev. Paint, Colour, Varnish*, 1934, 7, 102.

[172] E. M. Davidson, U. S. P. 2,091.966, Sept. 7, 1937, to Continental Can Co., Inc.; *Paint Tech.*, 1937, 2, 320; *Chem. Abs.*, 1937, 31, 7677; *Rev. Paint, Colour, Varnish*, 1937, 10, 413. J. H. Clewell, U. S. P. 1,806,965, May 26, 1931, to DuPont Viscoloid Co.; *Chem. Abs.*, 1931, 25, 4138; *Brit. Chem. Abs.* B, 1932, 234. Canadian P. 307,397, 1931, to Canadian Industries, Ltd.; *Chem. Abs.*, 1931, 25, 1108. P. L. Herbinet, *loc. cit.*

[173] E. M. Davidson, *loc. cit.* British P. 456.898. 1936, to British Celanese, Ltd.; *Chem. Abs.*, 1937, 31, 2457; *Brit. Chem. Abs.* B, 1937, 159; *Rev. Paint, Colour, Varnish*, 1937, 10, 25. British P. 287,124, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 349; *Brit. Chem. Abs.* B, 1928, 914.

[174] E. M. Davidson, *loc. cit.*

[175] H. Wobornik, Austrian P. 125,010, 1931; *Chem. Abs.*, 1932, 26, 860; *Rev. Paint, Colour, Varnish*, 1932, 5, 107.

[176] E. M. Davidson, *loc. cit.*

[177] J. H. Clewell, *loc. cit.*

[178] E. M. Davidson, *loc. cit.* British P. 456.898, 1936, to British Celanese, Ltd.; *Chem. Abs.*, 1937, 31, 2457. British P. 287,124, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 349. H. Wobornik, *loc. cit.*

[179] British P. 456,898, 1936, to British Celanese, Ltd.; *Chem. Abs.*, 1937, 31, 2457. J. H. Clewell, *loc. cit.* E. B. Middleton, U. S. P. 1,833,086, Nov. 24, 1931, to DuPont Film Mfg. Co.; *Chem. Abs.*, 1932, 26, 931.

[180] British P. 456,898, 1936, to British Celanese, Ltd.; *Chem. Abs.*, 1937, 31, 2457.

[181] H. Wobornik, *loc. cit.*

[182] M. Ernst, Swiss P. 126.212, 1927; *Chem. Abs.*, 1929, 23, 721.

[183] E. M. Davidson, *loc. cit.*

[184] British P. 456,898, 1936, to British Celanese, Ltd.; *Chem. Abs.*, 1937, 31, 2457. H. Lummerzheim and E. Schnitzler, U. S. P. 1,828,974, Oct. 27, 1931, to Agfa Ansco Corp.; *Chem. Abs.*, 1932, 26, 662; *Rev. Paint, Colour, Varnish*, 1932, 5, 90.

[185] British P. 287,124, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 349. British P. 456,898, 1936, to British Celanese, Ltd.; *Chem. Abs.*, 1937, 31, 2457.

[186] E. M. Davidson, *loc. cit.*

[187] A. A. Shannon, U. S. P. 1,880,502, Oct. 4, 1932, to Eastman Kodak Co.; *Chem. Abs.*, 1933, 27, 675; *Brit. Chem. Abs.* B, 1933, 837; *Rev. Paint, Colour, Varnish*, 1933, 6, 335.

[188] E. M. Davidson, *loc. cit.*

[189] British P. 456,898, 1936, to British Celanese, Ltd.; *Chem. Abs.*, 1937, 31, 2457. J. H. Clewell, *loc. cit.*

[190] E. M. Davidson, *loc. cit.*

[191] E. M. Davidson, *loc. cit.* E. B. Middleton, *loc. cit.*

[192] E. M. Davidson, *loc. cit.*

[193] E. M. Davidson, *loc. cit.* A. A. Shannon, *loc. cit.*

[194] E. M. Davidson, *loc. cit.*

carbons, such as benzene,[195] tetrahydronaphthalene and other hydrogenated derivatives of naphthalene, phenol or naphthol,[196] and nitrobenzene.[197]

An adhesive composition consists of a solution of ester gum in toluene; solutions of nitrocellulose and ethylcellulose in ethyl alcohol, toluene, and ethyl acetate; titanium dioxide; tricresyl phosphate, and methyl isobutyl ketone.[198]

The drying rate of inks may be varied by using two or more solvents. For example, mixtures boiling below 120° C. consist of amyl acetate, diacetone alcohol, methyl alcohol, butyl alcohol and butyl propionate. A similar composition includes diethylene glycol monobutyl ether with nitrobenzene, methyl alcohol, amyl acetate, butyl alcohol and furfuryl alcohol.[199] A mixture of equal quantities of methyl "Cellosolve" and its acetate has good solvent power.[200] An ink containing glycol acetate gives sharp impressions, and to increase the drying rate, ethyl alcohol or acetone may be added.[201] To decrease speed of drying of acetone, for example, a slowly evaporating solvent may be admixed, such as dichlorohydrin or isobutyl alcohol.[202] "Cellosolve" is especially useful in printing protein-coated photographic films, as it penetrates the protein layer.[203]

OTHER ADDITIONS TO THE VEHICLE

Various substances may be added to the vehicle to obtain the desired consistency of the ink, *e.g.*, small amounts of linseed oil or castor oil or resins, according to requirements.[204] To a vehicle consisting of a solution of cellulose ester and resin, mixed with a plasticizer, an amount of commercial soft soap or rosin soap may be added.[205]

For a coloring substance in the inks any kind of pigments or their mixtures may be used. Inorganic pigments are preferable to organic lakes or soluble dyestuffs; however, they may be added to or replace pigments.[206] As a black color, carbon black, lampblack, nigrosine base or other black azo dyes may be used. For other colors inorganic pigments or dyes such as Rhodamine, Chrysoidine and their lakes, Spirit Blues, Malachite and Diamond Green, Victoria Blue base or Cerasine Red may

[195] British P. 456,898, 1936, to British Celanese, Ltd.; *Chem. Abs.*, 1937, 31, 2457.

[196] P. Allman and H. N. Morris, British P. 206,461, 1927; *Chem. Abs.*, 1929, 23, 2541; *Brit. Chem. Abs.* B, 1928, 827.

[197] E. M. Davidson, *loc. cit.*

[198] British P. 482,436, 1938, to Shellmar Products Co.; *Rev. Paint, Colour, Varnish*, 1938, 11, 281.

[199] E. M. Davidson, U. S. P. 2,091,966, Sept. 7, 1937, to Continental Can Co.; *Chem. Abs.*, 1937, 31, 7677.

[200] A. A. Shannon, U. S. P. 1,880,502, Oct. 4, 1932, to Eastman Kodak Co.; *Chem. Abs.*, 1933, 27, 675.

[201] British P. 287,124, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 349.

[202] H. Wobornik, *loc. cit.*

[203] E. B. Middleton, U. S. P. 1,833,086, Nov. 24, 1931, to DuPont Film Mfg. Co.; *Chem. Abs.*, 1932, 26, 931.

[204] A. F. Caprio and W. Bowker, U. S. P. 1,931,485, Oct. 24, 1933, to Celluloid Corp.; *Chem. Abs.*, 1934, 28, 662; *Brit. Chem. Abs.* B, 1934, 685; *Rev. Paint, Colour, Varnish*, 1934, 7, 22.

[205] E. M. Davidson, U. S. P. 2,091,966, Sept. 7, 1937, to Continental Can Co.; *Paint Tech.*, 1937, 2, 320; *Chem. Abs.*, 1937, 31, 7677; *Rev. Paint, Colour, Varnish*, 1937, 10, 413.

[206] A. F. Caprio and W. Bowker, U. S. P. 1,931,485, Oct. 24, 1933, to Celluloid Corp.; *Chem. Abs.*, 1934, 28, 662.

be employed.[207] The pigment content of the inks may vary from 10 to 60 per cent, according to the strength of color desired and the applied printing method.[208] So-called body-forming substances may be added to the pigment, such as light magnesium carbonate.[209]

Ordinary oil-printing inks are also used; for example, in printing regenerated cellulose articles (*e.g.*, sausage casings). An illustration is an ink consisting of a pigment, *e.g.*, titanium white, in a vehicle comprising waterproof spar varnish, paraffin, petroleum jelly and lithographic boiled linseed oil.[210] Cellophane may be coated with an alcoholic solution of an appropriate resin to make it more water-resistant before printing.[211] Colored powder may be applied by sprinkling on a print made with lithographic or typographic ink containing a flatting varnish. A solution of white shellac may be used as a substitute for the ink if metallic powder is used.[212] Moisture-proof Cellophane surfaces may be prepared for printing by applying a pigmented adhesive to them. The adhesive comprises glucose and water, a small amount of glycerol, gelatin, very little castor oil, and a pigment. A paper label is coated with this mass and then pressed on the Cellophane by means of a heated die bearing the design. After that, the paper is removed and printing ink applied to the pigmented areas.[213]

Compositions having the ingredients mentioned above are applied to motion-picture films. As the films go through various mechanical and chemical operations, *e.g.*, polishing, developing, fixing and washing, inks must be resistant to certain agents employed in these operations.[214] The inscriptions are further protected by coating them with a colloid, such as benzylcellulose dissolved in a mixture of acetone and benzene, which is insoluble in any solvents used in the treatment of films and which does not affect the dye.[215] An ink used for printing on cellulose ester films, such as cellulose acetate, is composed of approximately equal volumes of methyl "Cellosolve" (ethylene glycol monomethyl ether) and its ace-

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[207] E. M. Davidson, *loc. cit.* A. A. Shannon, *loc. cit.* A. F. Caprio and W. Bowker, *loc. cit.* J. H. Clewell, U. S. P. 1 806,965, May 26, 1931, to DuPont Viscoloid Co.; *Chem. Abs.*, 1931, **25**, 4138; *Brit. Chem. Abs.* **B**, 1932, 234. E. B. Middleton, *loc. cit.* H., Lummerzheim and E. Schnitzler, U. S. P. 1 828,974, Oct. 27, 1931, to Agfa Ansco Corp.; *Chem. Abs.*, 1932, **26**, 662; *Rev. Paint, Colour, Varnish*, 1932, **5**, 90.

[208] W. W. Mock, U. S. P. 2,081,949, June 1, 1937, to International Printing Ink Corp.; *Chem. Abs.*, 1937, **31**, 5188; *Rev. Paint, Colour, Varnish*, 1937, **10**, 342.

[209] E. M. Davidson, *loc. cit.*

[210] J. Voss, U. S. P. 1,929,394, Oct. 3, 1933, to Visking Corp.; *Chem. Abs.*, 1934, **28**, 351; *Brit. Chem. Abs.* **B**, 1934, 571; *Rev. Paint, Colour, Varnish*, 1934, **7**, 23. British P. 380,317, 1932, to Visking Corp.; *Chem. Abs.*, 1933, **27**, 5994; *Brit. Chem. Abs.* **B**, 1932, 1041.

[211] H. Prüfer, Austrian P. 139,842, 1934; *Chem. Abs.*, 1935, **29**, 2763; *Rev. Paint, Colour, Varnish*, 1935, **8**, 209.

[212] P. Corombelle, Belgian P. 362,030, 1929; *Chem. Abs.*, 1930, **24**, 4647.

[213] A. D. Eisenberg, U. S. P. 1,891,323, Dec. 20, 1932, to Continental Process Corp.; *Chem. Abs.*, 1933, **27**, 2052.

[214] A. A. Shannon, U. S. P. 1,880,502, Oct. 4, 1932, to Eastman Kodak Co.; *Chem. Abs.*, 1933, **27**, 675; *Brit. Chem. Abs.* **B**, 1933, 837; *Rev. Paint, Colour, Varnish*, 1933, **6**, 335.

[215] British P. 287,124, 1927; *Chem. Abs.*, 1929, **23**, 349; British P. 295,578, 1927; *Chem. Abs.*, 1929, **23**, 2113; both to I. G. Farbenind. A.-G. Another method, which does not make use of printing, for inscribing titles on photographic films is to remove, wholly or partially, the emulsion layer by means of a solvent, after the development of the film. A mineral acid or an alkali is used. In colored films the dye may be bleached by the use of an oxychloride, a peroxide, chlorine water, a perborate, permanganate, or a dichromate. The letters thus formed are transparent and they may be, if desired, printed with an ink or dye. (R. Hruska. British P. 411,335, 1934; *Chem. Abs.*, 1934, **28**, 7187; British P. 438,272, 1935; *Chem. Abs.*, 1936, **30**, 2508.)

tate, containing in solution cellulose acetate and an azo dye.[216] Another composition comprises a nigrosine base and shellac dissolved in diacetone alcohol, the drying period of the latter being decreased by adding triacetin.[217]

Linseed oil should not be used in inks for printing on organic cellulose derivatives, as it renders the print transferable to polishing plates.[218]

To bring about quick setting of an ink, the undried print is dipped into molten wax (*e.g.*, paraffin) at 100 to 150° C. The ink should contain a relatively high-boiling solvent miscible with the hot wax and not evaporating when coming into contact with the latter. Such a solvent is, *e.g.*, dimethyl phthalate. When the wet print comes into contact with heated wax, the solvent is absorbed by the latter, thus bringing about precipitation of the pigment. To obtain a hard, adhesive and non-smearing film, a thickener may be admixed, *e.g.*, nitrocellulose.[219]

PRINTING ON GLASS AND CERAMICS

Printing on vitreous surfaces, such as glass and ceramics, is done in two steps, *i.e.*, first applying the ink to the surface, then fixing the impression by applying heat to fuse the surface material with the ink.[220] Other methods of applying marks and designs are known which, however, are not satisfactory in all instances. One of these is to form the design in the mold in which the article is cast and apply enamel by stencil or hand. The objection to this procedure is that it requires the skill of an artist; consequently it is too expensive and not applicable to articles of mass production. Etching with hydrofluoric acid or sand blasting is used to prepare glass bottles for printing, which is done by the "cold color" process. Cold-color printing is done by heating the ink to about 300° F. to set the lacquer after the impression is made. This procedure is different from the method used in which the ink is fused into the glass or china surface by raising the temperature to the fusing point of the material. After the ink has set, a heat, alkali, acid and abrasion-proof varnish is applied over the printed label.[221]

Another method, particularly for marking electric bulbs, involves the use of an ink containing glass enamel of low melting point. This is often unsatisfactory, too, since the heat used in the manufacture of lamps is too low to fuse the enamel satisfactorily with the glass; therefore the abrasion resistance of the print is relatively low. Also, the comparatively low heat applied results in residual carbon from the oil (ink vehicle) which is incompletely oxidized, leaving a more or less dark hue on the glass.

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[216] A. A. Shannon, *loc. cit.*

[217] J. H. Clewell, *loc. cit.*

[218] A. F. Caprio and V. Bowker, *loc. cit.*

[219] W. W. Mock, U. S. P. 2,081,949, June 1, 1937, to International Printing Ink Corp.; *Chem. Abs.*, 1937, 31, 5188; *Rev. Paint, Colour, Varnish*, 1937, 10, 342.

[220] For a discussion of printing on ceramic and glass articles see G. C. Müller, *Glas-ind.*, 1912, 23, 4; *Chem. Abs.*, 1912, 6, 1216. Also, *Glas-ind.*, 1913, 24, No. 17; *Chem. Abs.*, 1913, 7, 3004.

[221] D. W. Knaggs, U. S. P. 2,119,546, June 7, 1938, to Anigraphic Process, Inc.

Characters printed by this method are rather translucent and not clearly distinguishable from the glass. To increase opacity, various metallic oxides may be added, but these cannot be burned into the glass below a temperature which melts the glass.[222]

Transfer of the design to ceramic or glass ware may be accomplished by lithographic or relief printing.[223] In other instances an oil print of the design is made on the article with the aid of a rubber stamp.[224] Afterwards the oil film is dusted with the selected pigment and the printed object subjected to a heating or firing operation at a temperature of approximately 1050 to 1080° F. Another method involves etching the design on a steel plate, printing with the latter on thin sheets of paper, and transferring the ink from the paper to the ceramic article. It is advantageous that prior to the printing operation the paper be coated on one side with a thin film of soap and the ink applied to this side. By so doing, the ink does not come directly in contact with the paper and is more readily transferred to the ceramic or glass ware. Also, paper is easily removed from the latter by means of warm water which dissolves the soap film and thus destroys the medium connecting ink and paper.

In another procedure a composition is used which, after being printed, is burned into the article during an operation in the manufacturing process which requires heating, such as the sealing in of the stems of electric lamps to the bulbs.[225]

Inks for printing on glass consist of a fusible pigment in a vehicle which is burned off after the ink is applied. Pigments include a metal or metallic oxide as coloring substance, together with a flux for the metal and the glass. An enamel, incorporated into castor oil, may be composed of black copper (cupric) oxide, 1 pound, fused with boric acid, 1.5 pounds; litharge, 1 pound, and zinc oxide, 1.5 pounds, fused with boric acid, 6 ounces, and cryolite, 1.5 ounces. The two fuses are powdered and mixed in the proportion of 2:1. The powder is incorporated in $\frac{1}{5}$ its weight of castor oil.[226] Fredenburgh employs silver oxide with lead borate in a proportion of about 70:30. These are incorporated in a mixture of linseed oil and gum dammar or in glycerol. Both these vehicles provide an ink which is sufficiently tacky for glass surfaces. At the fusing temperature, between 400 and 500° C., the borate forms a colorless glass with metallic silver distributed in the molten mass. The silver gives to the markings a metallic white appearance of high opacity. Oxygen liberated during heating raises the temperature, thus assuring good fusion and also oxidizing carbon resulting from decomposition of the liquid vehicle.[227]

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[222] M. N. Fredenburgh, U. S. P. 1,538,890, May 26, 1925; *Chem. Abs.*, 1925, **19**, 2277.

[223] W. Schertel, *Ber. Tech.-wiss. Abt. Ver. keram. Gewerke in Deutschland*, 1919, **5** (5), 34; *Chem. Abs.*, 1921, **15**, 739.

[224] V. H. Remington, *Glass Ind.*, 1937, **18**, 267; *Chem. Abs.*, 1937, **31**, 8851.

[225] D. K. Wright, British P. 212,938, 1923, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1924, **18**, 2230.

[226] D. K. Wright, *loc. cit.*

[227] M. N. **Fredenburgh**, *loc. cit.*

Other metallic oxides such as those of cobalt, manganese, uranium[228] or metals such as nickel, iron, copper, chromium, selenium red,[229] the nitrate or other salts of cobalt[230] may be used as coloring agents. The powdered metallic pigment may be mixed with lead oxide, white lead or minium because lead compounds, when molten, adhere strongly to glass or other vitreous surfaces. Also, a flux such as borax, lead borate,[231] potassium carbonate,[232] as well as glass,[233] may be used to insure thorough amalgamation of the metallic oxides with the printed surface. By heating the vehicle (linseed oil) with minium or another lead oxide to secure a product having a high content of lead, the use of a flux is made unnecessary, since the lead present insures good adhesion.[234]

In applying the ink to the surface, the finely ground solid ingredients are suspended in a vehicle which usually consists mainly of linseed oil. The latter may be boiled[235] or raw.[236] The desired consistency for printing may be obtained by adding various substances to linseed oil, such as natural balsams, *e.g.*, capivi balsam; essential oils, *e.g.*, oil of amber,[237] lavender oil or clove oil, or animal fat.[238] The vehicle may be boiled while read lead is added. During simmering the metallic oxides are added, and after being cooled the mass is ground. As previously mentioned a flux may be avoided by boiling linseed oil with minium. The cooking is continued until the oil absorbs no more of minium and becomes dark and resinifies on cooling, thus furnishing a product similar in appearance to colophony. Coloring matter may be incorporated during the cooking and stirring of the mass.

A new preparation suitable for "cold-color" printing processes, or printing without subsequent baking or fusing, contains 1177 parts by weight of a heat-convertible phenol-aldehyde resin, 1002 parts of rosin-glycerol ester, 105 parts of rosin, 3109 parts of drying oil (tung oil, raw and cooked) and 178 parts of lead and cobalt naphthenate drier dissolved in 932 parts of chlorinated diphenyl having a distilling range of 278 to 360° C. This ink is resistant to abrasion and the action of dilute acids and alkalies.[239]

A vehicle for silver oxide and lead borate as coloring materials includes, as mentioned above,[240] either glycerol or a mixture of linseed

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[228] British P. 211,718, 1923, to Indelible Coloration Corp.; *Chem. Abs.*, 1924, 18, 1916. Also see W. C. Schroeder, U. S. P. 1,732,342, Oct. 22, 1930, to Indelible Coloration Corp.; *Chem. Abs.*, 1930, 24, 252.

[229] L. McLaughlin, U. S. P. 2.030,999. Feb. 18, 1936, to Western Electric Co., Inc.; *Chem. Abs.*, 1936, 30, 2411; *Rev. Paint, Colour, Varnish*, 1936, 9, 170. Canadian P. 337,714, 1933; *Chem. Abs.*, 1934, 28, 1879.

[230] H. G. Isbell, *Chemist-Analyst*, 1931, 20 (3), 20.

[231] M. N. Fredenburgh, *loc. cit.* L. McLaughlin, *loc. cit.*

[232] H. G. Isbell, *loc. cit.*

[233] L. McLaughlin, *loc. cit.*

[234] German P. 229,192, 1908, to Schmidt, Kassеker & Co.; *Chem. Abs.*, 1912, 6, 144.

[235] L. McLaughlin, *loc. cit.*

[236] H. G. Isbell, *loc. cit.*

[237] A. J. Q. Smith, British P. 211.718, 1923, to Indelible Coloration Corp.; *Chem. Abs.*, 1924, 18, 1916.

[238] German P. 229,192, 1908, to Schmidt, Kasseker & Co.; *Chem. Abs.*, 1912, 6, 144.

[239] F. G. Oswald, U. S. P. 2,111,802, March 22, 1938, to John W. Masury and Son; *Chem. Abs.*, 1938, 32, 3992.

[240] M. N. Fredenburgh, U. S. P. 1,538,890, May 26, 1925; *Chem. Abs.*, 1925, 19, 2277.

oil and gum dammar, in case of which equal parts of both ingredients are employed, and the total quantity is equal to that of the pigment. Gum dammar provides the tack necessary on glass surfaces. To facilitate milling of the ink, a small proportion of benzol, which is later evaporated, is added to the composition. If glycerol alone is used as a vehicle, its proportion may vary from 35 to 65 per cent by weight of the pigment. Methyl alcohol may be added to accelerate grinding and afterwards removed by evaporation.

Ink is applied to glass or ceramics by means of an ordinary rubber stamp,[241] or by a device which includes a rubber stamp adjusting itself automatically to curved surfaces.[242] Also, offset printing or transfers by decalcomania process,[243] autotypy or phototypy [244] may be used in applying inks to glass or ceramic surfaces.

It may be mentioned that a process of printing on artificial stone involves impregnating the surface with an insoluble compound of a heavy metal and coating the part of the surface to be printed with glue, gum dextrin or similar substance. Subsequent application of hydrogen sulphide solution, by dampening a stamp pad with the liquid, will precipitate the sulphide of the heavy metal on the coated areas.[245]

PRINTING ON METAL AND METAL FOIL

Metal foils, especially those of tin, lead and aluminum, are employed to a large extent in wrapping articles.[246] Since aluminum has a high affinity for greasy substances, ordinary lithographic or typographic ink [247] may be applied to the metal, which will properly hold the print. Alkaline pigments are likely to affect aluminum; therefore such pigments as laketine or magnesia should be controlled carefully. Acids in pigments in these circumstances have little or no effect.[248]

Transparent inks printed on metal foils often show a brilliant effect due to the metallic sheen of the surface. Inks must possess good adherence and great strength of color in order to attain the desired contrast with glossy foils.[249]

Since the surface is non-absorbent, the inks dry mainly by oxidation. As the same effects may be obtained with a few ink lines as with full coverage, the former is preferable because of faster drying. Drying

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[241] M. N. Fredenburgh, *loc. cit.*

[242] British P. 212,938, 1923, to British Thomson-Houston Ltd.; *Chem. Abs.*, 1924, **18**, 2230.

[243] L. McLaughlin, U. S. P. 2,030,999, Feb. 18, 1936, to Western Electric Co., Inc.; *Chem. Abs.*, 1936, **30**, 2409; *Rev. Paint, Colour, Varnish*, 1936, **9**, 170. Canadian P. 337,714, 1933; *Chem. Abs.*, 1934, **28**, 1879. For the discussion of decalcomania transfers see Chapter 12.

[244] German P. 229,192, 1908, to Schmidt, Kasseker & Co.; *Chem. Abs.*, 1912, **6**, 144. Discussion of the mentioned photographic transfers can be found in Chapter 11.

[245] A. N. P. Jacobs, British P. 211,896, 1923; *Chem. Abs.*, 1924, **18**, 2232.

[246] G. Wallace, *Am. Ink Maker*, 1936, **14** (3), 19; *Chem. Abs.*, 1937, **31**, 6034; *Brit. Chem. Abs.* **B**, 1936, 1217; *Rev. Paint, Colour, Varnish*, 1936, **9**, 377.

[247] See Chapter 9 and Chapter 7 for the description of lithographic and typographic inks, respectively.

[248] J. E. Filler, *Nat. Lithographer*, Feb., 1935; *Am. Ink Maker*, 1935, **13** (3), 23; *Rev. Paint, Colour, Varnish*, 1935, **8**, 207.

[249] For reviews of methods for printing on metal surfaces, see J. W. McHugh, *Ind. Finishings*, 1934, **10** (12), 15; *Rev. Paint, Colour, Varnish*, 1934, **7**, 508. Stefan, *Druck.-u.-Werbek*, 1938, **15**, 275; *Rev. Paint, Colour, Varnish*, 1938, **11**, 364.

troubles may be diminished by the use of 0.25 to 1 oz. of cobalt drier per pound of ink. Although it is possible to obtain dry prints within 5 to 8 hours, forced drying may result in crystallization, which makes application of successive colors difficult. One method is that of natural air-drying, which often requires about 24 hours.[250]

Good adhesion is obtained by exclusion of air and dust between foil and ink film.[251] The metal may be treated before printing with a solvent (for fats) containing a small proportion of an adhesive, *e.g.*, resin or a cellulose ester, dissolved in trichloroethylene (C_2HCl_3).[252] The surfaces also may be prepared by coating with varnish or solutions of cellulose or cellulose derivatives, vegetable drying oils or juices, rubber, resins, casein or glue.[253] Printing ink with amyl acetate solution of nitrated cotton may be applied to tin foil.[254]

Metal foils for wrapping may be printed in special color effects by applying the pattern desired with a lacquer containing a heat-hardenable resin and heating the foil to the setting temperature. A cellulose-derivative lacquer may be printed on the printed or on the unprinted area of the foil, depending upon the effect wanted.[255]

To reduce tack or prevent offsetting, particularly of an impression of heavy ink coverage, powdered cornstarch may be added to the ink. However, caution must be exercised as to the amount employed, since the ink is apt to lift off the foil surface on slight abrasion if adhesion of the former is too small. Addition of a very small quantity of cornstarch per pound of ink is reported as satisfactory.[256]

As a reducing agent (for tack) a scratchproof varnish may also be employed. Usually an addition of 1 to 2 ounces per pound of ink will produce the desired effect.[257]

The amount of ink required to cover a given area of embossed patterns is reported to be double the quantity needed for a plane surface of equal area.[258]

When the required number of prints is small (under about 2500), ordinary zinc printing blocks may be employed, but for printing on larger scale the use of copper electrotypes is considered to be better. Rubber plates are of advantage when the paper side of foils mounted on paper is printed. The handling of printed material depends upon ink coverage, method of printing and kind of stock used.[259]

Aluminum plates with an oxidized surface may be printed by a water-repellent, colored or colorless substance; then the unprinted parts are

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[250] R. E. Hunt, *Am. Ink Maker*, 1934, 12 (11), 27; *Rev. Paint, Colour, Varnish*, 1934, 7, 456.

[251] G. Wallace, *loc. cit.*

[252] J. Modern, Austrian P. 114,650, 1929; *Chem. Abs.*, 1930, 24, 817.

[253] G. Manetti, P. Benaglia and M. Luchsinger, British P. 314,635, 1928; *Chem. Abs.*, 1930, 24, 1529; Italian P. 266,782, 1934; *Chem. Zentr.*, 1934, 105 (2), 1030.

[254] I. Nemoto, Japanese P. 31,446, 1917; *Chem. Abs.*, 1918, 12, 86.

[255] German P. 658,578, 1936, to Nestlé and Anglo-Swiss Condensed Milk Co., Ltd.; *Modern Plastics*, Sept., 1938, 56.

[256] R. E. Hunt, *Am. Ink Maker*, 1934, 12 (11), 27; *Rev. Paint, Colour, Varnish*, 1934, 7, 456.

[257] R. E. Hunt, *loc. cit.*

[258] R. E. Hunt, *loc. cit.*

[259] R. E. Hunt, *Brit. Printer*, 1935, 48 (284), 88; *Rev. Paint, Colour, Varnish*, 1935, 8, 401.

covered with a water-soluble color to give the first print the proper background. Compositions for this procedure consist of colorless beeswax with 3 per cent grease or wax-soluble Chrysoidine.[260] The mixture is applied in the liquid state by means of heated dies and the printed plate immersed for 20 minutes in an aqueous solution of 3-per cent Alizarin Saphirol B,[261] a dye derived from anthrarufin (1,5-dihydroxyanthraquinone). The original yellowish-orange color of Chrysoidine, which is left unchanged, is surrounded by the deep blue of the unprinted areas. Other mixtures involve the application of 100 parts hard colorless paraffin wax colored by 10 parts chrome oxide green[262] and immersed in an aqueous solution of "milling orange,"[263] which procedure gives green designs against an orange background. A solution of aminoazotoluene (1 to 5 parts) dissolved in a mixture of 100 parts of ethyl alcohol, 20 parts of turpentine and 50 parts of linseed oil is also used. This composition is applied to the metal plate by means of a spray pistol and stencils, and the dry print is given a blue-red background by an aqueous solution of 2-per cent Azo Fuchsine.[264] Similarly, the color of the design printed first is left unchanged. Metallic bands may be coated with a sticky material such as varnish, then dusted with powdered pigment or metallic powder and excess powder wiped off.[265]

PRINTING ON LACQUER, VARNISH, AND COLLOIDS

Lacquers or varnishes may be printed with inks which amalgamate with the hardened surfaces by penetrating, softening or dissolving them. To illustrate, an ink to use on shellac or other varnish has a vehicle consisting of alcohol, diethyl phthalate and an ethyl ester, such as the lactate or oxalate, to soften and penetrate the varnish.[266] An ink for printing, for example, photographically reproduced leather designs on nitrocellulose lacquer-coated sateen consists of nitrocellulose dissolved in a mixture of ethyl alcohol, butyl alcohol and ethyl acetate, and a pigment and castor oil.[267] Nitrocellulose lacquer surfaces may be improved (for printing operations) by spraying thin films of solutions of soft resins on them or by incorporating soft oil-modified Glyptal resins into the lacquers.[268]

Other vehicles suggested for inks intended for printing on lacquers or varnishes consist of a cellulose ester or ether dissolved in water-soluble mono- or di-formates of polyhydric alcohols.[269] Examples of the latter

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[260] G. Schultz, "Farbstofftabellen," 5th ed., Berlin, Weidmann, 1914, No. 33.

[261] G. Schultz, "Farbstofftabellen," 5th ed., Weidmann, Berlin, 1914, No. 858. See also R. N. Shreve, "Dyes Classified by Intermediates," The Chemical Catalog Co., Inc., New York, 1922.

[262] G. Schultz, "Farbstofftabellen," 5th ed., Weidmann, Berlin, 1914, No. 971.

[263] G. Schultz, "Farbstofftabellen," 5th ed., Berlin, Weidmann, 1914, No. 147.

[264] British P. 439,403, 1935, to Peintal soc. anon.; *Chem. Abs.*, 1936, **30**, 3399; *Rev. Paint, Colour, Varnish*, 1936, **9**, 93. Swiss P. 176,415, 1935, to Peintal soc. anon.; *Chem. Abs.*, 1936, **30**, 75.

[265] Australian P. 12,342, 1933, to Gerrard Industries Ltd.; *Chem. Zentr.*, 1934, **105** (2), 1030; *Rev. Paint, Colour, Varnish*, 1934, **7**, 377.

[266] C. L. Cunningham, U. S. P. 1,562,514, Nov. 24, 1925; *Chem. Abs.*, 1926, **20**, 513.

[267] H. J. Jenemann, U. S. P. 2,102,715, Dec. 21, 1937, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1938, **32**, 1360; *Rev. Paint, Colour, Varnish*, 1938, **11**, 111.

[268] *Ind.-Lack-Betrieb*, 1937 (3/4), A22; *Rev. Paint, Colour, Varnish*, 1937, **10**, 95.

[269] British P. 311,795, 1928, to I. G. Farbenind. A.-G.; *Rev. Paint, Colour, Varnish*, 1929, **2**, 198; *Brit. Chem. Abs.* **B**, 1929, 609.

compounds (alcohols) which are applicable include ethylene-, propylene- or 1,3-butylene-glycol and also glycerol. Other water-soluble organic liquids, such as ethyl alcohol, acetone or ethylene chlorhydrin may be incorporated into the solution.

The printing of hydrophilic colloids has always been difficult; the impressions were made superficially, and, as a consequence, they tended to be diffused and easily rubbed off. Direct prints with opaque inks containing such pigments as titanium oxide frequently flaked off and exhibited considerable bleeding. Such difficulties are obviated, however, by printing upon the colloid when it is in the gel condition, thereby producing a print that is in some degree absorbed below the surface and in this way protected from abrasion. The gel is first conditioned by impregnating it with a water-miscible solvent for the dye to be used in printing it. The pigments which are used in the process may be Plutoform Black, Benzo Fast Red L and GL, Benzo Fast Yellow, Benzo Pure Blue, Columbia Blue, and Diamine Deep Black. The dye is dissolved in a vehicle consisting of a mixture of triethanolamine, butyl ether of diethylene glycol, methyl ether of glycol, diethylene glycol, and water. The proportions of the constituents may be varied, depending on the characteristics of the colloid to be printed. When used, the ink penetrates the gel, and as the vehicle evaporates, the dyes remain inside the colloid.

A second method of printing upon such hydrophilic colloids employs inorganic pigments. The colloid, in the gel condition, is impregnated with a salt solution, either throughout the body of the object, or in special areas which will form a design. A second salt, which will react with the first to form a precipitate, is then applied to the pellicle of colloid. Thus, if a colloid which has been conditioned with sodium dichromate is printed with a solution of lead acetate, an insoluble yellow precipitate of lead dichromate will be deposited in the interior of the material. Ferric ferrocyanide, lead sulphate, or cadmium sulphide, which form respectively blue, white and light yellow pigments, may be precipitated in the pellicle, and may be used as a background for printed matter as produced in the first procedure (above paragraph), or they may be employed by themselves to produce printed material.[270]

PRINTING ON RUBBER

Rubber printing inks should be free from pigments or driers containing copper, iron, lead or manganese, since they either affect the surface or form dark sulphides on vulcanization. For this reason also copper vessels or stirrers should be avoided in the manufacture of the inks. Red iron oxide free from copper or manganese may be used, also chrome yellow and chrome green. But the latter are often replaced by cadmium yellow mixed with ultramarine for green colors, since chrome pigments often

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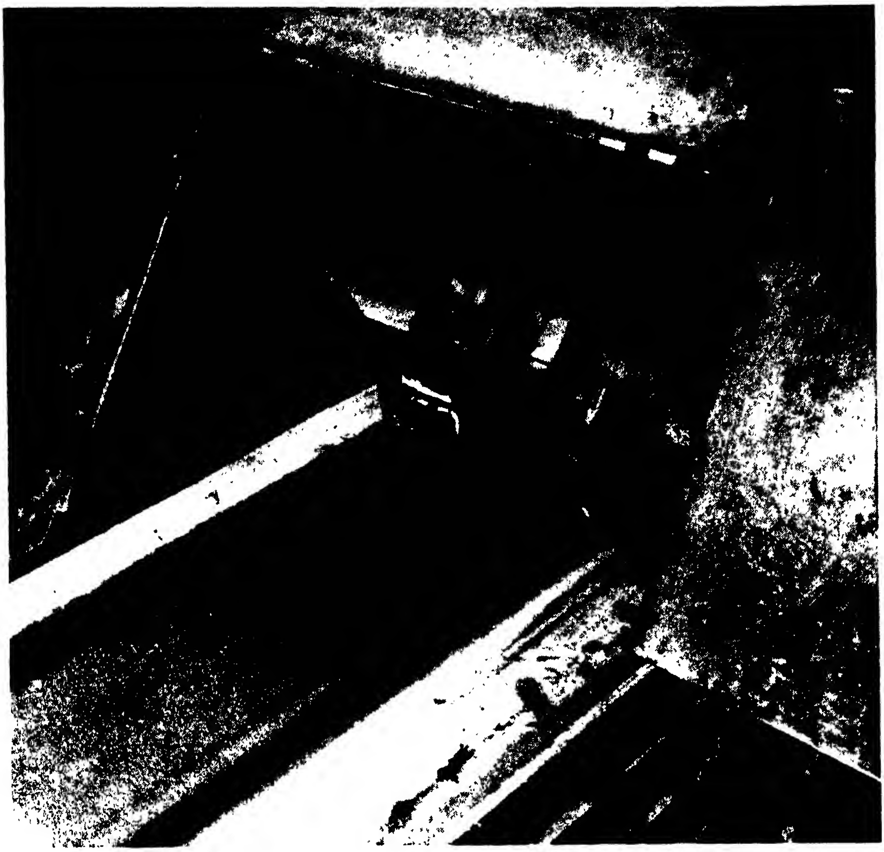
[270] T. K. Cornwell, U. S. P. 2,121,021 and 2,121,022, June 21, 1938, to Sylvania Industrial Corp.; *Chem. Abs.*, 1938, 32, 6083.



Courtesy The Rubber Age
Courtesy American Ink Maker

FIGURE 66. Direct Printing of Inner Tubes (R. A. Crawford and D. B. Forman).

render the finished article tacky. Solvents which tend to swell rubber, such as benzene, petroleum or turpentine, are to be avoided.[271]

The rubber may be dusted with powdered sulphur (which combines with the rubber on vulcanization), and ink or colored rubber composition [272] applied and the material then vulcanized.[273] Markings or designs may be applied by fixing a transfer sheet, marked with copying ink containing glycerol, gum or glucose, to the rubber surface, which is then vulcanized and the marking thus transferred. The process is applicable for marking rubber insulation of electric cables.[274] An ink containing

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[271] P. Kluckow, *Farben-Ztg.*, 1932, **38**, 380; *Chem. Abs.*, 1933, **27**, 855; *Rev. Paint, Colour, Varnish*, 1933, **6**, 3.

[272] S. Saul, British P. 275,298, 1927; *Chem. Abs.*, 1928, **22**, 2292.

[273] R. T. Griffiths, U. S. P. 1,516,598, Nov. 25, 1924; *Chem. Abs.*, 1925, **19**, 420.

[274] J. Bowyer, British P. 317,620, 1928, to Callender's Cable & Construction Co., Ltd.; *Chem. Abs.*, 1930, **24**, 2329; *Brit. Chem. Abs.* **B**, 1929, 864.

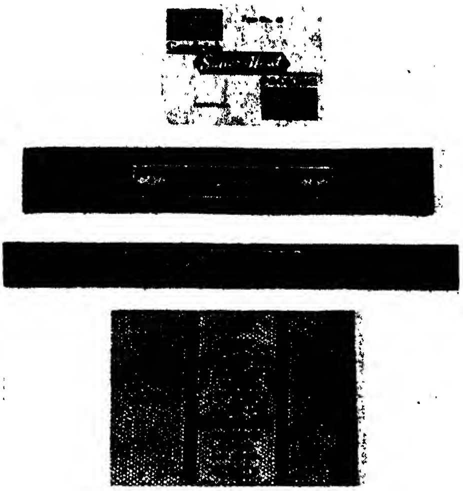


FIGURE 67.

Branding of Packings and Belts (R. A. Crawford and D. B. Forman).

Courtesy The Rubber Age
Courtesy American Ink Maker

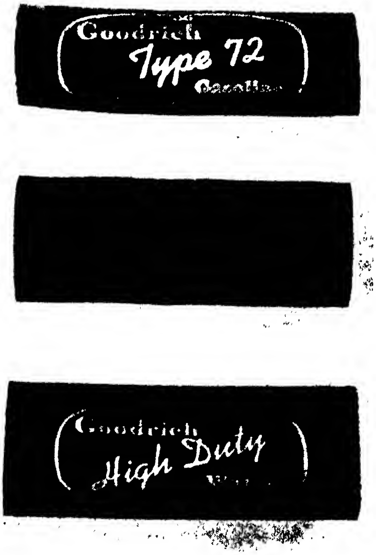
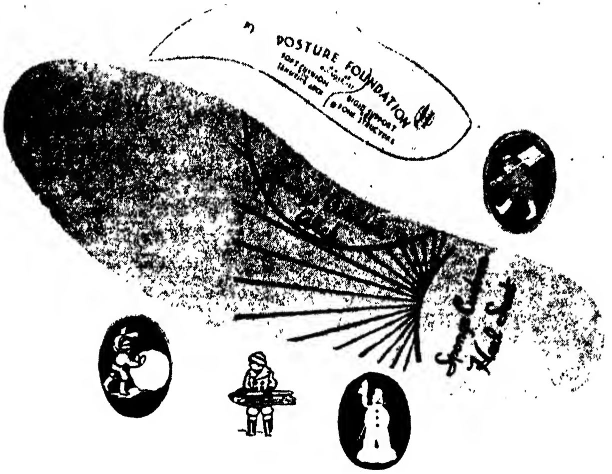


FIGURE 68.

Printed Mechanical Hose Labels (R. A. Crawford and D. B. Forman).

Courtesy The Rubber Age
Courtesy American Ink Maker



Courtesy The Rubber Age
Courtesy American Ink Maker

FIGURE 69. Assortment of Footwear Labels (R. A. Crawford and D. B. Forman).

glycerol as a vehicle and lead chromate is made by boiling precipitated lead chromate and, before it is quite dried, grinding it into the glycerol. The ink may be used with a stamp pad on rubber tensile strips and will not be absorbed by the surface on stretching the rubber several hundred per cent.[275] The ink is also reported to be highly resistant to heat and water.

Rubber may be printed with inks which penetrate the surface. Such a composition consists of an aqueous solution of an aniline dye admixed with a small amount of fat or naphtha, or a water-soluble pigment dispersed in latex. To promote penetration, the rubber may be warmed or covered with a film of latex.[276] Another ink acting by penetration of rubber surfaces consists of a soluble color substance, alcohol-soluble induline, dissolved in a hydrogenated derivative of phenol, naphthol or naphthalene, such as tetrahydronaphthalene.[277] To the hydrogenated solvent other volatile organic compounds, for example, acetone, or methylethyleneglycol, may be added. Also, heat-liquefied rubber has been utilized in printing on rubber.[277a]

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[275] C. G. Cashion, *Ind. Eng. Chem.*, 1927, **19**, 45; *Chem. Abs.*, 1927, **21**, 836; *Brit. Chem. Abs.* **B**, 1927, 147.

[276] M. M. Dessau, British P. 204,668, 1922, to Plantation Rubber Mfg. Co., Ltd.; *Chem. Abs.*, 1924, **18**, 1067; *J. S. C. I.*, 1923, **42**, 1187A.

[277] H. N. Morris, U. S. P. 1,715,209, May 28, 1929; *Chem. Abs.*, 1929, **23**, 3587; *Brit. Chem. Abs.* **B**, 1929, 651; *Rev. Paint, Colour, Varnish*, 1929, **2**, 283. P. Allman and H. N. Morris, British P. 296,461, 1927; *Brit. Chem. Abs.* **B**, 1928, 827; *Chem. Abs.*, 1929, **23**, 2541.

[277a] R. A. Crawford and D. B. Forman, *Am. Ink Maker*, 1939, **17** (3), 21. *The Rubber Age*, 1938, **43** (5), 281.

SPECIAL INKS FOR PRINTING ON SOFT PAPER

Inks applied to paper napkins are required to be resistant to water and may have binding media, *e.g.*, glue or albumin, which become insoluble by printing at high temperatures.[278] Another ink for paper napkins is prepared by dissolving water-insoluble tannin lakes of aniline dyes in a spiritous solvent such as alcohol.[279]

On colored paper a white or clear-tone ink may be used. An illustration of the latter is a composition which consists of 100 g. titanium dioxide dispersed in a solution of 100 g. casein in 1 liter water, the latter containing 13 g. ammonia per liter.[280]

Billings[281] suggests that inks intended for printing on paper towels can be rendered antiseptic by incorporating an appropriate proportion of a mixture consisting of 1 part nutgalls, 2 parts fir balsam, 2 parts extract of hemlock, 3 parts beeswax, 1 part pine balsam and 2 parts carbolated Vaseline.

PRINTING ON TEXTILE FABRICS

Designs or markings may be printed on textile fabrics with printing inks of widely varying compositions.[282] Possibly one of the first of these was that described by Reed and Eastwood,[283] which consisted of a coloring agent incorporated into a solution of nitrocellulose in alcohol and camphor. Drying was effected by allowing the solvent to evaporate.

Waterproof colored designs may be applied with the aid of a water-insoluble colored body, such as a "Sudan dye," which is oil- or fat-soluble and is incorporated into lithographic varnish.[284] Curd soap is added to the varnish in a proportion of 25 per cent of the latter.[285] A washable ink, which is removable also by brushing, but is resistant to hydrocarbons, contains zinc white and a small amount of gelatin glue dispersed in a solution consisting of thymol, glycerol and water.[286] Printing or marking resistant to reagents used in various fabric-treating processes may be effected by a composition including a pigment or dye dispersed in a stabilized emulsion of natural latex or prepared rubber. If necessary, a swelling agent, such as benzene, and a filler, such as china clay, may be added. For example, a paste of china clay with an aqueous solution of ammonium oleate is admixed with a coloring substance, *e.g.*, Monolite

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[278] M. Fleischer and H. C. Fleischer, British P. 268,340, 1926, to Seidenpapier Fabrik Eislingen; *Chem. Abs.*, 1928, 22, 1244.

[279] H. C. Fleischer, British P. 409,272, 1934; *Chem. Abs.*, 1934, 28, 6001.

[280] French P. 788,406, 1935, to P. Chouanard & Fils & Cie. (Soc. Veuve); *Chem. Abs.*, 1936, 30, 1595; *Rev. Paint, Colour, Varnish*, 1936, 9, 170.

[281] W. T. Billings, U. S. P. 1,233,962, July 17, 1917; *Chem. Abs.*, 1917, 11, 2619.

[282] For a number of formulas of such inks see *Tiba*, 1926, 4, 45; *Chem. Abs.*, 1926, 20, 1143.

[283] P. Reed and J. Eastwood, U. S. P. 256,596 and 256,597, April 18, 1882; *J. S. C. I.*, 1882, 1, 187.

[284] Lithographic varnish is prepared by bodying raw linseed oil. See Chapter 3.

[285] H. A. Wolinski, British P. 406,324, 1934; *Chem. Abs.*, 1934, 28, 4818; *Brit. Chem. Abs.* B, 1934, 413.

[286] C. J. Bullinger, U. S. P. 1,162,027, Nov. 30, 1915; *Chem. Abs.*, 1916, 10, 256.

Yellow G. Afterwards rubber latex is incorporated, and then benzene is added as an emulsifying agent.[287]

Textile fabrics coated with a cellulose ester, *e.g.*, cellulose nitrate, may be printed with a solvent-free ink. The latter composition includes 20 to 80 per cent of a pigment, and 0.015-2.0 per cent of a lead or cobalt drier dispersed in a drying oil-modified polyhydric alcohol-polybasic acid resin. The drying oil should be 45 to 60 per cent of the resin. This ink is said to dry tack-free in 12 to 16 hours and to remain plastic on the press for about 4 hours.[288]

Inks which are resistant to dyeing and bleaching operations are used for printing or marking cellulose acetate fabrics; they may consist of a cellulose derivative solution, drying or semi-drying oil and a pigment. Such an ink may be produced, for instance, by grinding a dispersion of lead chromate in linseed oil or tung oil into a solution of nitrocellulose in ethyl acetate or in a mixture of ether and alcohol.[289]

Another composition for marking cellulose ester textiles or other fabrics contains a pigment, *e.g.*, carbon black, suspended in a liquid which is a solvent or swelling agent for the cellulose derivative. (Liquids of this type have been discussed in the section dealing with inks for printing Celluloid and Cellophane.) The vehicle should have a boiling point higher than 150° C. and be free from film-forming substances and solid thickening agents. A partially esterified polyhydric alcohol mixed with a lower monocarboxylic acid is useful, for example, glycol monoacetate and acetic or formic acid.[290]

Suspensions of powdered aluminum, copper or brass dispersed in pastes of glue, gelatin or similar materials often serve for the production of metallic prints on cotton, rayon or other fabrics.[291] Following the printing operation and drying of the films, the printed material is subjected to pressure by passage between calender rollers. Cellulose or its esters, natural or synthetic rubber, albumin or casein may be incorporated into the paste as fixing agents.

One type of synthetic rubber, a polymerization product of diolefins, finds application as a bodying agent when used in a paste with such materials as zinc oxide, lampblack, and soluble or insoluble dyestuffs as fillers.[292]

Interpolymerization products of the various vinyl ethers, such as vinyl

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[287] L. P. Rendell and G. E. Scharff, British P. 405,315, 1934, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1934, **28**, 4614; *Brit. Chem. Abs.* **B**, 1934, 334. See also French P. 759,114, 1934; *Chem. Zentr.*, 1934, **105** (2), 183; *Rev. Paint, Colour, Varnish*, 1934, **7**, 294.

[288] D. McBurney and E. H. Nollau, U. S. P. 2,049,507, Aug. 4, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 6586; *Brit. Chem. Abs.* **B**, 1937, 947.

[289] H. Platt and C. Dreyfuss, British P. 396,759, 1927, to British Celanese, Ltd.; *Chem. Abs.*, 1929, **23**, 2585; *Brit. Chem. Abs.* **B**, 1929, 728. Canadian P. 317,112, 1931; *Chem. Abs.*, 1932, **26**, 1459.

[290] W. I. Taylor and L. B. Gibbins, British P. 473,627, 1937, to British Celanese, Ltd.; *Chem. Abs.*, 1938, **32**, 3176; *Brit. Chem. Abs.* **B**, 1938, 693. U. S. P. 2,165,522, July 4, 1939, to Celanese Corp. of America.

[291] P. Bellecour, *Industrie Textile*, 1937, **54**, 298; *J. Text. Inst.*, 1937, **28**, 556A; *Rubber Res. Abs.*, 1937, **15** (12), 795; *Rev. Paint, Colour, Varnish*, 1938, **11**, 108.

[292] British P. 334,961, 1930, and 373,233, 1932, to I. G. Farbenind. A.-G.; *Rev. Paint, Colour, Varnish*, 1930, **3**, 244; 1932, **5**, 276.

methyl ether, vinyl octadecyl ether, formaldehyde glycerol acetal vinyl ether, may be used with pigments to make pastes for printing on fabrics.[293]

It is recommended, when printing on fabrics is carried out with engraved cylinders, that mineral or tar oil, natural or paraffin wax, or mixtures of these be added to the ink to prevent corrosion of the cylinders or other parts of the apparatus.[294] If starch is employed as the thickening agent, oleic or other carboxylic acids of high molecular weight may be included also. The addition of the higher-boiling fractions of benzine is said to prevent foaming.

INKS FOR PACKAGES, WRAPPERS AND LABELS

Inks used in printing labels for cartons or wrappings must possess resistance to light, heat and water, and also must be reasonably resistant to any chemical action of the contained product.[295] Thus, resistance to various alkalies and acids may be necessary. Also, non-bleeding in alcohol is often required.[296] Soap-wrapper inks must be alkali resistant.[297] An example of an ink vehicle resistant to soap is one prepared by reacting an oil-soluble phenol-formaldehyde resin with China Wood oil and dissolving the reaction product in 0.5 to 1 part of a hydrocarbon oil.[298]

Cheese-wrapper inks are subjected to the action of free volatile acids, amino-acids, ammonia and compounds containing the latter,[299] these substances being produced by decomposition of various cheese products. Wrappers for meat products must be printed with inks which do not run, due to the action of lactic acid in the meat.[300]

Extremely odor-free inks are required for odor-sensitive products such as butter.

Most important is the question of toxicity. Distinction should be made between inks coming directly in contact with the wrapped product and those printed on the outside of wrapping material. Any possibility of ink offsetting should be carefully examined and preventive measures taken accordingly.[301]

The printing methods more frequently applied in this field are aniline printing (q.v.) for glassine, waxed paper and cellulosic, *e.g.*, Cellophane, wrappers. On the other hand, multicolor rotary printing is not objection-

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[293] W. Reppe, F. Hoelscher and A. Schneevoigt, U. S. P. 2,108,994, Feb. 22, 1938, to General Aniline Works, Inc.; *Chem. Abs.*, 1938, 32, 3166.

[294] British P. 226,164, 1923, to A. Holtman & Co.; *Chem. Abs.*, 1925, 19, 1784.

[295] *Paint Manuf.*, 1932, 2, 173; *Rev. Paint, Colour, Varnish*, 1932, 5, 232. E. F. Nurse, *Paper and Print*, 1939, 12 (1), 38; *Rev. Paint, Colour, Varnish*, 1939, 12, 180.

[296] C. E. Foss, *Am. Ink Maker*, 1932, 10 (4), 33; *Chem. Abs.*, 1932, 26, 5438; *Rev. Paint, Colour, Varnish*, 1932, 5, 116.

[297] L. F. Hoyt, *Oil & Soap*, 1935, 12, 48; *Chem. Abs.*, 1935, 29, 2768. Also, *Papier-Ztg.*, 1938, 63, 1288; *Rev. Paint, Colour, Varnish*, 1938, 11, 363.

[298] L. M. Larsen, Canadian P. 376,599, 1938, to Interchemical Corp.; *Chem. Abs.*, 1938, 32, 9530.

[299] W. Kühn, *Farben-Chem.*, 1934, 5, 205; *Brit. Chem. Abs.* B, 1934, 636; *Molkerei-Ztg.*, 1934, 48, 1882; *Chem. Abs.*, 1935, 29, 1526.

[300] R. Roley, *Am. Ink Maker*, 1938, 16 (6), 18.

[301] R. Roley, *loc. cit.*

able in the case of folding cartons, paper milk containers and other heavier varieties of paper.[302]

In formulating the vehicles for the inks for food wrappers, certain types of oils must be excluded. Those considered undesirable because of their toxicity are tung oil and rosin oil; and fish oils, because of their penetrating odor. Mineral oils are not employed, since they do not dry to hard, insoluble films. Rapeseed oil should be avoided because of its bitter taste and slightly rancid odor. Oils commonly used are linseed. soybean and perilla. The last is favored, as it yields practically odorless varnishes.[303]

Selection of resins also should be carefully considered, especially for food wrappers. Synthetic resins, which are entirely odorless and nontoxic, are those of the pale ester gum or maleic anhydride-rosin-glyceride type.[304] With regard to natural resins, those of the copal type, particularly "Manila Loba C" and "Run Congo No. 11," are reported[305] as most suitable to be employed in inks for wrappers of odor-sensitive products. Loba resins, being of light color, are desirable where the proper color of ink is important. Natural resins of the dammar variety have been found to impart a definite odor to the wrapped material, especially to butter.[306] The odor in many cases can be removed from varnish oils by blowing superheated steam through them.[307]

Driers which may be used with safety are soaps of cobalt and manganese. Lead and cerium driers are to be avoided in food-wrapper inks, since they are considered highly toxic. Linoleates possess less odor than resinates or naphthenates. A mixture of cobalt linoleate and manganese borate ground into a perilla oil (which has been bodied) is said to be a satisfactory varnish.[308]

Toxic pigments, of course, must be similarly avoided, such as those containing lead, cadmium, mercury, copper or arsenic. Many organic lakes and toners free of lead salts may be used, for example, phosphotungstic and phosphomolybdic pigments. Generally speaking, all pigments free from heavy metals and arsenic, and that are insoluble in water and oils, may be regarded as nontoxic.[309]

Another satisfactory variety of pigments in this field is the phthalocyanine blues. Their properties, which are especially appropriate, are fastness to acids, alkalies and light, as well as resistance to reducing and mild oxidizing agents. Phthalocyanine blues may be employed in inks for printing soap wrappers, parchment paper, posters, bags containing various chemicals, such as lime, salt, acid powders, fertilizers, etc., medi-

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[302] R. Roley, *loc. cit.*

[303] R. Roley, *loc. cit.*

[304] R. Roley, *loc. cit.*

[305] J. H. Holzberger, *Am. Ink Maker*, 1938, 16 (4), 25; *Chem. Abs.*, 1938, 32, 5086.

[306] J. H. Holzberger, *loc. cit.*

[307] R. Roley, *Am. Ink Maker*, 1938, 16 (6), 18.

[308] R. Roley, *loc. cit.*

[309] R. Roley, *loc. cit.*

cinal labels, metal foils for cheese wrappers. Their resistance to heat makes them useful for printing paper which is afterwards coated with molten wax, such as caps for milk bottles or drinking cups.[310] In the cap-drawing process the cardboard, when in contact with the stamp, is subjected for a short time to a heat of about 220° C. Therefore inks for printing bottle caps must be resistant to heat and not contain softening substances.[311]

MEAT-MARKING INKS

An ink for stamping meat products may contain spirit-soluble nigrosine, which, after being digested with a mixture of glycerol and glacial acetic acid, is admixed with ethyl alcohol.[312] Another composition consists of Methyl Violet base dissolved in oleic acid and ether.[313]

Animal products may be marked with an agent which penetrates the surface and changes the color of the tissue or walls of fat cells.[314] Sulphuric or nitric acid may be used for this purpose. A composition of this type consists of hydrochlorate of nitrobenzene, induline or nigrosine as coloring agents, incorporated with a mixture of glycerol and hydrochloric acid.[315] An ink which contains a protein precipitant, *e.g.*, formaldehyde, may be employed for marking sausage skins and other animal matter. The vehicle consists of waterproof spar varnish, petroleum jelly and boiled linseed oil in which powdered alum or a formaldehyde solution is incorporated as a protein precipitant. At least 50 per cent by weight of pigment, *e.g.*, titanium dioxide, should be present.[316] The applied marking is reported to be water- and smoke-resistant.

PRINTING ON FRUITS

An ink for printing on fruits consists of coloring matter, *e.g.*, phenolic solution of a spirit color, a color lake, a vehicle of amyl acetate and methyl alcohol and a phenol-formaldehyde resin, such as Bakelite A.[317]

The printing of vegetable fibers is improved by inclusion in the ink of a water-soluble salt of cymenesulphonic acid. The salts which may be used are those of copper, iron, potassium, sodium, ammonium, and also those of aniline, ethanolamine and pyridine. Glycerol, ethylene glycol, and thiodiglycol, and a hydrotropic agent such as urea, diethylmetanilic

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[310] *Am. Ink Maker*, 1937, **15** (8), 17.

[311] W. Kühn, *Papier-Ztg.*, 1937, **62**, 1448; *Chem. Zentr.*, 1938, **109** (1), 741; *Rev. Paint, Colour, Varnish*, 1938, **11**, 109.

[312] L. S. Paddock, U. S. P. 1,895,641. Jan. 31, 1933, to Swift & Co.; *Chem. Abs.*, 1933, **27**, 2505; *Brit. Chem. Abs.* **B**, 1934, 28; *Rev. Paint, Colour, Varnish*, 1934, **7**, 22.

[313] L. S. Paddock, U. S. P. 1,868,071, July 19, 1932, to Swift & Co.; *Chem. Abs.*, 1932, **26**, 5220; *Brit. Chem. Abs.* **B**, 1933, 436.

[314] R. W. Johns, U. S. P. 1,863,903, June 21, 1932, to Swift & Co.; *Chem. Abs.*, 1932, **26**, 4390.

[315] J. Hauser, U. S. P. 875,174, Dec. 31, 1907; *Chem. Abs.*, 1908, **2**, 1204.

[316] C. T. Walter, British P. 447,368, 1935, to Industrial Patents Corp.; *Brit. Chem. Abs.* **B**, 1936, 652; *Chem. Abs.*, 1936, **30**, 7884. See also U. S. P. 2,119,729, June 7, 1938; *Chem. Abs.*, 1938, **32**, 5953; Canadian P. 373,465, 1938; *Chem. Abs.*, 1938, **32**, 5098. Both patents to Industrial Patents Corp.

[317] M. Sinozaki, Japanese P. 93,651, 1931; *Chem. Abs.*, 1933, **27**, 1529. See also Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935, 453.

acid, or benzylanilinesulphonic acid may be included in the ink. Anthraquinone, or its derivatives, used as a reducing catalyst, sodium hyposulphite, as a reducing agent, and an alkali are also used in producing the vehicle. To the mixture made by these materials, a dyestuff is added to complete the paste which is used as a basis for the ink.[318]

INK FOR LINOLEUM

In printing designs on linoleum or other floor coverings of like character, the usual practice has been to employ an enamel (*i.e.*, drying oil varnish and pigment) and apply such to the covering with the aid of wooden blocks. The disadvantage connected with the use of such printed films is the long time required for their drying. Several compositions have been proposed in the endeavor to overcome or mitigate this objectionable feature.

Whitescarver and Hopkins[319] suggest employment of a varnish consisting of a glycerol-phthalic anhydride resin modified with rosin and dissolved in a drying oil. This varnish then may be admixed with an appropriate quantity of pigment. However, in some cases the varnish may be diluted with approximately an equal quantity (by weight) of a hydrocarbon solvent, either aliphatic, aromatic, or a mixture, boiling at 150 to 200° C.

Printing lacquers applicable for floor coverings and containing nitrocellulose have been described also. A typical example is one containing the following ingredients:[320] 10 parts of nitrocellulose, 25 parts of ester gum, 30 parts of xylene, 30 parts of fenchone, 5 parts of dibutylphthalate, and 25 parts of pigment. Semi-drying oils, for example castor oil,[321] or drying oils, *e.g.*, linseed oil,[322] as well as esters such as ethyl or butyl lactate and triphenyl phosphate may be incorporated also.

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[318] O. Albrecht and M. Bommer, U. S. P. 2,128,599, Aug. 30, 1938; British P. 486,445, 1938; *Chem. Abs.*, 1938, 32, 8795; both to Soc. pour l'ind. chim. à Bâle.

[319] W. F. Whitescarver and H. H. Hopkins, U. S. P. 1,942,736, Jan. 9, 1934; *Chem. Abs.*, 1934, 28, 1880.

[320] D. R. Wiggam, U. S. P. 1,966,846, Apr. 9, 1935, to Hercules Powder Co.; *Chem. Abs.*, 1935, 29, 3539; *Rev. Paint, Colour, Varnish*, 1935, 8, 221.

[321] British P. 275,949, 1926, to Armstrong Cork Co.; *Chem. Abs.*, 1928, 22, 2476; *Brit. Chem. Abs.* B, 1928, 866.

[322] F. T. Walker and A. C. Hetherington, British P. 360,815, 1930, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1933, 27, 1222.

Chapter 15

Printing Inks for Miscellaneous Purposes

SPECIAL PRINTING PROCESSES

The preceding chapters have discussed the more frequently employed printing processes, such as typographic, planographic, lithographic, offset, photogravure and intaglio, the main constituents of inks—their vehicles, their pigments, and other constituents employed in them—and emulsion inks. In this chapter are reviewed the more unusual inks and printing effects. Many of the ink compositions to be discussed, such as those for wood grain effects and embossing, and bleachable and safety inks, find only limited applications. Others are novel in that they are intended for such purposes as the preparation of games, trick displays, and unusual advertising schemes. These inks are the fluorescent, sympathetic, and phosphorescent types. Included also are types of composition which may be designated "semi-printing" inks. These are neither press inks, nor are they actually writing inks, but they are employed nevertheless in what may be called printing, or at least duplicating, processes. Therefore their inclusion is made to cover completely the field of inks used in making (by duplication or otherwise) printed pages or illustrations.

Wood Grain Effects. By various methods an imitation wood grain may be printed on metals, paper, stone and cheap wood. Many times such cheap woods as pine and maple are printed with a graining to simulate rarer and more expensive wood, such as mahogany or oak. Wallpaper may be printed so as to give the effect of wood panelling. Objects made of metal, such as safes and metal sills and window frames, are sometimes made to look like wood by graining or veining them.

One method for printing grained effects employs an ink composed of 60 per cent ethylene glycol, 7.5 per cent water with 30 per cent pigment and 2.5 per cent gum arabic. This ink can be applied on wood, metal or Pyroxylin (nitrocellulose) finishes.[1] The wood or metal surface may be covered first with a coat of nitrocellulose lacquer and then the graining imprinted with an oil paste to which has been added acetone or some other solvent for nitrocellulose.

Graining may be done by first printing on the material the basic color of the wood, that is, the shade of the lightest parts. Over this the veining is printed in a darker shade. The wood to be counterfeited is photo-

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[1] J. M. Verderosa, British P. 315,214, 1928, and French P. 673,452, 1929, to E. I. du Pont de Nemours and Co.; *Chem. Abs.*, 1930, 24, 1753, 2622.

graphed and this photograph is made into a half-tone block for printing. The impression is made by the intaglio offset process.[2]

In some instances, prior to the printing operation, the surface of the wood may be prepared by coating it with a foundation containing gelatin, albumin or other similar colloidal substance mixed with a hardening agent, such as chrome alum, formalin, or potassium dichromate. The wood is then printed with a greasy ink by a half-tone prepared from a photograph, as mentioned above.[3]

Another procedure provides a permanent, non-bleeding pigment, imitating the grain of wood in printing, dispersed in a vehicle composed of about 4 per cent of a resin, such as shellac, accroides, kauri or elemi, and a small amount of alkali resin solvent, such as ammonium hydroxide. The solvent consists of a mixture of terpineol and higher alcohols of a boiling point ranging from 150 to 230° C. The vehicle should be a non-solvent for cellulose esters.[4]

Printing on Leather. In the printing of leather, special precautions have to be observed as to the preparation of the surface to receive the ink. The leather is sometimes tanned with formalin vapor instead of by the usual tanning methods.[5]

Sometimes the tanned skin may be treated with a solution of nitrocellulose or other cellulose derivative which will serve as a color-retaining base. The design is printed on this priming layer with a casein-carried pigment and, after it has dried, the leather is given another thin coating of the material used in priming. The printed object then is finished by glazing.[6] By the condensation of aromatic hydrocarbons with cellulose waste products in the presence of normal aliphatic alcohols, neutral or slightly acid vegetable oils and naphthenesulphonic acid, a filler or bodying agent for a leather-printing ink is said to be formed. In the preparation of the condensation product, 5 parts of collodion are mixed slowly with 25 parts of a slightly acid vegetable oil and 5 parts of cellulose waste products until the mass is homogeneous. To this mixture 1 part of methyl or ethyl alcohol is added and the whole is emulsified with a mixture containing 12 parts of tetrahydronaphthalene, 5 parts of water, and 0.5 part of alkylated naphthenesulphonic acid. The tetrahydronaphthalene may be replaced as solvent by an organic solvent, such as benzene, toluene, xylene, trichloroethylene, or carbon disulphide.[7] A solution of nitrocellulose to which coloring matter and alcohol have been added may be used for printing on skins.[8]

[2] British P. 318,554 and 319,000, 1929, to Masa Ges. m. b. H. Zur Herstellung Künstlicher Oberflächen; *Rev. Paint, Colour, Varnish*, 1929, 2, 332. French P. 681,214. 1929; *Chem. Abs.*, 1930, **24**, 4409.

[3] L. J. Francis, British P. 322,279, 1928; *Chem. Abs.*, 1930, **24**, 2857.

[4] C. B. Hemming, U. S. P. 2,008,018, July 16, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1936, 652; *Rev. Paint, Colour, Varnish*, 1935, 8, 348; *Chem. Abs.*, 1935, **29**, 6082.

[5] Y. Matsukane, Japanese P. 31,733, 1917; *Chem. Abs.*, 1918, **12**, 1259.

[6] P. Blatz, U. S. P. 1,985,675, Dec. 25, 1935; *Rev. Paint, Colour, Varnish*, 1935, 8, 161; *Chem. Abs.*, 1935, **29**, 1278.

[7] French P. 678,685, 1929, to Soc. anon. pour l'ind. chim. à Saint-Denis; *Chem. Abs.*, 1930, **24**, 3662.

[8] P. Reid and J. Eastwood, U. S. P. 256,596 and 256,597, April 18, 1882, to Celluloid Mfg. Co.; O. A. G. Mandelsloh, German P. 560,469, 1929; *Chem. Abs.*, 1933, **27**, 1216.

A procedure for printing with a glossy finish on leather consists of three steps. First the material is coated (by hot calendering) with a lacquer composed of 12.1 parts of nitrocellulose, 18.6 parts of pigments, 27.5 parts of castor oil, tricresyl phosphate or dibutyl phthalate, and 41.8 parts of solvent. A second lacquer is applied containing blown cottonseed oil in place of the castor oil. The last coat consists of blown castor oil or rapeseed oil.[9] Silver or bright impressions may be made on leather using a vehicle of gum dammar thinned with China Wood oil and having a powdered metal pigment.[10]

Printing on Wood. Special consideration must be taken in the printing of wood, the surface of which is so absorbent that a priming coat must always be applied to prevent the ink from soaking in too much. The surface, after being smoothed, is sponged with a mixture of ammonium hydroxide and hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), and then with hot water. In case the wood does not absorb water readily, 10 per cent of glycerol may be added to the hot water.[11]

An alternative procedure involves the use of a coating preparation consisting of a solution of 50 parts of rubber, 30 parts of white wax and 60 parts of Canada balsam in 700 parts of turpentine, 20 parts of linseed oil, and 650 parts of benzene. Afterwards the wood may be printed with a fatty ink and subsequently coated with a varnish or lacquer for protection against mechanical and chemical deterioration.[12]

Printing on Wall Paper. The inks employed in printing wall papers are made usually of pigments mixed with starch paste, glue, gum or some other adhesive material. A mixture consisting of powdered casein in 3 to 7 times its volume of water, and borax to the extent of 12 to 18 per cent of the casein may serve as a binder. The mixture is heated to dissolve the casein and borax, and the desired pigment is incorporated. After the paper is printed, the casein is made relatively insoluble either by passing the paper through a solution of formaldehyde or by allowing it to come into contact with the aldehyde vapors.[13] A good binding agent is said to be prepared by emulsifying 3 gal. of water, 2 qts. of kerosene, and 1 qt. of linseed oil with the aid of 1½ lbs. of soap powder and adding 2 lbs. of tapioca flour. The mixing is done in the cold and the composition is boiled until it becomes pasty.[14] Most wall paper printing must be done in two steps because of the necessity of printing a ground (background) color and a design on top of it. However, by printing the ground color with an oil ink and the overdesign with a water-soluble pigment, it is reported that the two operations may be done at the same time without fear of blurring the colors. The oil color, dissolved in turpentine, is applied with a smooth roller, while the paste color for the

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[9] Australian P. 22,568, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Zentr.*, 1936, 107 (2), 3208; *Rev. Paint, Colour, Varnish*, 1936, 9, 381.

[10] F. A. Putman, U. S. P. 1,203,779, Nov. 7, 1916; *Chem. Abs.*, 1917, 11, 104.

[11] J. Richardson, British P. 409,424, 1934; *Chem. Abs.*, 1934, 28, 6260.

[12] E. Josz, U. S. P. 902,886, Nov. 3, 1909, to Soc. anon. du Joxyl; *Chem. Abs.*, 1909, 3, 694.

[13] A. Fleury, French P. 350,249, 1904; *J. S. C. I.*, 1906, 25, 71; *Chem. Abs.*, 1907, 1, 1196.

[14] C. J. Heidorf, U. S. P. 1,358,151, Nov. 9, 1921; *Chem. Abs.*, 1921, 15, 438.

second printing may be thinned with glycerin and printed on the undried ground.[15]

Color differences in printed matter are obtained by increasing pressure on different parts of the print while passing through the press.[16]

The use of waste vulcanized rubber as a fixing agent [17] has come to be well known. Old automobile tires may be used and the waste mixed with enough fresh rubber to give the product stability. The mixture is dissolved in a solution of camphor oil and naphtha, and copal varnish added as a diluent. Aside from being rather economical, the main advantage claimed for rubber is that it renders the printed material very flexible so it can be bent without cracking. The rubber solution is found also to be a protective agent against mildew and rust. Metal powders such as bronze and aluminum may be added as pigments for unusual effects in the wall paper.[18]

Embossing Inks. Although genuine embossing is a distinct art in itself and not strictly related to printing, except in the case of what is called color embossing, many types of inks have been composed which imitate the appearance of a raised finish. In plain embossing, a crest or design is cut in a steel die or plate and the impression made by the use of a die upon the paper, which is backed by a relief die faced with gutta-percha. In color embossing, the ink is brushed on the die and the surface cleaned, leaving ink only in the depressed portions of the plate. In what is called cameo embossing, the ink is applied only to the flat parts of the die with a small roller and the depressed portions are left uncolored. Small hand-embossing presses often are used by notary publics to imprint their seals on documents.

The expense and slowness of embossing has caused the search for cheaper and mass-production means of producing the same effect. Most of this pseudo-embossing is done either by thermography, a process by which an ink, usually oily and slow-drying, is coated after printing with a fusible material, which is molded by means of a heated die,[19] or by the use of an ink which contains a swelling agent which will be affected by heat. Powdered shellac may be fused on the characters printed in an ink composed of 73 per cent boiled linseed oil, 8 per cent rosin, 12 per cent carbon black, and 6 per cent Prussian Blue. Another composition which may be used consists of 1½ pounds of glycerol, 1 pound of dextrin, and 4 ounces of aniline color. Many viscous liquid materials which are hygroscopic may be used as substitutes for glycerol.[20] The fusing agent to be applied may be a powdered polymerization product of hydrocarbons of the diene series, or more specifically, of those compounds initially containing the group $:C:CH_2$.[21]

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[15] H. Burmann, French P. 378,680, 1907; *J. S. C. I.*, 1907, **26**, 1137.

[16] C. Bittinger, U. S. P. 1,629,250, May 17, 1927; *Chem. Abs.*, 1927, **21**, 2194.

[17] See Chapter 5.

[18] G. Rice, *The Rubber Age*, 1931, **28**, 611. For a general discussion of wall paper printing and coloring, see F. Kuhne, *Farbe und Lack*, 1931, **36** (46), 514; (47), 520; (48), 530.

[19] D. G. Elson, U. S. P. 1,438,815, Dec. 12, 1923; *Chem. Abs.*, 1923, **17**, 888.

[20] S. Lipsius, British P. 10,089, 1915; *Chem. Abs.*, 1917, **11**, 104.

[21] German P. 576,889, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, **27**, 3790.

Other compositions which are useful as embossing inks, which are reported to be very slow-drying, and which contain paracoumarone, are described by Schneider.[22] One is composed of 100 parts of dibutyl phthalate, 100 parts of paracoumarone resin, and 2½ parts of a drier; the other of 100 parts of paracoumarone, 50 parts of dibutyl phthalate, 50 parts of butyl stearate, and 2½ parts of a drier.

An example of the type of ink which is self-expanding is one composed of 10 parts of yellow dextrin, 1 part of sodium bicarbonate, 0.5 part of a pigment, and water. The leavening agent is the bicarbonate which decomposes when heated, releasing carbon dioxide.[23]

A vehicle is used that will dissolve shellac. The colored granular shellac is spread on the wet print and then fused.[24]

Tighe [25] reports the use of rosin admixed with aluminum oxide as an embossing medium. A resinous thermographic base is used and the mixture of rosin and aluminum oxide dusted thereon. Aluminum oxide of such grain size as to be visible to the naked eye is used.

INDELIBLE AND RESISTANT INKS [26]

Fabric and Laundry Marking Inks. Indelible inks were developed for the purpose of marking raw fabrics for identification and having the ink remain uneradicated during bleaching and subsequent processes. These inks are also needed for use in modern commercial laundries where articles should have identifying marks stamped or printed on them which will remain for the life of the fabric.

An ink for marking cotton and linen which are to be bleached is composed of 1 part of coal tar thinned with 1 part of naphtha and 1/10 part pine soot.[26a] The material is stamped with this ink and dried. Another formula requires 1 liter of a solution of 200 g. of tartaric acid in 1 liter of hot water, to which 100 g. of aniline oil are added, and, after this mixture becomes homogeneous, due to vigorous stirring, 100 g. of potassium chlorate are dissolved in the solution. It may be necessary to add more hot water to dissolve all of the chlorate. When the solution has cooled, it is allowed to stand about 24 hours and afterwards is filtered from the crystals of potassium bitartrate which have formed. The density of the clear solution of aniline chlorate (so-called) should be 7° Bé. The liquid is thickened to the desired viscosity with gum arabic, and immediately before use 20 g. of copper sulphate are added. The printed areas should be allowed 24 hours to dry, after which they may be bleached. The alkaline bleaching material and the chlorite of lime acting upon the ink develop and make permanent the black color.[27] An easily prepared mark-

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[22] A. Schneider, U. S. P. 1,992,016, Feb. 19, 1935; *Chem. Abs.*, 1935, 29, 2375. U. S. P. 1,966,907, July 17, 1934; *Rev. Paint, Colour, Varnish*, 1934, 7, 483; *Chem. Abs.*, 1934, 28, 6002.

[23] G. W. Brenizer and C. C. Hutson, U. S. P. 1,436,856, Nov. 28, 1923; *Chem. Abs.*, 1923, 17, 642.

[24] S. Lipsius, U. S. P. 1,928,668, Oct. 3, 1933.

[25] J. J. Tighe, U. S. P. 2,128,105, Aug. 23, 1938, to Norton Co.: *Chem. Abs.*, 1938, 32, 8174.

[26] F. Marginol, "Encres Speciales," Desforges, Girardot, and Cie, 1928; *Rev. Paint, Colour, Varnish*, 1929, 2, 303.

[26a] See also A. I. Kosoi, Russian P. 46,647, 1936.

[27] *Reimann's Farberzeitung; Pol. C.-Bl.*, 29, 652; *Chem. Zentr.*, 1875, 6 (3), 576.

ing ink that is reported to be used in Hawaii on sugar bags consists of one pound of glue dissolved in one gallon of hot water, to which one pound of lampblack is added. It is stated that after two years of use, printing made with this ink would not smear with handling and was practically indelible.[28]

The crushed fruit of *Semecarpus anacardium* may be extracted with a liquid such as methylated spirit, gasoline, benzene, naphtha, ether, alcohol or carbon tetrachloride and the resulting solution treated with an alkali, *e.g.*, sodium carbonate, to neutralize the free acid. The liquid may then serve as an indelible marking ink when the mark, after being printed, is touched with dry soda ash or with a dilute solution of the salt.[29]

There are many indelible inks containing metals as the pigments. In most of them the desired metal is in the form of an unstable salt that decomposes and deposits the metal in the fibers of the cloth. Silver, gold, platinum, manganese, chromium, and lead salts are often employed. The formulas usually include gum arabic as a thickener, sodium carbonate, and some organic acid or a salt.[30]

A laundry marking ink is composed of hematin extract, potassium dichromate, dilute hydrochloric acid, tannin and ferric chloride.[31] An ink which is invisible except when made fluorescent by ultraviolet light is used sometimes. The ink is very viscous and contains a dissolved fluorescent substance such as petrolatum or xylene. During dry cleaning or laundering practically all of the composition is removed except minute particles of the fluorescent substance, which are left in the fabric.[32]

Indelible Inks for Paper. There are many inks for the printing of permanent records and for the prevention of fraud in connection with documents, checks, and various other securities.[33] Ferrous and ferric salts may be added to black printing inks, and since these salts form compounds with the cellulose of the paper and the substances used in sizing, it is easy therefore to detect any attempt to remove the black.[34] By adding a dye to a mixture of turpentine, asphaltum, resin, alum, and beeswax, an indestructible ink for paper may be made. In this case, however, it is the vehicle which protects the dye, and not the pigment itself which is indelible.[35] Another such ink may be made by dissolving 2 parts of asphalt and one part of aniline oil in 16 parts of a solvent, *e.g.*, carbon tetrachloride, and adding enough methyl salicylate (oil of wintergreen) to perfume the mixture.[36]

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[28] J. P. F., *Hawaiian Planters' Monthly*, 28, 424; *Chem. Abs.*, 1910, 4, 397.

[29] J. M. H. de Bretton, British P. 190,232, 1921; *J. S. C. I.*, 1923, 42, 151A; *Chem. Abs.*, 1923, 17, 2941.

[30] A. Chaplet, *Rev. mensuelle du blanchissage, blanchiment, apprets*, 1921, 15, 19, 23, 29, 32; *Chem. Abs.*, 1922, 16, 504.

[31] M. Shinozaki, Japanese P. 101,700, 1933; *Chem. Abs.*, 1934, 28, 5262.

[32] L. S. Smith, Jr., U. S. P. 2,056,809, Oct. 6, 1936; *Chem. Abs.*, 1936, 30, 8648.

[33] See also the section in this chapter on "Safety Inks and Paper."

[34] W. Reussig, German P. 17,462, 1881; *J. S. C. I.*, 1882, 1, 145.

[35] F. L. Leech and A. Horrobin, British P. 1616, 1891; *J. S. C. I.*, 1892, 11, 446.

[36] L. W. Luscher, U. S. P. 1,320,631, Nov. 4, 1920; *Chem. Abs.*, 1920, 14, 277.

By impregnating sized paper with sodium nitrite and using an ink containing dianisidine, β-naphthol, and oleic acid, a permanent printed record is obtained.[37] Lactic acid and a phenol or aromatic amine may be employed in an indelible ink which forms an insoluble azo color within the fibers of the paper.[38] The sensitizing agent may be an aqueous or alcoholic solution of tannic or gallic acid, with which a printing material is used containing ferrous nitrate or a chromate, such as that of potassium, dissolved in water or some other appropriate solvent.[39]

Diphenylamine is often a component of indelible inks, as for example, one containing 15 parts of castor oil, 15 parts of glycerol, 3 parts of aniline oil, 5 parts of diphenylamine, and a small amount of Methyl Violet. Another ink comprises 15 parts of soybean protein, 15 parts of aniline oil, 1 part of β-naphthol, 5 parts of diphenylamine, and 5 parts of varnish.[40]

A quick-drying ink consists of water, Lysol, sodium nitrate, gum arabic, and a water-soluble dye.[41] A mixture of 300 parts of Methylene Blue, 740 parts of powdered talc, 55 parts of gum tragacanth, 25 parts of Japan wax, 100 parts of calcium stearate and 80 parts of ether-purified tannic acid forms a base for an indelible ink.[42] A composition which, when used in printing mechanisms such as check-writers, will resist removal by organic detergents is composed of glycerol and a water-soluble leuco-ester salt of a vat dye, such as soluble Ponsole Jade Green. If the dye becomes colorless in the reduced state, it is advantageous to add an auxiliary organic dye or pigment.[43]

Waterproof Inks. One type of vehicle for waterproof inks is composed of an aqueous dispersion of an oily or resinous condensation product which forms a water-insoluble resin when exposed to air. Drying oil-modified synthetic resins obtained from polyhydric alcohols, polybasic acids and unsaturated higher fatty acids (*e.g.*, linoleic acid), or from phenol or urea, formaldehyde and drying oils are examples of condensation products which may be employed.[44]

By using a printing paste containing a solution of a water-soluble acid dye and water-soluble salts of amines (having at least one basic nitrogen atom and derived from an aliphatic hydrocarbon possessing 10 or more carbon atoms per molecule) in an organic solvent which will dissolve basic dyes, a waterproof ink is obtained. For example, a composition made of Fast Blue Cloth GTB [45] and *p*-stearylaminophenyltrimethylam-

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[37] W. J. Murray, U. S. P. 1,509,872, Sept. 30, 1924; *Chem. Abs.*, 1924, **18**, 3720.

[38] W. J. Murray, U. S. P. 1,514,222, Nov. 4, 1925; *Chem. Abs.*, 1925, **19**, 178.

[39] U. A. D'Inzeo, British P. 280,088, 1927; *Chem. Abs.*, 1928. **22**, 3055.

[40] Z. Hattori, Japanese P. 91,387, 1931, to Syotaro Ohara; *Chem. Abs.*, 1932, **26**, 1810.

[41] J. Rochat, Swiss P. 153,496, 1931, *Chem. Abs.*, 1933, **27**, 1217.

[42] Italian P. 286,597, 1936, to Soc. Anon. Matita Nazionale, Pennino Nazionale Prebistero; *Chem. Zentr.*, 1936, **107** (2), 877; *Rev. Paint, Colour, Varnish*, 1936, **9**, 316.

[43] B. W. Smith, U. S. P. 2,068,204, Jan. 19, 1937, to Todd Co., Inc.; *Brit. Chem. Abs.* **B**, 1938, 1334; *Chem. Abs.*, 1937, **31**, 2030.

[44] W. Lützkendorf, German P. 585,167, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1556. For the preparation of such resinous bodies, see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[45] "Schultz Dye Tables," 7th Ed., **1**, 552.

monium sulphomethylate was dissolved in a mixture of ethyl alcohol and glycerol to form a paste which may serve as a base for waterproof inks.[46]

FLUORESCENT AND PHOSPHORESCENT INKS

The phenomenon of fluorescence has been known for centuries, mostly as a curiosity and a plaything for magicians. The complete explanation is not entirely understood, however, even at present. Certain materials possess fluorescence, which is the property of absorbing light rays of one wave length and emitting those of a different, and usually longer, wave length. Fluorescein possesses this property to a great degree and can be used in very small quantities to test for leakage and seepage in pipes and underground passageways. Phosphorescence is very closely allied to fluorescence, and is thought to be merely a variation of the same phenomenon. Phosphorescence is the property of a material whereby it continues to emit light, which it absorbed at an earlier time, after the original source of light has been extinguished.

Many materials, such as collodial zinc, barium, strontium and calcium sulphides, become fluorescent when affected by energy in the form of radium or uranium emanations, or by ultraviolet light rays. The use of this property has been made in the production of fluorescent paints and printing inks.[47]

When radioactive material, such as a uranyl or radium salt, is incorporated into the ink with a fluorescent material, such as colloidal zinc sulphide, the printed matter produced by the ink will fluoresce independently of any light source, and the poster or sign printed will glow in a dark room, or even slightly in the light. When 50 parts of one of these radioreceptive materials are mixed with 40 parts of a radioactive salt, such as radium-barium sulphate or carbonate, or the salts of actinium, ionium, mesothorium, uranium, or polonium, a fluorescent mixture is secured, which, when incorporated with a pigment and a resin in hempseed or tung oil, will form an ink for printing. The drying oil chosen must be as colorless as possible so it will not interfere with the fluorescence.[48]

Most fluorescent inks, however, contain merely the radio-excited material, which is made to fluoresce by means of "black light," or invisible ultraviolet rays. This method of activation is simpler and much more useful in that the design printed may be changed by switching from visible illumination to ultraviolet rays, thus creating an interesting display for advertising purposes or for amusement.

One printing may be done in regular ink for illumination by visible light, while a second impression may be made in fluorescent ink for illumination by ultraviolet. Often the practice is to have a light burning in the vicinity of the printed matter, for example, a Cooper-Hewitt arc

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[46] Swiss P. 173,767, 1935, to Soc. pour l'ind chim. à Bâle; *Rev. Paint, Colour, Varnish*, 1935, 8, 403; *Chem. Abs.*, 1935, 29, 5681

[47] German P. 510,565, 1928, to Deutsche Gasglühlicht-Auer-G. m. b. H.; *Chem. Abs.*, 1931, 25, 879. A. Wakenhut, *Papier-Ztg.*, 1938, 63 (49), 1000; *Rev. Paint, Colour, Varnish*, 1938, 11, 280. See also *Deutscher Drucker*, 1937, 44 (518), 76; *Rev. Paint, Colour, Varnish*, 1938, 11, 24.

[48] E. F. Krapf, U. S. P. 1,097,981, May 26, 1914, to Joseph M. Flannery; *Chem. Abs.*, 1914, 8, 2627.

lamp, enclosed in a deep purple glass tube to exclude all or most of the visible rays.[49]

To prepare the ingredient for a fluorescent paint, one part of dry benzanthrone, finely powdered, is intimately mixed with 5 parts of zinc powder and the mixture is heated in a current of hydrogen, nitrogen, or carbon dioxide. The product of the reaction distills off as a heavy yellow vapor and condenses on the cold portions of the vessel in rather large crystals which may be recrystallized from acetone or alcohol. The yield is about 80 per cent.

The crystals so obtained have a yellowish green fluorescence and are very soluble in many organic solvents. The product is very stable thermally and is resistant to hot or cold acids and alkalies. When added in the proportion of about 1 to 10,000 to paraffin wax, it imparts to the latter a greenish yellow fluorescence.

Fifty parts of this product are dissolved in 1 liter of toluene and 20 per cent of Glyptal resin modified by a siccative acid. A varnish is obtained that will be strongly fluorescent when exposed to ultraviolet light. A 2-per cent solution gives a bluish green color, and a 0.2-per cent solution, a blue fluorescence.[50]

The double sulphate of uranyl and potassium can also be used as a fluorescent ingredient of ink. The salt is ground dry until it will pass through a screen of 150 meshes per square inch. It is then mixed with a vehicle which must be transparent to ultraviolet rays to cause fluorescence. Although the double sulphate of uranyl and potassium is the most desirable material, any uranyl salt, chemically stable and non-corrosive, may be employed. By dissolving 55 grams of the sulphate and 25 grams of a hydrocarbon polymerization product in 20 grams of toluol, a fluorescent ink is produced. A phthalic resin or Manila gum may be substituted as the bodying agent.[51]

A fluorescent ink can be made by dissolving anthracene and rubber in benzene, and adding a material such as sulphur chloride to the solution to vulcanize the rubber after printing.[52]

BLEACHABLE, SYMPATHETIC AND SAFETY INKS

Bleachable Ink. The economic value of bleachable inks is marked. Material, such as telephone books, printed with an ink which is easily obliterated, can be used over again by bleaching the ink and pulping the paper for the production of new sheets. One of the best pigments for such bleachable inks is a logwood-iron lake. Logwood contains considerable tannic acid which forms a pigment with ferrous salts and which may be ground with a mixture of blown castor oil and dibutyl phthalate to furnish a paste.[53] When printing is done with inks containing this

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[49] R. F. Salade, *Paper Conv. En. Ind.*, 1937, 11 (2), 10; *Rev. Paint, Colour, Varnish*, 1937, 10, 175.
[50] French P. 815,841, 1937, to Cie. Nat. de Mat. Col. du Nord; *Chem. Abs.*, 1938, 32, 1919.
[51] E. Schueller and L. Granderye, French P. 818,826, 1937; *Chem. Abs.*, 1938, 32, 2767.
[52] L. J. Buttolph, U. S. P. 1,658,476, Feb. 7, 1928; *Chem. Abs.*, 1928, 22, 1244.
[53] R. L. Drew, *Am. Paint J.*, 1936, 20 (36), 54; *Rev. Paint, Colour, Varnish*, 1936, 9, 220.

material in the form of a lake, the paper may be bleached by the application of sulphur dioxide.[54]

Several water-insoluble dyes, such as Palatine, Agalma, Brilliant or Diamond Black may be employed alone or with other water-insoluble dyes for making bleachable inks. The pigments may be used in the form of a lake or as the insoluble material precipitates from an acid solution. By preparing the dyes in the presence of such dispersing agents as Turkey-red oil, glue, or sulphonic acids or their salts, *e.g.*, alkylnaphthalene sulphonic acid, they will be precipitated in a more nearly colloidal state, making their application easier. Agalma black may be dissolved in water and precipitated by the addition of barium chloride, filtered, and mixed with a varnish. Any water present may be dispelled by warming or with the aid of drying rollers. Any of the pigments mentioned above may be bleached by the application of chlorine or of hypochlorites.[55]

Dyes that react with formaldehyde to give insoluble compounds may be used when hexamethylenetetramine is incorporated into the ink. Formaldehyde is liberated from the hexamethylenetetramine in the presence of water and heat of the press. The insoluble dyes formed are easily bleachable.[56] A bleachable ink is made by double printing so that an insoluble sulphide is formed by the action of the two inks used. An impregnated paper can be substituted for the first printing.[57]

Sympathetic Inks. Although sympathetic or invisible inks have been known and used for centuries, their extended and practical commercial use has been feasible only relatively recently. Their main advantage is their novelty. By printing part of an advertisement in invisible ink and giving simple directions for developing the material, the advertiser can call attention to his product in a way that will make the customer remember the message. However, one important fact to be taken into account is that unless the process of making the ink visible is quite simple, the experiment will not be done by many people. Besides the advertising value of sympathetic inks, there are other uses for them. Patterns for dresses may be printed across several pages of a newspaper to be brought forth if desired, and various games, toys, and novelty greeting cards may be made. Another application of such inks is in the making of tests and examinations for schools. The student answers the questions by applying

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[54] *Am. Ink Maker*, 1936, **14** (7), 23; *Rev. Paint, Colour, Varnish*, 1936, **9**, 315. See also *Z. Angew. Chem.*, 1926, **39**, 269; *Chem. Abs.*, 1926, **20**, 2071. *Paper Trade J.*, 1934, **98** (10), 41; *Chem. Abs.*, 1934, **28**, 2901. *Chem. Met. Eng.*, 1933, **40**, 634; *Rev. Paint, Colour, Varnish*, 1934, **7**, 22.

[55] British P. 320,430, 1928, to I. G. Farbenind. A.-G.; *Rev. Paint, Colour, Varnish*, 1929, **2**, 331; *Brit. Chem. Abs.* **B**, 1929, 1047. See also, French P. 657,516, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, **23**, 4356. Italian P. 340,553, 1937; *Chem. Zentr.*, 1937, **108** (2), 3967; *Rev. Paint, Colour, Varnish*, 1938, **11**, 25; Italian P. 340,159, 1937; *Chem. Zentr.*, 1937, **108** (2), 3967; *Rev. Paint, Colour, Varnish*, 1938, **11**, 26. Italian P. 342,214, 1937; *Chem. Zentr.*, 1937, **108** (2), 3676; *Rev. Paint, Colour, Varnish*, 1938, **11**, 25. German P. 225,275, 1908, to Aktein-Gesellschaft für Anilin-Fabrikation; *Chem. Abs.*, 1911, **5**, 1195. J. Hope, British P. 117,023, 1917; *Chem. Abs.*, 1918, **12**, 2451. E. Schering, British P. 239,113, 1925, to Chemische Fabrik auf. Aktein vorm; *Chem. Abs.*, 1926, **20**, 2082. L. L. Alsted, French P. 744,940, 1933; *Chem. Abs.*, 1933, **27**, 4400. E. Wydler, Swiss P. 179,454, 1936; *Chem. Zentr.*, 1936, **107** (2), 876; *Rev. Paint, Colour, Varnish*, 1936, **9**, 299..

[56] British P. 116,109, 1916; *Chem. Abs.*, 1918, **12**, 2056.

[57] R. Jeannin, J. Bouillon and C. Bouillon, British P. 344,431, 1928; *Chem. Abs.*, 1932, **26**, 3943. Harry E. Brookly, U. S. P. 1,763,291, June 10, 1930, to U. S. Gypsum Co.; *Chem. Abs.*, 1930, **24**, 3877.

a reagent to the specified place and the color of the ink appearing announces the veracity of his choice.[58]

There are three general types of sympathetic inks. The first is a heat-sensitive ink that will appear upon gentle warming. The second is an ink that owes its properties to its waterproofing character. It keeps parts of a page dry when the paper is immersed in water or sponged, thereby causing a difference in color between the wet and dry portions of the paper. The third type is an ink containing a reagent which will react with a second one that is applied and thereby cause a color change.

The most common example of the heat-sensitive inks is that type which contains cobalt chloride, a salt which in its hydrated (water-containing) condition is a pale pink only barely visible, especially in a thin layer such as on a printed page. In its anhydrous (dry) state the salt is a fairly dark blue. The substance is often used as a rain gauge because of this peculiar property. Cobalt chloride may be ground into a vehicle composed of a pale lithographic varnish, or in a water-type vehicle consisting of straw-colored dextrin which has been slowly and carefully cooked with glycerol. A considerable amount of the chloride must be included to insure sufficient concentration. Aluminum hydroxide is added to the vehicle to render the ink viscous enough for press work. Upon heating for a few seconds, the printing changes from an invisible state to a light blue color.[59] Other effects, such as changing from yellow to a green upon heating, may be caused by the inclusion of a colored dye in the ink; a yellow pigment, when heated, will cause a change to green, and when cooled, a reversion to yellow.[60]

An ink of the cobalt chloride type is composed of 60 parts of denatured alcohol, 10 parts of cobalt chloride, 10 parts of glycerol and 20 parts of water.[61]

The second type of sympathetic ink, in which the ink stays the same color, but the background changes, is practical in that the procedure may be repeated as often as desired, merely by wetting the paper and allowing it to dry after the effect is obtained. The use of nitrocellulose as a constituent of the ink along with "Cellosolve" acetate in the ratio of from 95 to 98.75 per cent of nitrocellulose, and the remainder "Cellosolve" ester, lowers the permeability of the paper to water.[62] Another mixture used is a 5 per cent solution of paraffin wax in a mixture of equal parts of xylene and acetylene tetrachloride.[63]

The best use of this water-impermeable ink is with colored papers, especially antique papers, the dye of which, however, should be fast, for a soluble color would spoil the ink by running into it when the paper is wet. Magnesium carbonate mixed with slightly bodied tung oil or with

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[58] H. Peterson and J. Person, U. S. P. 1,884,197, Oct. 25, 1933; *Chem. Abs.*, 1933, 27, 891.

[59] R. Roley, *Am. Ink Maker*, 1938, 16 (4), 18. A. Rogers, British P. 235,922, 1933, to Mimo Corp.; *Chem. Abs.*, 1926, 20, 997.

[60] H. Wyse, British P. 12,872, 1906; *J. S. C. I.*, 1907, 26, 821.

[61] W. Ellins, British P. 466,181, 1937, to John Dickinson & Co.; *Chem. Abs.*, 1937, 31, 8231.

[62] W. Guthmann, U. S. P. 2,083,372, June 15, 1937; *Rev. Paint, Colour, Varnish*, 1937, 10, 341; *Chem. Abs.*, 1937, 31, 5605.

[63] H. Pearson, U. S. P. 1,401,593, Dec. 27, 1922; *Chem. Abs.*, 1922, 16, 996.

light-bodied, water-white linseed oil lithographic varnish, to which is added some hygroscopic salt, such as calcium chloride, which becomes white when wet, is reported to be a suitable base for a sympathetic ink.[64]

The third type of sympathetic ink may be composed of various materials which will react when treated to form a colored product. The principal reagent used in the body of the ink is phenolphthalein, a dye which is colorless in the acid condition, but which turns a brilliant red when in the presence of alkalies. The ink may be brushed over or dabbed with a dilute solution of any alkaline material, *e.g.*, sodium carbonate, borax, soda or potash lye, or ammonia. This type of ink is comparatively easy to colorize. Other inks contain a material such as ferrous sulphate, which forms a blue color when in contact with a ferricyanide such as that of potassium. Ferrous salts also form colored dyes when they react with gallic or tannic acids. The main objection to the use of these inks is the difficulty in obtaining the chemical necessary to bring forth the color, and the usual procedure is to include with the piece of printed material an envelope containing a small amount of the required reagent. Aluminum hydroxide must be added to all the inks prepared, as stated above, to thicken them, and some opaque white must be added to cover the color of the chemical used. When the ink contains a ferrous salt and the printed matter is treated with ammonium sulphocyanide, a brilliant red color is produced. In the case of all of the inks of this third type, except those containing phenolphthalein, the color, once produced, is permanent, and the action cannot be repeated.[65]

An ink composed of phenolphthalein, glycerol, alcohol and carbon tetrachloride may be used to print patterns for garments on the pages of a newspaper, as is sometimes done in foreign practice.[66]

When a card sensitized with a gelatin solution of an alkali halide or an alkali salt of an organic acid, *e.g.*, sodium or potassium bromide, chloride, iodide or acid tartrate or citrate, is printed upon with an ink containing silver nitrate, the image, which originally is invisible, will be made to appear black by the use of one of the ordinary photographic developers, such as hydroquinone, elon, or pyro. In the procedure, the card, after being sized and printed, is exposed to light and then bleached. A second piece of paper, attached to the first so it may be folded over upon it, is impregnated with the developer and requires but a wetting with water to bring out the image when pressed to the printed card. The ink employed contains 100 parts of distilled water, 250 parts of silver nitrate, 75 parts of alcohol, and 200 parts of glycerol.[67]

The effect of iodine upon starch has served as the basis for the manufacture of one variety of sympathetic inks. One procedure is to print upon a starch-saturated card or paper a solution of 1/10 g. of iodine in

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[64] R. Roley, *loc. cit.*

[65] R. Roley, *loc. cit.* Also A. Rogers, British P. 235,922, 1923, to Mimo Corp.; *Chem. Abs.*, 1926, **20**, 997.

[66] H. Collins, British P. 235,968, 1923; *Chem. Abs.*, 1926, **20**, 998.

[67] W. F. Mansell and W. H. Mansell, British P. 27,233, 1908; *Chem. Abs.*, 1910, **4**, 2191.

water-saturated benzene. The characters appear purple or blue, but disappear quickly. Thereafter a piece of blotting paper soaked with a solution of iodine in water will, when brought into contact with the printed matter, bring out the color again. This step may be repeated as often as desired.[68] Another action producing the same effect consists of bringing one paper, printed with starch and an acid, into contact with a second which is saturated with a water-soluble iodide and a water-soluble nitrite. The iodine set free in the reaction colors the starch.[69]

When paper, pretreated with a dilute salt solution, is printed upon with an ink containing silver sulphate or basic mercuric nitrate and treated with a solution of sodium or potassium sulphide, a black color results due to the formation of silver or mercuric sulphide.[70]

A rather unique type of sympathetic ink is one that does not change color at all. It is a white ink with a clay-like texture that is composed of Paris white or titanium dioxide as a pigment, a colorless lithographic varnish and a small amount of drier, which may be lead naphthenate or manganese borate. The safety of this ink is its best feature, and it may be employed in children's picture books and various other toys. It is applied to a high-gloss paper, and when a soft pencil is lightly rubbed across the paper, the ink, being of a rough texture, rubs the lead off the pencil, and becomes blacker than the paper, thus indicating the material printed. A sympathetic ink, related in a way to what is known as "touch-paper," contains a considerable proportion of potassium nitrate (saltpetre) in a transparent lithographic varnish to which is added some paraffin wax and also some aluminum hydroxide as a filler or thickener. The ink is applied to a fireproof paper and when the film is touched with a match or cigarette, the ink will burn along the lines of the design, leaving a back trail of ash.[71]

Safety Inks and Paper. The principle of practically all of the so-called "safety" inks is not their indelibility, but their peculiar ability when tampered with to exhibit tell-tale reactions. They are a sort of warning bell of fraud. Some of these inks change color when treated with acids and bleaching agents, while others blur and diffuse throughout the area in contact with the reagent used. Some of the safety papers are colorless until an attempt is made to alter the document, when they become colored as evidence of the tampering. By including about 10 per cent of a mixture of a water-soluble dyestuff and an oil vehicle in the inks used in printing revenue stamps, the use of any water for the purpose of removing the stamp will be shown by a smudged effect due to the running of the water-soluble pigment.[72]

By using an ink the color of which is a function of the acid concentration, any employment of an acid bleaching agent may be detected by a

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[68] A. Gawalowski, *Pharm. Monatshefte*, 1926, 7, 47; *Chem. Abs.*, 1926, **20**, 1913.

[69] F. Baggaley, British P. 415,535, 1934, to McCorquodale & Co., Ltd.; *Chem. Abs.*, 1935, **29**, 860.

[70] A. Gawalowski, *loc. cit.*

[71] R. Roley, *loc. cit.*

[72] A. Wittnebel, U. S. P. 2,116,374, May 3, 1938, to American Bank Note Co.; *Chem. Abs.*, 1938, **32**, 5237. British P. 469,232, 1937; *Chem. Abs.*, 1938, **32**, 814.

variation in the shade of the ink. An indicating ink of this type is made from the zinc chloride salts of a mixture of hexamethyl- and pentamethylmonoethyl-*p*-rosaniline, the diazo dye from tetrazotized *o*-tolidine, sodium naphthionate, sodium hydroxide and monosodium phosphate.[73]

An ink which contains a metallic salt of a fatty acid (such as oleic or palmitic) will change its tint when treated with a detergent agent.[74] This ink is applicable for printing on fiduciary paper or other valuable documents. By using colorless inks to print concealed figures on checks showing the valuation in case of any alteration, the application of ink eradicators will be shown by the coloring and ensuing visibility of the inscriptions.[75]

Dianisidine and β-naphthol, an amine and a developer, are dissolved in oleic acid and a nitrite added to form a solution usable for safety inks. The action of any bleach will cause a discoloration of the dianisidine, thereby staining the paper.[76] Aniline hydrochloride may be used also and will discolor by the decomposition of the hydrochloride when a bleach comes in contact with paper.[77] The action of a hypochlorite or a weak acid will discolor water-soluble indigosols (sodium salts of leuco-sulphuric esters of various vat dyes), in the presence of an oxidizing agent.[78] The application of a different principle is made by impregnating the paper (to be printed) with potassium prussiate (cyanide) and including ferric perchlorate in the ink vehicle. The two salts, which produce a strong color upon coming together, are separated only by the oily medium of the ink, and will interact when any acid or alkali reagents (used to tamper with the paper) decompose this vehicle. The addition of magenta to the ink will intensify the discoloration thus produced.[79] An improvement is said to be noted with any of the foregoing inks used for safety purposes if a wetting agent such as triethanolamine oleate is added to the vehicle.[80]

A "fugitive" or "security" ink is made by mixing 83 parts of dextrin with 17 of treacle or golden syrup, adding 50 parts of glycerol and enough aniline dye to give the desired color. These proportions may vary with the temperature, and in summer some salicylic acid or phenol should be added as a preservative.[81]

Inks for Recording Instruments. Either water-glycerin or water-ethylene glycol vehicles may be used. The percentage of water varies from about 25 to 50 per cent. Direct dyes give better results than other dyes. Enough ethyl alcohol to keep the ink fluid at very low temperatures is added to the vehicle when necessary.[82]

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[73] E. Bayle, H. George and A. Maché, U. S. P. 1,899,452, Feb. 28, 1933; *Rev. Paint, Colour, Varnish*, 1933, **6**, 335; *Brit. Chem. Abs.* **B**, 1933, 978. British P. 305,028, 1928; *Chem. Abs.*, 1929, **23**, 4836.

[74] A. Azam and A. Schwartz, French P. 799,948, 1936; *Chem. Abs.*, 1936, **30**, 8663.

[75] R. Bohrer, U. S. P. 1,799,499, April 7, 1931; *Chem. Abs.*, 1931, **25**, 3170.

[76] W. Murray, U. S. P. 1,462,613, July 4, 1923; *Chem. Abs.*, 1923, **17**, 3105.

[77] J. Neff, U. S. P. 1,578,908, March 30, 1926; *Chem. Abs.*, 1926, **20**, 1926.

[78] F. Neuber, *Mitt. tech. Vers.*, 1931, **20**, 63; *Chem. Abs.*, 1932, **26**, 3665.

[79] J. Rowan, British P. 3,909, 1904; *J. S. C. I.*, 1904, **23**, 453.

[80] German P. 579,117, 1933, to Lövinsohn and Co.; *Rev. Paint, Colour, Varnish*, 1933, **6**, 265; *Chem. Abs.*, 1933, **27**, 4699.

[81] R. Webb, British P. 19,783, 1897; *J. S. C. I.*, 1897, **16**, 1012.

[82] C. E. Waters, *J. Research Natl. Bur. Standards*, 1936, **17**, 651.

Inks for Printing Currency and Securities. One of the most exacting types of printing is that done in the production of paper money and securities, such as bonds and stock certificates. Engraved copper and steel plates, which are very delicately etched, are employed in this work; therefore an ink must be used that will not cause unnecessary wear over long periods and that will bring out, upon printing, the fine lines of the plate without smudging or smearing. The inks must show very fine gradations of color shade in order to prevent photomechanical counterfeiting. The vehicle of the ink must be short, buttery and greaseless. Certain pigments that easily become black cannot be incorporated because they would greatly simplify the practice of photomechanical counterfeiting, which consists of photographing a piece of paper money and etching a plate from the photograph. When paper money is printed in a green that is of different shades, counterfeiting cannot be effected very easily because the camera will not differentiate between two or more shades, but the process will work to advantage if the ink can be converted to a solid black, thereby simplifying the photographic process.

Security and currency inks are manufactured by mixing a light-fast, water-insoluble ink with well burnt linseed oil, or plate oil, and adding Paris white. Small amounts of driers may be included as needed. Ochres and colored earths are not satisfactory as pigments because of their harsh texture; zinc, lead and cadmium colors, cobalt blue and red, chromium oxide green, Paris green, and basic copper carbonate are not desirable because they can be turned black very easily by the action of hydrogen sulphide gas or by a solution of sodium or potassium sulphide. Zinc yellow is too soluble in water to be employed. Bronze blue, Milori Blue, and Prussian Blue are fairly good as pigments, but by a complicated chemical process it is possible likewise to make them black. The application of aluminum and calcium salts of organic acid dyes as pigments was formerly quite widespread, but these materials have been supplanted to a considerable degree by synthetic dyestuffs. Simmonds reports the use of orchil as a pigment for inks used in printing stamps, checks and drafts.[83]

The second most important ingredient of security inks is the filler or extender. It is necessary that the material give a dilution high enough to prevent all the lines of the plate from printing deep blue or black. The use of gypsum or calcium sulphate is not recommended because slightly alkaline water (frequently used to clean the plates and press) acts upon the salt and the linseed vehicle to furnish a variety of cement, thus making it difficult to clean the plate, and streaks appear across the surface. Both barium sulphate and aluminum hydroxide are undesirable because they make for difficulty in cleaning the plate; kaolin or china clay imparts a greasiness to the ink. Zinc white and titanium dioxide make for a good working quality in the ink, but they do not give a good

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[83] J. P. Simmonds, U. S. P. 101,170, Mar. 22, 1870.

gradation of color. As mentioned above, lead-containing whites can be easily darkened and, too, they have a tendency to attack and darken copper plates. Paris white (calcium carbonate) is the extender most commonly employed.

The vehicle most frequently found in ink for printing currency is refined linseed oil that has been burned to the degree desired. The burning operation consists in heating raw oil until the vapors will ignite. Combustion is continued until a sample drawn off is of the consistency required. The sample to be tested is cooled and spread on a plate and examination made of it for tack, consistency and length. If the oil is too thin it will not adhere properly to the paper; if too thick, it will gum the plates and show a tendency to smear on the paper. Of the driers, manganese borate seems to be one of the most desirable that can be found.[84]

A bank note ink containing barium chromate is reported by Eaton.[85]

Tannic acid and chromium oxide were suggested for use in ink for bank note printing.[86]

Various Printing Inks

Inks for Printing from Rubber Type. As a rule, inks for printing from rubber printing plates are not as viscous as are those for metallic type faces. No material which would dissolve the rubber or cause it to swell may be included in the ink.[87] A light-resistant ink used with rubber plates is composed of a highly dispersed suspension of a water- and alcohol-insoluble pigment in an aqueous-alcoholic solution of shellac. The ink is fast-drying and the rate of drying may be controlled by the proportion of water and alcohol in the mixture.[88]

The manufacture of bronze ink for printing from rubber type is aided by the inclusion of highly viscous polymerization products of aliphatic vinyl compounds (soluble in alcohol) as the binding agent for the powder. A typical ink may be composed of copper bronze, polyvinyl methyl ether, ethyl alcohol, and the acetate of glycol ethyl ether.[89]

To the aqueous-alcoholic shellac vehicle mentioned above, there may be added an alkali as an aid for dissolving the shellac or other plastic.[90] Included in the ink is a pigment not affected by alkali, such as Hansa Yellow, Methyl Violet, soot, chrome yellow, ultramarine, Milori Blue, Lake Red, or Permanent or Lithol Red. Borax is recommended, but

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[84] K. H. Bettner, *Am. Ink Maker*, 1935, 13 (11), 15. For a discussion of various tests for ink, see Chapter 17.

[85] A. K. Eaton, U. S. P. 38,298, April 28, 1863.

[86] T. S. Hunt, U. S. P. 40,839, Dec. 8, 1863.

[87] See J. D. Cohen, *Paper and Print*, 1937, Spring, 22; *Rev. Paint, Colour, Varnish*, 1937, 10, 260. See also *Am. Ink Maker*, 1932, 10, 11; *Rev. Paint, Colour, Varnish*, 1932, 5, 173.

[88] German P. 649,474, 1937, to Kast and Ehinger G. m. b. H.; *Papier-Ztg.*, 1937, 62 (93), 1613; *Rev. Paint, Colour, Varnish*, 1937, 10, 414; *Chem. Abs.*, 1938, 32, 1123.

[89] W. Lützkendorf, German P. 619,501, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, 30, 1595. See also French P. 774,851, 1935; *Chem. Abs.*, 1935, 29, 2265.

[90] E. Loevinsohn, H. Loevinsohn and M. Schnelling, British P. 405,483, 1934; *Brit. Chem. Abs.* B, 1934, 334; *Chem. Abs.*, 1934, 28, 4614. French P. 749,241, 1933; *Rev. Paint, Colour, Varnish*, 1934, 7, 135; *Chem. Abs.*, 1933, 27, 5989.

ammonia, inorganic or organic bases (other than alkyl hydroxyamino compounds) or ammonium carbonate may be substituted.

Miscellaneous. An ink which is said to be non-inflammable is composed of a manganese pigment with a binder of shellac, borax and water.[91] By mixing an aqueous emulsion of white starch and Turkey-red oil with an ordinary printing ink, a frosting ink is secured.[92] An electrically conductive ink consists of a mixture of carbon black, powdered graphite, a dilute colloidal solution of glue or gum arabic, sodium chloride, and an organic acid, which may be citric or tartaric acid.[93] A rather novel type of ink having sulphite liquor as a basis is said to dry on paper only, and not on metals, cloth, or the hands of the operator, because of the chemical action of the vehicle upon the fibers of the paper.[94]

Rubber and Latex Inks. Rubber and latex inks contain as a bodying agent raw rubber that is vulcanized after being printed, either by a second process or by incorporating a vulcanizing agent in the ink itself. The advantages claimed for rubber inks are that they are capable of absorbing a greater amount of pigment than those inks containing nitrocellulose, cellulose acetate or benzyl cellulose, therefore making for better covering power; that they are non-conductive of electricity, thereby reducing the fire hazard caused by static electricity when the ink contains benzene, xylene, toluene, etc.; that the impressions are impervious to rubbing as a cause of removing the print; that the inks containing rubber are light-fast, and that there is no striking through on the paper because the rubber has a sizing action upon the fiber.

Rubber may be employed in both oil-containing and oil-free inks. Both types are reported to be resistant to acids, alkalies, salts, corrosive gases, and water, and yield ink films which remain more or less elastic, thus making for greater durability when this property is required. Impressions of the ink are highly lustrous, but may be subdued by the addition of chalk, magnesia, or blanc fixe. The inks dry faster than those containing resins. When rubber inks are used, the press generally is fitted with gelatin rollers.[95]

Although inks containing chlorinated rubber are apt to give off free chlorine due to the decomposition of the halogenated ingredient, there is no corrosive effect upon the plates or upon the vehicle because of the protective action of the fillers and other substances present in the ink. Chlorinated rubber is soluble in practically all solvents used in printing, as well as in tung, soybean, and linseed oils. It can be used with many natural and artificial resins, with the exception of shellac, acaroid resin, ceresin wax and paraffin.[96]

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[91] H. A. Buck, U. S. P. 1,421,125, June 27, 1922; *Chem. Abs.*, 1922, **16**, 3004.

[92] T. Morobosi, Japanese P. 93,295, 1931; *Chem. Abs.*, 1933, **27**, 1529.

[93] K. Suzuki, Japanese P. 109,595, 1935; *Rev. Paint, Colour, Varnish*, 1935, **8**, 403; *Chem. Abs.*, 1935, **29**, 4958.

[94] *Paint, Varnish Production Mgr.*, 1932, 7 (2), 19; *Rev. Paint, Colour, Varnish*, 1932, **5**, 89.

[95] R. A. Crawford and D. B. Forman, *Am. Ink Maker*, 1939, 17 (3), 21.

[96] H. Hadert, *Am. Ink Maker*, 1933, 11 (11), 9. T. V. Binmore, U. S. P. 1,552,907, Sept. 8, 1925, to N. Y. Belting and Packing Co.; *Am. Ink Maker*, 1939, 17 (3), 25. T. P. Sanguinetti, British P. 472,684, 1936.

Fingerprint Record Inks. The requirements of fingerprint inks are that they be non-smearing, tacky enough to secure a complete impression of the prints, and that they be non-fading when kept on file. Most such inks should be non-staining so they will be rather easy to remove from the fingers after the impression has been made. A mixture of glycerol, gelatin, alcohol, and a colored earth pigment is made for securing print impressions. In preparing the ink, one part of gelatin is dissolved in 10 parts of heated glycerol and the mixture allowed to cool to 20° C. Half as much alcohol as glycerol is added and the mixture is ground with 5 parts of a blue pigment of the naturally colored earth materials.[97] Another formula consists of 50 per cent lanolin, or natural skin oil, 10 per cent glycerol, and 40 per cent carbon black.[98]

Amalgam Inks. Amalgam inks are those that dry and set by means of the hardening of an amalgam rather than primarily by the drying of the vehicle. They contain a mercury salt and any salt of a metal with which mercury will form an amalgam, such as silver, cadmium, tin, or zinc. These salts are usually suspended or dissolved in glycerol.[99]

Another type of ink closely related to the amalgam ink is one containing mercury in the metallic state and designed to be used with a plate having mercurized or amalgamated non-printing areas. These plates are closely allied to those for offset and the lithographic presses in which the non-printing areas are coated with a gum, such as gum arabic.[100] Partially polymerized linseed oil, pigments, and mercury usually make up the ink. Linseed oil is heated to 315° C. without burning and without carbonization taking place (usually in a non-oxygen atmosphere) until the desired proportion of fatty acid, about 7 per cent, is obtained. The amount of mercury needed can be reduced by incorporation of an aqueous solution of borax and shellac with the ink. If no borax is used. the ink may consist of 52 parts of linseed oil, 35 parts of carbon black, 9 parts of Prussian Blue and 35 parts of mercury. If the borax and shellac solution (2.5 to 5 per cent borax and 5 to 10 per cent of shellac) is included to the extent of 52 parts, the proportion of mercury can be reduced to 1.5 parts.[101] The amalgam on the plate is regenerated by including the mercury in a finely divided state in the ink. The amalgam usually employed is one which contains silver, tin or cadmium, and which hardens on exposure to air.[102]

Water Color Inks. Water color inks are employed in the printing of wall paper by the rotary photogravure (rotogravure) process and also for stencil printing. In the photogravure process, the plate is etched

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[97] E. Reitze and E. Trujillo, British P. 208,930, 1923; *Chem. Abs.*, 1924, **18**, 1597. U. S. P. 1,506,082, August 26, 1924; *Chem. Abs.*, 1924, **18**, 3282.

[98] T. M. Price, U. S. P. 1,088,840, March 3, 1914; *Chem. Abs.*, 1914, **8**, 1515.

[99] H. Renck, French P. 810,129, 1937; *Chem. Abs.*, 1938, **32**, 814. German P. 646,845, 1937; *Chem. Abs.*, 1937, **31**, 6490. Dutch P. 41,981, 1938; *Chem. Zentr.*, 1938, **109** (1), 1232; *Rev. Paint, Colour, Varnish*, 1938, **11**, 194. Norwegian P. 59.521, 1938; *Chem. Abs.*, 1938, **32**, 8808.

[100] For a discussion of the offset and lithographic processes, see Chapter 9.

[101] A. R. Trist, British P. 307,535, 1929; *Rev. Paint, Colour, Varnish*, 1929, **2**, 151.

[102] H. Renck, British P. 474,680, 1937; *Chem. Abs.*, 1938, **32**, 3644. British P. 493,502, 1938; U. S. P. 2,154,866, Apr. 18, 1939.

to make the surface water-receptive and then it is inked with an aqueous solution of a dye.[103]

In one procedure for the manufacture of a water color ink, 2 parts of gum arabic are dissolved in 2 parts of water, and 18 parts of glycerin are added. The mixture is dehydrated by heat until the product attains a specific gravity of about 1.28. Pigment is then added and the mixture thoroughly ground.[104] Aluminum soaps precipitated from the potassium soaps with $Al_2(SO_4)_3$ are also reported to be used.[105]

Water-soluble inks are suggested for gummed labels to prevent their detachment or re-use, the water-soluble ink being on the gummed side and showing up when the label is wet.[106]

When a gloss finish is desired, the composition may consist of a varnish, stearin, cod-liver oil, turpentine, a volatile mineral oil, and a pigment, such as Bolognese chalk, or kaolin. An oil-soluble aniline dye may be added, thereby producing a colored impression.[107] Dean[108] recommends a mixture containing 25 pounds of gum arabic, 1 gallon of liquid soap, 100 pounds of dextrin, 20 pounds of starch, 40 pounds of glucose, and 10 gallons of water, with a half pint of a preserving agent, such as Lysol.

Aluminum hydroxide, freshly precipitated by soda ash from solutions of alum, may be incorporated with dyestuffs to furnish the pigmenting material.[109] Another starch base ink made by the action of perborates and honey, dextrin or molasses has been reported.[110] Millet jelly, starch, and a silicate sol, admixed with a pigment, illustrates a variation in the formulas for water-soluble inks.[111]

SEMI-PRINTING INKS

Although these inks are not in a technical sense true printing inks, their inclusion is warranted to insure complete coverage of the field of what might be called duplicating inks. They are used in duplicating processes, such as stamping, mimeographing, typewriting, multigraphing and hectographing, and are more liquid in character than many printing inks, as they usually must permeate a cloth or paper-fiber medium by means of which the type is inked; or the material, such as paper, leather or cloth, is printed upon directly. In the case of hectograph ink, no type

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[103] W. Gamble, *Brit. Printer*, 1930, **42**, 265; *Rev. Paint, Colour, Varnish*, 1930, **3**, 176. H. N. Durham, U. S. P. 1,838,218, Dec. 29, 1931; *Chem. Abs.*, 1932, **26**, 1459. For the preparation of such plates see Chapter 11 on photomechanical processes.

[104] J. Hoeffler, U. S. P. 1,660,196, Feb. 21, 1928, to J. Hoeffler & Co.; *Rev. Paint, Colour, Varnish*, 1928, **1**, 172; *Brit. Chem. Abs.* **B**, 1928, 614; *Chem. Abs.*, 1928, **22**, 1486.

[105] Talsuzo Sato, Japanese P. 37,198, 1920; *Chem. Abs.*, 1921, **15**, 3758.

[106] Franz Krell, German P. 671,305.

[107] Swiss P. 75,976, 1917, to Firma Gustav Ruth; *Chem. Abs.*, 1918, **12**, 1128.

[108] C. T. Dean, U. S. P. 1,607,060, Nov. 16, 1926; *Chem. Abs.*, 1927, **21**, 333.

[109] N. Akaike, Japanese P. 90,835, 1931, to Sitizaemon Mori; *Rev. Paint, Colour, Varnish*, 1931, **4**, 250; *Chem. Abs.*, 1931, **25**, 5048.

[110] A. F. Ware, British P. 346,311, 1928; *Chem. Abs.*, 1933, **27**, 1529.

[111] S. Kurotaki and T. Ito, Japanese P. 94,742, 1932, to Tinokiti Kobayasi; *Chem. Abs.*, 1933, **27**, 2050.

or printing plate is employed in the actual process, a gelatin film being the medium of transfer.

Stamp-pad Inks. Stamp-pad inks are of a non-drying or slowly drying type and are held for use in a thick permeable pad of soft cloth, or fibers covered with cloth. Frequently the type is made of soft rubber, but sometimes metallic faces are employed, especially when the material to be printed is soft and will accommodate its surface to the type, insuring intimate contact with every portion of the plate. Stamping is most frequently used in cancelling checks, printing meat or vegetables, numbering cards or papers with a hand-numbering machine, and printing cloth and irregularly shaped objects, such as bottles or jars.[112] An ink that dries fast to light, water, and rubbing is made by dissolving a dye (*e.g.*, Xylene Fast Blue BL) in ethyl alcohol, butylglycol, glycerol and water.[113]

Some hygroscopic agent, such as glycerol, is added to slow down or inhibit drying of the ink on the pad. The United States Bureau of Standards requires that 5 grams of dye can be dissolved in 100 cc. of 55-per cent glycerol (sp. gr. of 1.1415 at 20° C.) to make a stamp-pad ink.[114]

It is suggested that, because glycerol is held by some to be not sufficiently hygroscopic, some other agent should be included in the ink to retain moisture. Among those proposed as substitutes, ethylene glycol[115] has been mentioned, as well as cresol, creosote or phenol,[116] oleic acid,[117] tricresyl phosphate,[118] and various esters and salts of organic acids, such as butyl lactate, amyl tartrate, dimethylcyclohexanol oxalate, and potassium lactate solution. The main advantage of these liquids is that they are not for the most part, at least, easily volatile.[119]

The Bureau of Standards specification makes provision for the use of the following standard pigments for stamp-pad inks:[120]

Black—Nigrosine	Schultz No. 700
Blue—Sol. blue	Schultz No. 539
Green—Light green	Schultz No. 505
Red—Magenta	Schultz No. 512
Violet—Acid violet	Schultz No. 530

Other dyestuffs are used, such as Methyl Violet, and the ferro-tannate

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[112] See C. Becher, Jr., *Seifenzieder Ztg.*, 1934, **61** (11), 209; (12), 230; (13), 247; *Rev. Paint, Colour, Varnish*, 1934, **7**, 195; W. Hacker, *Farben-Ztg.*, 1921, **26**, 1508; *Chem. Abs.*, 1921, **15**, 2197. A. Langer, *Chem.-Ztg.*, 1920, **44**, 951; *Chem. Abs.*, 1921, **15**, 1081.

[113] British P. 443,294, 1936, to Soc. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1936, **30**, 5415. Swiss P. 173,767, 1935; *Chem. Abs.*, 1935, **29**, 5681.

[114] *Circ. of Bur. of Stand.* No. 185, 1924; *Chem. Abs.*, 1924, **18**, 3282.

[115] German P. 309,911, 1917, to Th. Goldschmidt A.-G.; *Chem. Abs.*, 1919, **13**, 1772.

[116] Y. Aoyama and S. Yasojima, Japanese P. 35,607, 1919; *Chem. Abs.*, 1920, **14**, 3163. I. Siga, Japanese P. 100,572, 1933, to Toyo Seikan K. K.; *Chem. Abs.*, 1934, **28**, 2553. C. M. Higgins, British P. 93, 1892; *J. S. C. I.*, 1892, **11**, 362; I. Sharov, Russian P. 28,266, 1929; *Chem. Abs.*, 1933, **27**, 3835.

[117] C. M. Higgins, British P. 15,857, 1890; *J. S. C. I.*, 1891, **10**, 252. British P. 15,858, 1890; *J. S. C. I.*, 1891, **10**, 253.

[118] W. D. Potapov and I. Y. Postofskii, Russian P. 37,781, 1936; *Chem. Zentr.*, 1936, **107** (1), 198; *Rev. Paint, Colour, Varnish*, 1936, **9**, 22.

[119] British P. 156,212, 1921, to Chem. Fabriken Worms A.-G.; *Chem. Abs.*, 1921, **15**, 1821. A. L. Glover, British P. 424,628, 1935; *Chem. Abs.*, 1935, **29**, 5682.

[120] *Circ. Bur. of Stand.*, No. 185, 1924.

and ferro-gallate lakes. Schiffman [121] recommends incorporating a small quantity of carbon black with a mixture of a tannate or gallo-tannate of iron and a water-insoluble dye dissolved in acetin. An ink made of 65 parts of crude cresol, 30 parts of cacao fat, 15 parts of raw lacquer, 5 parts of Methyl Violet, and 5 parts of a perfume is said to be resistant to water, acids and alkalies.[122]

Carbolin, an oily black aniline dye, can be used in ink for stamping cloth. It does not decompose, and will not affect metallic dies.[123]

For use with wooden inking pads, an ink may be manufactured composed of a dye and a carrier containing cyclohexylidenecyclohexanone and a derivative, methylcyclohexylidenemethylcyclohexanone, dissolved in benzyl alcohol, diacetone alcohol, or some other solvent which will not warp the pad, injure the rubber stamps, or rapidly evaporate.[124] The inclusion of diethyl phthalate, a softening agent for cellulose esters and other cellulose derivatives, softens the wood of the pad and effects greater penetration of the ink.[125]

A solvent very penetrating to paper fibers, but which will not evaporate readily when exposed to air, is "butyl Carbitol" or monobutyl ether of diethylene glycol. It is best used in a concentration of 40 per cent water and 20 per cent "butyl Carbitol." According to Waters, an inking pad saturated with this liquid mixture did not dry after weeks of exposure.[126]

A black stamping ink for printing on linen and cloth is prepared by coarsely crushing anacardium nuts and extracting the dyestuff from them with petroleum ether. When the material is printed the color will first be a yellowish brown, but upon the application of ammonium hydroxide or lime water, the impression will turn to a resistant black, which will be impermeable to saturated solutions of many bleaching agents, potassium cyanide, acids and alkalies.[127]

Mimeograph or Stencil Inks. The medium for stencil duplication consists of an impermeable sheet of paper, through which lettering or drawings are cut, wrapped around an ink drum. The drum has around it a blanket of soft cotton or some other fabric through which the ink soaks and comes into contact with the stencil sheet. The ink goes through the openings cut and reproduces the design on paper which is run through the machine as the drum is rotated or oscillated. The ink is a non-drying or slowly drying variety, and its method of setting consists of the dispersion of the solvent into the fibers of the paper printed upon. The stencil paper is usually a thin tissue impregnated with a wax-like material which renders it impermeable, but which is easily broken by a

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[121] J. Schiffman, British P. 172,588, 1921; *Chem. Abs.*, 1922, 16, 1512.

[122] Y. Aoyama and S. Yasojima, *loc. cit.*

[123] Jacobsen, *Ind.-Bl.*, 14, 12; *Chem. Zentr.*, 1877, 8 (3), 96.

[124] A. L. Glover, *loc. cit.*

[125] J. Ehrlich, Austrian P. 130,240, 1932, to Firma W. Koreska; *Chem. Abs.*, 1933, 27, 1216. French P. 726,220, 1931; *Chem. Abs.*, 1932, 26, 4969. British P. 376,612, 1932; *Chem. Abs.*, 1933, 27, 3627. German P. 576,190, 1933; *Chem. Abs.*, 1933, 27, 3835.

[126] C. E. Waters, *J. Research Natl. Bur. Standards*, 1938, 20 (4), 543; *Chem. Prod. and Chem. News*, 1938, 1 (2), 47; *Rev. Paint, Colour, Varnish*, 1938, 11, 194; *Chem. Abs.*, 1938, 32, 5234.

[127] R. Böttger, *Jahresber. Physikal. Ver.*, 1870-71, 23; *Chem. Zentr.*, 1872, 3 (3), 743.

blow of a typewriter key or by the pressure of a stylus point. Most stencil inks contain a high percentage of soap, or a resin, or both.[128]

A composition of syrup, molasses or honey mixed with coloring matter and, if desired, glycerin or oil was suggested by Loewenberg.[129]

Calcium soaps derived from animal or vegetable oils are employed in many instances. These may be prepared by heating a mixture of one part of calcium hydroxide and three parts of an oil to about 300° C. Afterwards the soap is cooled and powdered, and mixed, at about 100° C., with 12 parts of a mineral oil. A mixture of one part of an ammoniacal solution of gluten, 3 parts of resin oil, and one of lampblack is added to the first solution to prepare a stencil ink.[130] As the soap constituent for mimeograph ink, Kruse [131] uses a varnish that has been partly saponified, and includes in his ink Turkey-red oil (sulphonated castor oil). The ammonium soap of Turkey-red oil is sometimes employed as the soap constituent.[132] Turkey-red oil is used with gum tragacanth and a varnish gum, and glycerol. The inclusion of mineral, peanut and citronella oils is sometimes made in a stencil ink.[133] Stevenson prescribed a mixture of equal parts of a saturated solution of calcium chloride and a 33⅓-per cent aqueous solution of a gum with lampblack or some other coloring material.[134] Green soap, with Turkey-red oil, rosin oil, paraffin oil, water, and aluminum phosphate, forms the vehicle for a stencil or mimeograph ink, to which is added a pigment, such as Milori Blue or carbon black.[135]

An ink that is reported not to corrode the metallic portions of the machine is composed of a mixture of linseed, castor and soybean oils, wax, a soap of organic bases, such as ethanolamine oleate or hydroxyethylamine naphthenate, a dye, and water.[136]

Another composition, the color of which depends upon the dye used, consists of 32 ounces of liquid shellac, 5 to 6 ounces of turpentine, 2 ounces of beeswax, 5 to 8 ounces of pigment, and 80 to 167 ounces of alcohol.[137]

The use of hexamethylenetetramine or one of its salts,[138] or a direct substantive coloring matter, such as Benzo Fast Scarlet 2, mixed with

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[128] *Seifensieder-Ztg.*, 1936, 63, 149; *Rev. Paint, Colour, Varnish*, 1936, 9, 92. Also see W. G. Fuerth, U. S. P. 970,439, Sept. 13, 1910, to Equilibrator Co.; *Chem. Abs.*, 1910, 4, 3306. R. W. Hochstetter, U. S. P. 928,915, 1909, to Ault & Wiborg Co.; *Chem. Abs.*, 1909, 3, 2389.

[129] H. Loewenberg, U. S. P. 63,733, April 9, 1867.

[130] F. Yamanouchi, Japanese P. 40,608, 1921; *Chem. Abs.*, 1923, 17, 1896. *Cf.* Japanese P. 40,804, 1921; and Japanese P. 41,033, 1921; *Chem. Abs.*, 1923, 17, 2197; and Japanese P. 42,414, 1922; *Chem. Abs.*, 1924, 18, 760. All additions to 40,608.

[131] H. Kruse, U. S. P. 1,515,123, Nov. 11, 1925; *Chem. Abs.*, 1925, 19, 185. *Cf.* H. Kruse and W. C. Kruse, U. S. P. 1,464,944, Aug. 14, 1923; *Chem. Abs.*, 1923, 17, 3261; U. S. P. 1,381,648, June 14, 1921; *Chem. Abs.*, 1921, 15, 3560; and U. S. P. 1,309,292, July 8, 1919; *Chem. Abs.*, 1919, 13, 2292.

[132] R. W. Hilton, U. S. P. 1,499,943, March 27, 1923; *Chem. Abs.*, 1923, 17, 1896.

[133] R. Hochstetter, U. S. P. 928,450, July 20, 1909, to Ault and Wiborg Co.; *Chem. Abs.*, 1909, 3, 2389; German P. 226,003, 1909; *Chem. Abs.*, 1911, 5, 1195. *Cf.* U. S. P. 1,158,131, Oct. 26, 1915; *Chem. Abs.*, 1915, 9, 3370; U. S. P. 1,226,884, May 22, 1917; *Chem. Abs.*, 1917, 11, 2157.

[134] J. Stevenson, British P. 104,429, 1916, to Roneo, Ltd.; *Chem. Abs.*, 1917, 11, 1894.

[135] A. B. Dick and E. W. Hill, U. S. P. 1,439,356, Dec. 19, 1923; *Chem. Abs.*, 1923, 17, 888. A. B. Dick, Canadian P. 236,471, 1923; *Chem. Abs.*, 1924, 18, 477. E. W. Hill, U. S. P. 1,824,995, Sept. 29. 1932, to A. B. Dick Co.; *Chem. Abs.*, 1932, 26, 323.

[136] S. Horii, Japanese P. 99,266, 1933; *Rev. Paint, Colour, Varnish*, 1935, 8, 402; *Chem. Abs.*, 1934, 28, 2553. Japanese P. 91,209, 1931; *Chem. Abs.*, 1932, 26, 1459. Japanese P. 109,804, 1935; *Rev. Paint, Colour, Varnish*, 1935, 8, 403; *Chem. Abs.*, 1935, 29, 4958.

[137] W. Ernest and R. H. Baer, U. S. P. 2,002,939, May 28, 1935; *Am. Ink Maker*, 1935, 13 (7), 35; *Rev. Paint, Colour, Varnish*, 1935, 8, 337; *Chem. Abs.*, 1935, 29, 4958.

[138] J. B. Hurwitz, A. S. Hurwitz, and M. Garfunkel, British. P. 264,712, 1926, to H. Hurwitz and Co.; *Chem. Abs.*, 1928, 22, 174.

formaldehyde, sodium chloride, glycerol and gum arabic or gum tragacanth, is suggested for stenciling compositions.[139] Dextrin and acetated glycerin dissolved in blown rapeseed oil form the vehicle for an emulsion ink, the body of which consists of blanc fixe and a pigment.[140]

A non-cracking, non-chipping, flexible slow-drying stencil ink is said to be made from 5 parts glue, 1 part glycerin and 1 to 4 parts water-color paint.[141]

Ribbon Inks. Inks used for ribbons of various machines are very closely allied to stamp-pad inks in their qualities and characteristics. They must be non-drying and very diffusable into the paper fibers when they are printed. There are several types of ribbon-employing machines, among which are the typewriter, multigraph machine, time clocks, and telegraph machines of the type that automatically register the signals received. The ribbons are usually of a tightly woven, highly flexible fabric which is cut into strips of the width required for the machine. They are inked by passing them on rollers through a vessel of the ink solution and removing the excess ink by squeegee rollers. The edges of the ribbon are kept from fraying by the impregnation of a binding agent, such as glue and glycerol.[142]

Various methods serve to inhibit both evaporation of the solvent on the ribbon and the loss of too much ink to the paper when printing. These include the coating of each face of the ribbon with aluminum powder,[143] the imposition of a Pyroxylin layer on the ribbon,[144] and the addition of a very small proportion of oil in relation to the amount of pigment present so the particles of pigment will stay near one side of the ribbon and not go through to the type side.[145]

An ink for ribbons is prepared by mixing an ammonium salt, such as the chloride or carbonate, with wax, oleomargarine, or stearin, and a coloring material, such as carmine or cochineal.[146] An ink not influenced by temperature or humidity and containing palm oil and aniline is reported by Bailey.[147]

In another procedure a salt of copper, iron, manganese, or aluminum is added to a solution of an aniline dye in a resin soap and the mixture dissolved or suspended in turpentine. Castor oil or whale oil is added to inhibit drying and spreading of the pigment.[148]

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[139] G. S. Whitty, U. S. P. 953,110, March 29, 1910; *Chem. Abs.*, 1910, 4, 1530. J. T. Humes, U. S. P. 2,163,601, Oct. 21, 1937.

[140] W. G. Fuerth, U. S. P. 1,013,544, Jan. 2, 1912; *Chem. Abs.*, 1912, 6, 688.

[141] G. R. Stocker, U. S. P. 2,136,985, Nov. 15, 1938; *Am. Photo-Engraver*, 1939, 31, 33; *Rev. Paint, Colour, Varnish*, 1939, 12, 20; *Chem. Abs.*, 1939, 33, 1421.

[142] B. Walther, *Chem.-Ztg.*, 1921, 45, 169; *Chem. Abs.*, 1921, 15, 1630. C. Becher, *Seifensieder-Ztg.*, 1928, 55; *Der. Chem.-techn. Fabr.*, 1928, 25 (9), 25; (10), 29; (11), 31; (12), 33; *Rev. Paint, Colour, Varnish*, 1928, 1, 20. P. J. Hassett, *Am. Dyestuff Reptr.*, 1922, 10, 403; *Chem. Abs.*, 1922, 16, 2611.

[143] L. C. Antrim, Canadian P. 354,228, 1935, to Autographic Register Co.; *Chem. Abs.*, 1936, 30, 1908.

[144] S. E. Miller, U. S. P. 1,962,082, June 5, 1934, to L. C. Smith and Corona Typewriters, Inc.; *Rev. Paint, Colour, Varnish*, 1934, 7, 377; *Chem. Abs.*, 1934, 28, 4923.

[145] G. W. Shaefer, U. S. P. 2,103,275, Dec. 28, 1937; *Am. Ink Maker*, 1938, 16 (2), 37; *Rev. Paint, Colour, Varnish*, 1938, 11, 111.

[146] A. F. O. Nardi, French P. 665,319, 1928; *Chem. Abs.*, 1930, 24, 979.

[147] L. Bailey, U. S. P. 224,477, Jan. 3, 1888.

[148] I. A. M. Korolev and I. P. Bocharov, Russian P. 23,508, 1931; *Chem. Abs.*, 1932, 26, 2070. Russian P. 22,596, 1931; *Chim. et Ind.*, 1932, 28 (3), 659; *Rev. Paint, Colour, Varnish*, 1932, 5, 276.

Ultramarine, the presence of which, it is said, enables the vehicle to absorb a larger amount of the readily printing dye, often is included in ribbon ink, along with waxy or oleaginous materials, used to lessen the likelihood of smearing or smudging of the composition.[149]

Both tricresyl phosphate[150] and higher molecular alcohols having at least 12 carbon atoms[151] are used as plasticizers for ink compositions. The proportion of tricresyl phosphate may be sufficient for it to serve as a vehicle in which the pigment is dispersed, while the higher aliphatic alcohols permit a high proportion of color value.

Typewriter ribbons may be rejuvenated by subjecting the old ribbon to the action of hydrocarbon vapors.[152]

Hectograph Inks. In the hectograph process of duplication, a master sheet is printed with a highly tinctorial ink containing a dye such as Methyl Violet. This sheet is then laid face down on a layer of tough gelatin which may be cast in a trough or impregnated on a roll of fabric. Methyl Violet is readily absorbed by the gelatin and from 50 to 100 printed pages may be made by laying and pressing sheets of paper successively upon the gelatin and removing them. The master sheet may be typewritten in a machine fitted with a special ribbon, or may be prepared by writing upon it with a fluid hectograph ink. Although the ink usually contains Methyl Violet, other dyes may be employed when other colors are desired, such as Malachite Green, Methylene Blue, Magenta (for red) and nigrosine black.[153] The dye can be incorporated with such modifying agents as water, alcohol, glycerol, hydrochloric, oxalic, or lactic acid, tannic acid, and *o*-dihydroxybenzene.

Gum arabic is used to make the ink more viscous. When this gum is mixed with an aniline pigment, alcohol, and water, the mixture should be strained through flannel or cotton; otherwise very small particles of undissolved dye make the copies appear smeary.[154]

A pigment which is found applicable is the product resulting from the reaction of *p*-aminodimethylanilinethiosulphonic acid and methyl-*o*-toluidine. This dyestuff is converted to a water-soluble dye by hydrolysis with an acid.[155]

Sorbitol and acetyl sorbitol mixed with acetic acid, glycerol, water, and a dye furnish a hectograph ink.[156]

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[149] R. Jarmai and E. Lorand, French P. 642,349, 1927; *Chem. Abs.*, 1929, 23, 1293. British P. 279,403, 1926; *Chem. Abs.*, 1928, 22, 2819. German P. 523,226, 1926; *Chem. Abs.*, 1931, 25, 3502.

[150] S. A. Neidich, U. S. P. 2,139,092, Dec. 6, 1938, to Underwood Elliott Fisher Co., Inc.; *Chem. Abs.*, 1939, 33, 2354.

[151] E. Schwabe, U. S. P. 2,135,735, Nov. 8, 1938, to Am. Hyalsol Corp.; *Chem. Abs.*, 1939, 33, 1525.

[152] Hugo Graf, U. S. P. 2,155,653, April 25, 1939.

[153] M. Shinozaki, Japanese P. 109,351, 1935, to Shinozaki Ink Seizo K. K.; *Rev. Paint, Colour, Varnish*, 1935, 8, 307; *Chem. Abs.*, 1935, 29, 3863.

[154] E. Stormer, *Pharm. Z.; Polyt. Notizbl.*, 35, 31; *Chem. Zentr.*, 1880, 11 (3), 175.

[155] French P. 792,689, 1936, to I. G. Farbenind. A.-G.; *Rev. Paint, Colour, Varnish*, 1936, 9, 224; *Chem. Abs.*, 1936, 30, 4335.

[156] K. H. Meyer, J. Müller and U. Hoffman, U. S. P. 1,756,951, May 6, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 3387. British P. 292,655, 1927; *Chem. Abs.*, 1929, 23, 1517.

Chapter 16

Printing Ink Problems

MANUFACTURING, STORAGE AND SHIPPING PROBLEMS

Many difficulties and problems arise in connection with the manufacture, storage, shipping and use of printing inks. A great number of troublesome features have been mentioned in connection with the various types of ink; others, more universal in nature, will be discussed in relation to the general field of inks and printing. Some of these problems are chemical in nature, others physical, and still others mechanical.

The difficulties attendant upon the manufacture of inks are neither as numerous nor as important as those connected with printing, but a knowledge and understanding of the problems is essential in order that the processes involved in the manufacture of inks be comprehended.

Two methods of grinding and mixing pigments are in common use, the roll mill and the pebble mill. The roll mill usually comprises from two to nine steel rollers which turn upon each other to grind and disperse the pigments. The several rollers do not revolve at the same rate; the first drum usually has a speed of about 300 r.p.m. and the ratio of the others is 1:3:9 in a 3-roll mill, and 1:3:6:12 in a 4-roll type. A 9-roll mill is really a series of three separate 3-roll machines arranged so that the product of each mill successively is treated by the next until dispersion is complete. The advantages of this type of mill are its efficiency and speed, which are relatively higher than those of the pebble or ball mill. The main disadvantage of the roll mill is the heat created because of friction. For this reason the steel rolls must be hollow to allow for constant water cooling. The rolls may be set at a desired distance apart and the magnitude of the particles produced so regulated.[1]

In pebble or ball mills, pigments are ground by rolling balls over each other as the drum, in which they are encased, revolves. The "pebbles" are usually made of flint, Belgian buhrstone, silex or steel, and are about 1 to 1½ inches in diameter. The barrel of the drum is lined with soft rubber or some other material to protect it and to subdue the noise. Most of the grinding is done between the balls rather than against the side of the drum. Eccentric balls have been utilized to make the work more efficient, and the walls of the drum have been fitted with water coils for

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[1] R. Berger, *Farbe u. Lack*, 1930, 35, 18; *Rev. Paint, Colour, Varnish*, 1930, 3, 44. J. M. Sanderson, *Paint, Oil, Chem. Rev.*, 1931, 91 (22), 8; *Rev. Paint, Colour, Varnish*, 1931, 4, 210; *Chem. Abs.*, 1931, 25, 4416. F. de M. Tubman, *J. S. C. I.*, 1932, 51, 330; *Rev. Paint, Colour, Varnish*, 1932, 5, 176; *Chem. Abs.*, 1932, 26, 3311. H. J. Wolfe, *Am. Ink Maker*, 1934, 12 (12), 18; *Rev. Paint, Colour, Varnish*, 1935, 8, 62.

cooling. Although the process is slower than the roll mill, it is said to be cheaper because less power is needed to run the apparatus. One of the disadvantages encountered is the chipping of the surfaces of the balls and the resulting discoloration of the pigments, especially those light in color, such as whites and yellows.[2]

Special difficulty arises when colors must be matched to correspond to those used by an artist in a water color or an oil painting. The ink manufacturer is required to duplicate, or match as closely as possible, the colors of the painting and at the same time to produce an ink that has good printing qualities. If necessary, special characteristics for a desired paper surface, or unusual permeability and resistance must be held to in case the printed material is to be varnished or shellacked over. When a previously compounded ink is to be matched, the difficulties increase because the exact qualities of the original ink, such as tack, length, gloss, and drier content, in addition to color, must be met.[3]

Inks that are improperly manufactured tend to cause difficulties when stored. When in the store-room for a length of time, some inks exhibit a thickening effect ("livering," to be discussed later) because of saponification of the fatty acids present in the vehicle, and other chemical action within the material. A high drier content catalyzes the oxidation of the drying oil and tends to thicken the ink. Other inks with pigments improperly dispersed become thinner upon storage because the vehicle and the pigment tend to separate into two layers.[4]

Without the observance of special precautions, there is a frequent danger of spontaneous ignition or combustion occurring in linseed oil varnishes, paints and inks. There are numerous causes for the occurrence of fire, among which are the presence of excess drier, and of extremely fine pigments which tend to act as catalyzers for the oxidation of the varnish, a low relative humidity of the atmosphere, and temporary stoppage and inefficient cooling of the grinding mills. Slight traces of impurities in an ink, such as sulphur and potassium chlorate, act as very potent catalysts in the oxidation of the linseed oil. Zinc white has been found

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[2] P. O. Abbé, *Drugs, Oils & Paints*, 1933, **48** (1), 16; *Rev. Paint, Colour, Varnish*, 1933, **6**, 27. *Official Digest Federation Paint and Varnish Production Clubs*, 1932 (120), 1047; *Rev. Paint, Colour, Varnish*, 1933, **6**, 27. F. Hebler, *Chem. Fabr.*, 1928 (47), 665; *Rev. Paint, Colour, Varnish*, 1928, **1**, 219; *Chem. Abs.*, 1929, **23**, 2047. S. W. Kendall, *Chem. Trade J.*, 1932, **90** (2235), 191; *J. Oil Colour Chem. Assoc.*, 1932, **15**, 66; *Rev. Paint, Colour, Varnish*, 1932, **5**, 93; *Chem. Abs.*, 1932, **26**, 3145.

[3] R. Fanelli, *Am. Pressman*, 1937, **48** (1), 25; *Rev. Paint, Colour, Varnish*, 1938, **11**, 108. For a general treatment of the manufacture of inks, see H. Hadert, "Handbuch über die Herstellung und Verwendung der Druckfarben," 2nd Ed., Verlag von Otto Elsner, Berlin, 1931; *Rev. Paint, Colour, Varnish*, 1931, **4**, 169; *Chem. Abs.*, 1931, **25**, 2864. *Mod. Lith. and Offset Printer*, 1932, **27** (3), 50; *Rev. Paint, Colour, Varnish*, 1932, **5**, 90. H. Hadert, *Paint Manuf.*, 1933, **3** (1), 5; (2), 37; *Rev. Paint, Colour, Varnish*, 1933, **6**, 25; *Chem. Abs.*, 1933, **27**, 1526. O. Prager, *Seifensieder-Ztg.*, 1930, **57**, 551; *Rev. Paint, Colour, Varnish*, 1930, **3**, 177. O. Preiszer. *Farben-Ztg.*, 1924, **29**, 1841; 1925, **30**, 453; *Chem. Abs.*, 1925, **19**, 408, 901. H. E. Rice, *Paint, Oil Chem. Rev.*, 1935, **97** (11), 16; *Chem. Abs.*, 1935, **29**, 4956. C. K. Sloan, *Am. Ink Maker*, 1937, **15** (2), 16; *Rev. Paint, Colour, Varnish*, 1937, **10**, 132. H. J. Wolfe, *Paint Manuf.*, 1934, **4** (10), 321; *Rev. Paint, Colour, Varnish*, 1934, **7**, 456. French P. 42,820, 1933, to Anciens établissements le Clezio (S. a. r. l.); *Chem. Abs.*, 1934, **28**, 1555. H. P. Benner and J. C. Morrell, U. S. P. 1,848,100, March 8, 1932, to Universal Oil Products Co.; *Chem. Abs.*, 1932, **26**, 2879. R. L. Cawood, U. S. P. 1,992,290, Feb. 26, 1935; *Rev. Paint, Colour, Varnish*, 1935, **8**, 253; *Chem. Abs.*, 1935, **29**, 2406. P. Mitchell, British P. 409,752, 1934; *Chem. Abs.*, 1934, **28**, 6327. B. C. J. Selier, British P. 426,621, 1935; *Chem. Abs.*, 1935, **29**, 6445. British P. 410,427, 1934, to Franz Zimmers Erben A.-G.; *Chem. Abs.*, 1934, **28**, 6351. H. Zimmer, German P. 602,593, 1935, to Paul Buschmann; *Chem. Abs.*, 1936, **30**, 632.

[4] R. F. Bowles, *Penrose's Annual, London*, 1935, 111; *Am. Ink Maker*, 1935, 13 (4), 13; *Rev. Paint, Colour, Varnish*, 1935, **8**, 207.

to cause a considerable amount of heating of linseed oil over a period of 9 or 10 hours. One of the most dangerous pigments is said to be Prussian Blue, which is the cause of much fire hazard in inks.[5]

Livering. One of the more troublesome phenomena which occur in inks is what is known as "livering," or flocculation of the vehicle, which causes the ink to coagulate and become in some cases very hard and non-liquid. It usually occurs while the ink is in the warehouse and not being moved. It is possible both to prevent and to remedy livering of ink by various methods, many of which are preventive rather than corrective.[6]

Pigment Flotation. Pigment flotation occurs when a material somewhat soluble in the vehicle is used as the pigment. When there is an excess of colloidally dispersed particles of one color, or when the dyestuff has not been sufficiently ground, the phenomenon will appear. The elimination of floating may be effected by a thorough grinding and dispersion, by the use of insoluble dyestuffs, and by the selection of compatible materials for the pigment, in that they have the same dispersion qualities.[7] The mottling and powdering of inks may be obviated by the addition of a greater amount of vehicle.[8]

"Doping" or "doctoring" inks in the pressroom to change their properties should be resorted to only in case of absolute necessity, and, if possible, the ink should be sent back to the ink maker for correction. Changes often are made when the humidity is high, the temperature low, and the paper not of workable quality. These are all objectionable. Certain substances, such as driers, mineral oil, beeswax, kerosene (for thinning gloss inks), and varnish, may be added to overcome difficulties in the pressroom.[9]

Pressroom Problems. Having discussed some of the problems connected with the ink itself, we now turn to the questions of pressroom technique, that is, the cleaning of type, presses and other machinery, and the use of various appliances (such as ink fountains) in the print shop.

Of the solvents used for cleaning type, the organic liquids, such as gasoline, benzene, toluene, xylene, kerosene, and alcohol are most commonly used. Emulsion-type cleaners, however, also find application, mostly because they are non-inflammable and do not cause a swelling of rubber surfaces as the organic solvents do. Tests were made by the Japanese Government Printing Bureau[10] at Tokyo to determine the swelling effect on rubber and the solvent power of a number of solvents. Strips of rubber 1 × 4.5 cm. were used and their elongation was measured when treated with various solvents. Liquids of high volatility, such as

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[5] *Farbe u. Lack*, 1933, **38** (11), 129; *Chem. Trade J.*, 1933, **92** (2394), 278; *Rev. Paint, Colour, Varnish*, 1933, **6**, 91, 111.

[6] See Chapter 5.

[7] *Am. Paint J. Conv. Daily*, 1930, **14** (52D), 27; *Rev. Paint, Colour, Varnish*, 1930, **3**, 229.

[8] *Am. Pressman*, 1937, **47** (2), 30; *Rev. Paint, Colour, Varnish*, 1937, **10**, 95.

[9] W. Foxglove, *Mod. Lith. and Offset Printer*, 1929, **25**, 78; *Rev. Paint, Colour, Varnish*, 1929, **2**, 150. E. A. Kilheffer, *Am. Pressman*, 1938, **48** (2), 19; *Rev. Paint, Colour, Varnish*, 1938, **11**, 109.

[10] M. Ogura and K. Nakazima, *Res. Bull. Govt. Printing Bur., Tokyo*, 1937 (3), 7, 21; *Rev. Paint, Colour, Varnish*, 1938, **11**, 193; *Brit. Chem. Abs.* B, 1938, 407; *Chem. Abs.*, 1938, **32**, 3988.

gasoline and petroleum ether, were best because they did not remain on the rubber long enough to be absorbed, while of the materials of low volatility, dichloroethane caused least swelling, whereas xylene and toluene were not considered satisfactory.

Other experiments showed the desirability of using gasoline with a specific gravity of .72 for cleaning forms; petroleum naphtha with 10 per cent petroleum for rollers, and 80 per cent petroleum naphtha, 15 per cent xylene, and 5 per cent petroleum as a general cleaner. Light gasoline is also recommended for offset work, and a mixture of 80 per cent naphtha and 20 per cent tetralin for cleaning intaglio plates.[11]

When benzene, gasoline, and other organic solvents are used to clean the press, they dissolve some of the substance out of the rollers and thereby roughen the surface and reduce the life of the material; therefore the use of water emulsion cleaners has been advised.

Kerosene is emulsified with water by the agency of ammonium linoleate and a stable mixture produced which cleans the type and also tends to prolong the life of the rollers. The slight amount of ammonia gas given off by the linoleate is said to be of value because the gas, when dissolved in water, is a good emulsifying agent and tarnish remover. The water in the emulsion does not swell the glue constituent of the rollers because it evaporates before any appreciable degree of absorption can take place.[12] Sodium or ammonium hydroxide may be employed as emulsifying agents in the preparation of a type cleaner containing a water-insoluble detergent. Among the solvents used are *p*-cresol, *p*-oxytoluene, *p*-methylphenol and phenol. The rollers are soaked with the solution, after which they are washed with water.[13]

The application of collodion as an ink remover has been suggested. Chalk is suspended in the solution and the whole is spread on the surface to be cleaned, allowed to dry and harden, and then stripped off, removing with it the ink layer.[14]

When only a portion of the ink is to be removed, as when there is an excess, a roller made of a composition of whiting, wax, glycerol, gelatin and water is employed to collect some of the ink from the plate.[15] If a certain area of a plate is to be freed of ink, a shield is used to enclose that portion and an atomized spray of a solvent is applied to the plate (Figure 70).[16]

A composition added to drying inks and reported to inhibit drying on

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[11] J. Albrecht, W. Abitz, and W. Schuhbardt, *Z. deut. Buchdrucker verwandte Gewerbe*, 1934, **46**, 229; *Chem. Zentr.*, 1934, **105** (2), 517; *Rev. Paint, Colour, Varnish*, 1934, **7**, 305; *Chem. Abs.*, 1935, **29**, 6667. Dutch P. 36,673, 1936, to American Petroleum Co.; *Chem. Zentr.*, 1936, **107** (1), 900; *Rev. Paint, Colour, Varnish*, 1936, **9**, 22. H. G. Ghegan, U. S. P. 1,406,183, Feb. 14, 1922; *Chem. Abs.*, 1922, **16**, 1328.

[12] H. Bennett, *Am. Ink Maker*, 1931, **9** (6), 21; *Rev. Paint, Colour, Varnish*, 1931, **4**, 216.

[13] L. Minton, British P. 429,377, 1935; *Rev. Paint, Colour, Varnish*, 1935, **8**, 403.

[14] G. K. H. Améen and C. E. V. Dahlquist, Swedish P. 91,936, 1938; *Chem. Abs.*, 1938, **32**, 6779.

[15] S. Beaune, U. S. P. 2,043,604, June 9, 1936, to Soc. des Procédés Serge Beaune; *Chem. Abs.*, 1936, **30**, 5334.

[16] C. Henderson, U. S. P. 996,642, July 4, 1911; *Chem. Abs.*, 1911, **5**, 2744.

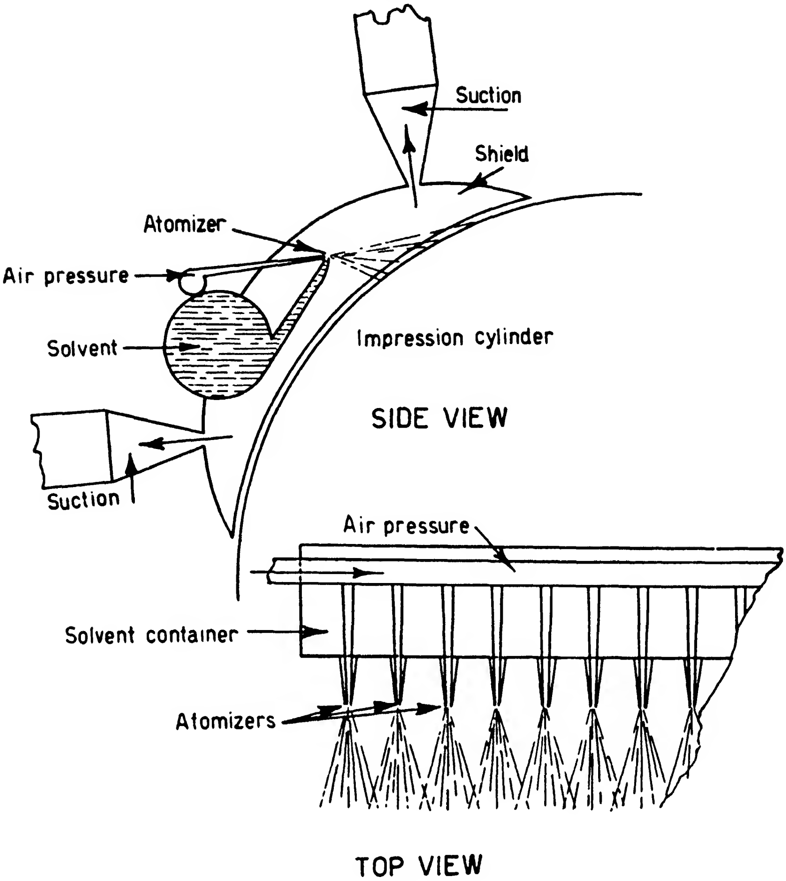

FIGURE 70. Diagrammatic Sketch of Apparatus for Selectively Removing Ink from Plate (C. Henderson).

the press while it is idle is made up of 1 part of turpentine, 2 parts of castor oil, and 5 grams of oil of cloves.[17]

The level of ink in the fountain may be kept constant by the use of an electrically operated shut-off system which regulates the flow of ink from a storage tank into the ink fountain on the press (Figure 71). When the height of the ink in the fountain exceeds a set level, thereby contacting two electric terminals, a shut-off is effected in the pipe from the reservoir. When the ink level lowers, the tap is turned on to allow more of the ink to flow into the press fountain. In this way the ink pressure is kept constant and an even flow of liquid is assured.[18]

The printing process might be called the least scientific of all the phases connected with ink. It is almost purely an art, and consequently

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[17] L. Dejardin, Belgian P. 355,723, 1928; *Chem. Abs.*, 1929, 23, 4356.

[18] W. Thomas, U. S. P. 1,981,530, Nov. 13, 1934, to Pneumercator Co.; *Chem. Abs.*, 1935, 29, 384

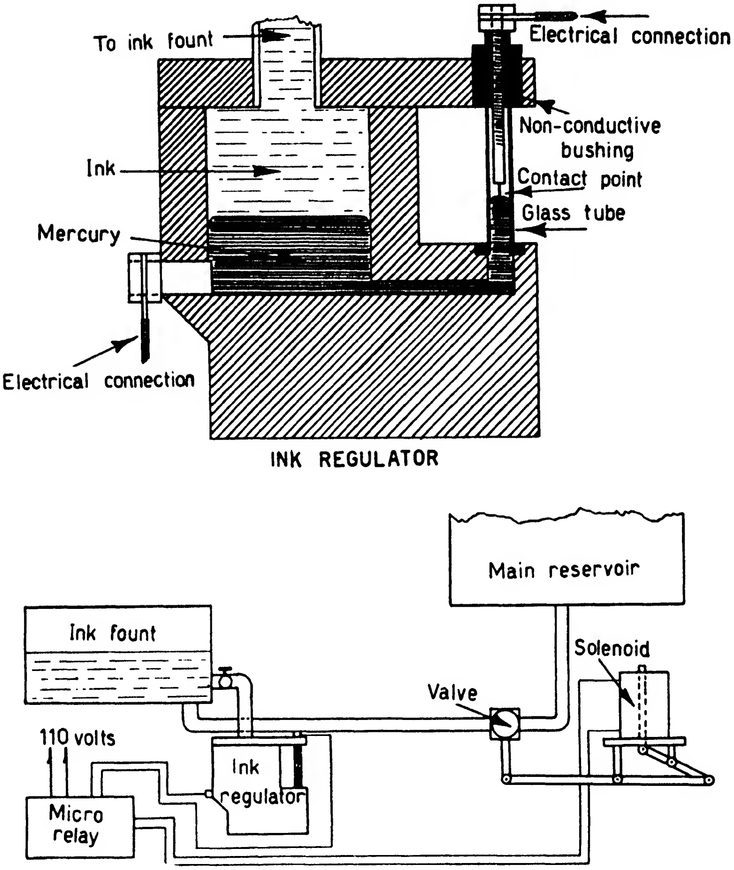

FIGURE 71. Sketch of Apparatus for Maintaining Constant Ink-Level in Fountain (W. Thomas).

little in the way of rules or laws can be formulated for practice, although some of the more specific problems have been investigated and are easily avoidable if general precautions are followed. On the problem of offset, for instance, extensive work has been done, and numerous processes and treatments have been devised to minimize the difficulty or to remove it entirely.

Humidity and Temperature Control. The scientific control of atmospheric humidity and temperature has been practiced as a means of securing the most advantageous conditions of printing. The relative humidity controls the rate of drying of inks and also the tendency for adhesion to the surface of material upon which printing is to be done. The viscosity of inks is a function of the temperature, so a control of the latter regulates their tackiness and printability. A different temperature has been found to be the optimum in each of the various operations connected with printing, such as etching, retouching, etc. Jacobsen[19] has prepared a table (Table 38) of the best temperature and humidity conditions for the various departments of a photogravure plant.

Many problems arise with colored inks. Care must be taken with a double-toned ink to see that cobalt and lead driers are not used, as oil-soluble pigments tend to react with them and produce colored compounds. Color printing in newspapers was long a source of trouble, mainly because colored inks are not as durable or as covering as black. Also, the speed for printing with such inks must be much slower than with carbon pigment inks. When natural or inorganic pigments are used, the inks produced are more durable and are resistant to many reagents, but a smaller variety of shades is available than when synthetic organic dyestuffs are employed.

Numerous difficulties arise in the drying of inks. When drying is delayed, a greater amount of absorption of the vehicle takes place, leaving the pigments of the ink more or less unprotected on the surface, and causing a chalking effect. Moreover, certain papers contain ingredients which may accelerate or retard the drying rate of the inks used on them. Therefore it is essential that, in manufacturing inks, the type of paper to be printed be taken into account in order to determine the proportions of drier, drying oil and fillers. The oils used should be bodied, either by blowing or by heating processes.

Various specific troubles in connection with inks may arise, such as the abrasion of copper plates and cylinders by coarse pigments, the filling in of half-tone blocks, which causes a spoilage of the impression, and other problems which arise from time to time.[20]

[19] H. E. Jacobsen. *Heating, Piping, Air Conditioning*, 1935, **7**, 423; *Chem. Abs.*, 1936, **30**, 1268.

[20] For general discussion of printing inks and their problems, see the following: *J. S. C. I.*, 1928, **47**, 1147; *Rev. Paint, Colour, Varnish*, 1928, **1**, 216. *Chronique Graphique*, 1938, **13**, 3993; *Rev. Paint, Colour, Varnish*, 1938, **11**, 107. *Am. Ink Maker*, 1932, **10** (3), 17; *Rev. Paint, Colour, Varnish*, 1932, **5**, 89. F. F. Barmeier, *Share Your Knowledge Rev.*, 1937, Nov. 28; *Rev. Paint, Colour, Varnish*, 1938, **11**, 24. J. Bekk, *Angew. Chem.*, 1933, **46**, 125; *Chem. Abs.*, 1933, **27**, 1960. R. F. Bowles, *Brit. Printer*, 1931, **44** (259), 9; *Rev. Paint, Colour, Varnish*, 1931, **4**, 207. *Penrose's Annual*, 1937, London; *Am. Ink Maker*, 1937, **15** (4), 25; *Rev. Paint, Colour, Varnish*, 1937, **10**, 174. *Mod. Lith. and Offset Printer*, 1930, **26**, 288; 1931, **27**, 16; *Rev. Paint, Colour, Varnish*, 1931, **4**, 35. L. Coates, *Indian Print and Paper*, 1937, **3** (2), 40; *Bull. Inst. Paper Chem.*, 1938, **8** (8), 306; *Rev. Paint, Colour, Varnish*, 1938, **11**, 192. A. J. England, *Oil Colour Trades J.*, 1930, **78**, 1679; *Rev. Paint, Colour, Varnish*, 1930, **3**, 262. H. A. Idle, *Oil Colour Trades J.*, 1937, **91**, 197; *Chem. Abs.*, 1937, **31**, 2026. G. F. Jones, *J. Oil Colour Chem. Assoc.*, 1933, **16** (155), 149; *Rev. Paint, Colour, Varnish*, 1933, **6**, 135; *Chem. Abs.*, 1933, **27**, 3625; *ibid.*, 1935, **18** (182), 269; *Rev. Paint, Colour, Varnish*, 1935, **8**, 401; *Chem. Abs.*, 1935, **29**, 7675. G. L. Riddell, *Oil Colour Trades J.*, 1937, **91** (2001), 602; *Paint Manuf.*, 1937, **7** (4), 110; *Chem. Age*, 1937, **36** (921), 169; *Rev. Paint, Colour, Varnish*, 1937, **10**, 96; *Chem. Abs.*, 1937, **31**, 3308. *J. Oil Colour Chem. Assoc.*, 1937, **20**, 220; *Brit. Chem. Abs.* **B**, 1937, 945; *Chem. Abs.*, 1937, **31**, 7268. R. Sanderson, *Brit. Printer*, 1935, **48** (284), 100; *Rev. Paint, Colour, Varnish*, 1935, **8**, 402; *Chem. Abs.*, 1936, **30**, 4342. A. de Waele, *J. Soc. Dyers Colourists*, 1927, **43**, 42; *Chem. Abs.*, 1927, **21**, 1362; *Am. Ink Maker*, 1939, **17** (5), 31. L. Coates, *Paper Market Printing Tech.*, 1939, **95**, 87, 123; *Rev. Paint, Colour, Varnish*, 1939, **12**, 180. *Am. Ink Maker*, 1939, **17** (5), 37. K. Stephan, Canadian P. 276,638, 1927; *Chem. Abs.*, 1928, **22**, 2071; *Rev. Paint, Colour, Varnish*, 1928, **1**, 136. *Brit. Printer*, 1937, **49**, 251; *Rev. Paint, Colour, Varnish*, 1937, **10**, 95. L. Auer, *Paint, Varnish Production Mgr.*, 1937, **17**, 12; *Chem. Abs.*, 1938, **32**, 8168. G. F. Jones, *Oil Colour Trades J.*, 1935, **87**, 1073; *Chem. Abs.*, 1935, **29**, 3859. L. Coates, *Paper, Market & Printing Tech.*, 1938, **104**, 191; *Rev. Paint, Colour, Varnish*, 1939, **12**, 19; *Chem. Abs.*, 1939, **33**, 4441. R. F. Bowles, *Penrose Ann.*, 1939, **41**, 162; *Rev. Paint, Colour, Varnish*, 1939, **12**, 19; *Chem. Abs.*, 1939, **33**, 4442.

Table 38.—Optimum Temperature for Printing Operations.

Department	Temperature (° F.)	Humidity (%)
Etching	72	50
Photo gallery	74	50
Retouching	75	50
Sensitizing of carbon printing	72	50
Dark rooms	74	50
Drying rooms	75	50

Offset. With the speeding up of printing processes, especially in newspaper work, the problems of ink drying and offset have become increasingly difficult. Offsetting is described as the tendency of an undried ink to be transferred from the printed sheet to any other surface with which it comes in contact. The ink may offset to the back of the adjacent sheet of paper, to a roll over which the paper passes, or to any object touching the paper. A printer often wears a small piece of sandpaper folded over the tip of his finger and held on with a rubber band when manually retrieving the sheets from the press, to prevent the offsetting of inks to his skin. In news printing, where the paper is to be printed on both sides in fast succession, and then folded, precautions must be taken, although the ink may be absorbed at a high rate, to prevent the ink from smudging and offsetting. As the speedup of printing goes on, the ink has less time to reach a state of dryness wherein the surface is tacky before the sheets are either stacked or rolled. The simple expedient has been tried of having the web of paper travel along for a distance before it is rolled on the drum, in order to allow more time for drying. No sacrifice in speed is made by this procedure, but considerable space is taken up, so it proves to be an unsatisfactory arrangement.

Many methods have been devised to eliminate offset, among which are spraying a liquid on the sheet of paper, the use of a powder to cover the ink film, the inclusion of a special substance in the ink itself, the appli-

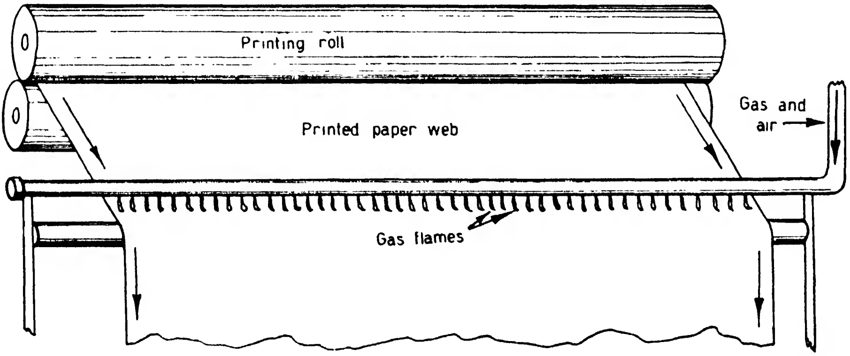

Figure 72. Diagrammatic Sketch of Apparatus for Removing Solvent from Inks by Burning.

cation of a gas to dry the ink (Figure 72), the use of rough rollers, and the reduction of the static electricity in the vicinity of the paper.[21]

Materials that cause a skin to form rapidly on the surface of the wet ink also eliminate offset. Milk when incorporated into the ink helps it to form a skin.[21a]

Various materials are used to spray or cover the sheet in order to cover the ink film and inhibit the tendency of the ink to smudge. Gum arabic and gum tragacanth, glucose, paraffin, and cellulose esters and ethers often are dissolved in quick-drying solvents, and applied to the

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[21] See also Chapter 8.

[21a] M. E. McMaster, U. S. P. 877,212, Jan. 21, 1908; *Chem. Abs.*, 1908, 2, 1502.

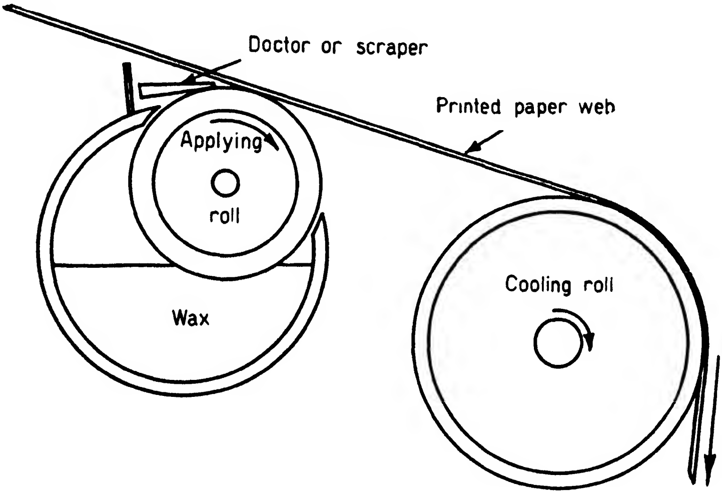

FIGURE 73. Sketch of Apparatus for Waxing Printed Webs to Prevent Offset (E. C. Francoise).

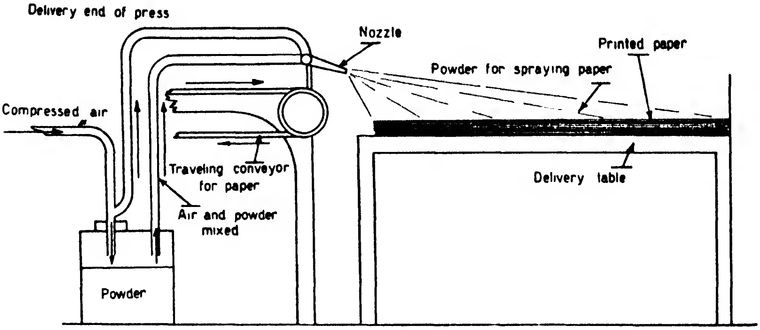

FIGURE 74. Apparatus for Preventing Offset by Spraying Printed Sheets with Powder (R. Blow).

sheet after printing. Some of the solvents used are methyl or ethyl alcohol, carbon tetrachloride, organic esters, or water.

The liquid may be sprayed from an atomizer, either from above or below the paper. Sometimes the substance which sets upon the paper does not completely cover the sheet, but forms small knobs which keep the sheets apart when they are stacked or rolled. Liquids containing the protective substance may be applied to the web by means of a roller over which the paper passes (Figure 73), the roller being fed by means of a hopper or fountain placed above it.[22]

Powder often is applied to the web of a paper as it passes along, so as to have a layer of material between the ink surface and the back of the paper as it is rolled upon itself. Powdered talc, soapstone, aluminum hydroxide, magnesia, starch, chalk, kaolin, and several other substances are employed. The material may be kept in a hopper above the web and sifted out upon a rotating drum which distributes it upon the paper surface. Occasionally the powder may be blown against the paper by air pressure and in this manner be distributed over the surface (Figure 74).[23]

Elimination of offset is sought by causing the ink to dry quickly. Different means of accelerating the drying or oxidation reaction have been devised, including exposure of the printed paper to ozone and heating. Ozone may be passed over the sheets or web, or may be produced *in situ* by means of an electric discharge near the web. An arrangement of condensers or the use of vacuum tubes has been suggested to produce nascent oxygen and ozone, both of which serve to increase the rate of oxidation of the drying oil.[24] By substituting a mixture of nitrogen peroxide and nitric oxide mixed with air for the ozone, the oxidation of the drying oil is catalyzed and offset is said to be prevented. The gases

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[22] Various methods of covering the ink film are discussed in the following: H. M. Barber, U. S. P. 1,470,344 and U. S. P. 1,470,345, Oct. 9, 1923; and U. S. P. 1,524,163, Jan. 27, 1925, to C. B. Cottrell and Sons. E. H. Bucy, U. S. P. 2,078,790, April 27, 1937; *Rev. Paint, Colour, Varnish*, 1937, **10**, 261; *Chem. Abs.*, 1937, **31**, 4416; U. S. P. 2,142,667 and 2,142,668, Jan. 3, 1939; *Chem. Abs.*, 1939, 33, 3039; all to Atlas Powder Co. A. S. Duncan, French P. 361,444, 1905; *Chem. Abs.*, 1908, **2**, 1359. E. C. Francoise, British P. 380,244, 1931; *Brit. Chem. Abs.* **B**, 1932, 978. U. S. P. 1,831,624, Nov. 10, 1931; U. S. P. 1,845,260, Feb. 16, 1932; U. S. P. 1,921,313, Aug. 8, 1933; *Chem. Abs.*, 1933, **27**, 5189; all to Kalamazoo Paper Parchment Co. A. L. Grammer, U. S. P. 1,445,273, Feb. 13, 1923. V. G. Green and E. Gustafsson, U. S. P. 2,110,218 and 2,110,219, March 8, 1938, to Binks Mfg. Co.; *Chem. Abs.*, 1938, **32**, 3525. R. A. Habermaier, U. S. P. 2,101,999, Dec. 14, 1937; *Chem. Abs.*, 1938, **32**, 1023; Canadian P. 367,983, 1937; *Chem. Abs.*, 1937, **31**, 7152; both to De Vilbiss Co. J. A. Paasche, British P. 439,078, 1936; *Rev. Paint, Colour, Varnish*, 1936, **9**, 93. Canadian P. 373,457 and 373,458, 1938; *Am. Ink Maker*, 1938, **16** (9), 71; *Chem. Abs.*, 1938, **32**, 5237. French P. 784,826, 1935; *Rev. Paint, Colour, Varnish*, 1936, **9**, 93; *Chem. Abs.*, 1936, **30**, 632. A. K. Taylor, U. S. P. 2,078,742, April 27, 1937, to U. S. Printing and Lithograph Co. B. A. Young, U. S. P. 2,114,792, April 19, 1938, to R. R. Donnelley & Sons; *Chem. Abs.*, 1938, **32**, 4697. German P. 699,386; *Rev. Paint, Colour, Varnish*, 1939, **12**, 181. L. Lemaire, *Bull. soc. franc. phot.*, (3), **5**, 39; *Chem. Abs.*, 1914, **8**, 1244. E. A. Albrecht, Swiss P. 167,823, 1934; *Chem. Zentr.*, 1934, **105** (2), 3851; *Rev. Paint, Colour, Varnish*, 1935, **8**, 26.

[23] H. M. Barber, U. S. P. 1,428,931, Sept. 12, 1922, to C. B. Cottrell & Sons. R. Blow, U. S. P. 2,093,995, Sept. 28, 1937, to W. F. Hall Printing Co. R. J. Greenway, U. S. P. 1,638,572, Aug. 9, 1927; and U. S. P. 1,949,102, Feb. 27, 1934, to C. B. Cottrell & Sons. C. J. MacArthur, U. S. P. 1,566,800, Dec. 22, 1925, to Charles Eneu Johnson and Co. *Am. Ink Maker*, 1939, **17** (3), 29; *Rev. Paint, Colour, Varnish*, 1939, **12**, 179.

[24] W. W. Allen and A. L. Grammer, British P. 415,885, 1934. U. S. P. 2,000,684, May 7, 1935; *Chem. Abs.*, 1935, **29**, 948. J. R. Blaine, U. S. P. 1,503,224, July 29, 1924, to Miehle Printing Press & Mfg. Co. R. L. Fearn, Jr., U. S. P. 1,388,418, Aug. 23, 1921; *Chem. Abs.*, 1921, **15**, 4058. T. F. Pinder, U. S. P. 1,842,195, Jan. 19, 1932; *Chem. Abs.*, 1932, **26**, 1810. U. S. P. 2,017,257, Oct. 15, 1935. F. E. Hartman, U. S. P. 1,993,404, 1935, to W. R. and F. H. Montgomery; *Chem. Abs.*, 1935, **29**, 2763; *Rev. Paint, Colour, Varnish*, 1935, **8**, 208.

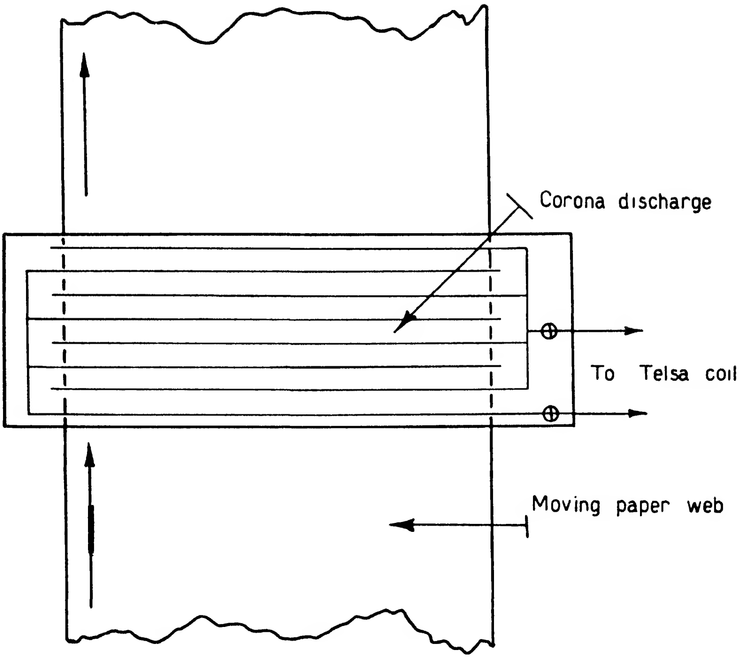

FIGURE 75. Sketch of Apparatus for Preventing Offset by Corona Discharge (J. R. Blaine).

are passed over the web in a confined space and come into contact with the undried ink film. Also, the gloss of the ink is said to be increased by the use of the nitrogen oxides.[25]

As an alternative method of causing the ink to dry faster, a compound such as "rubrene peroxide" may be incorporated into the ink before printing. When the paper is heated afterwards, the peroxide decomposes, releasing nascent oxygen, which accelerates the drying of the varnish vehicle.[26]

The smudging of paper and offsetting of the ink may be minimized or eliminated by the use of tympans covered with sandpaper or thin metal sheets. The tympan is the roller opposite the printing roller on a rotary press. When such work as newspapers must be printed in quick succession on both sides, the tympan of the second type roller often causes trouble because it comes into contact with the freshly printed first side of the sheet as the second impression is being made. Sandpaper offers a rough surface to the paper which prevents any slipping and also keeps

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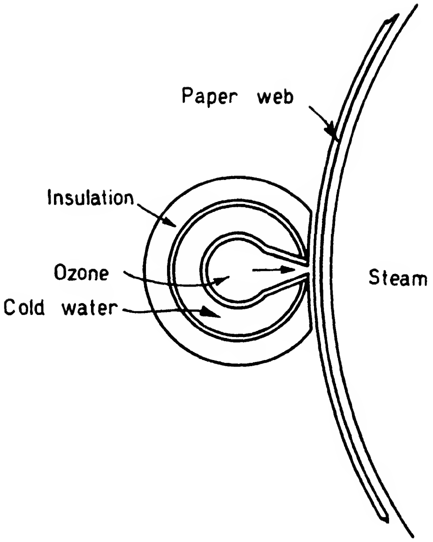
[25] W. W. Allen and A. L. Grammer, U. S. P. 2,077,624, April 20, 1937, to Curtis Pub. Co.; *Chem. Abs.*, 1937, 31, 4022.

[26] T. F. Pinder, U. S. P. 1,842,196, Jan. 19, 1932; *Chem. Abs.*, 1932, 26, 1810. "Rubrene peroxide" is also discussed in Chapter 8.

FIGURE 76.

Diagrammatic View of Ozonator for Effecting Rapid Drying of Prints (T. F. Pinder).



a great proportion of the sheet out of contact with the surface of the roller (Figure 77).[27]

By removing the static electricity from the surface of a printed sheet, thus allowing the air to come into contact with the paper and dry the ink, the tendency to offset is decreased. The use of a row of gas flames just

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[27] T. E. Knowlton, U. S. P. 1,731,467, Oct. 15, 1929. U. S. P. 1,922,372, Aug. 15, 1933. R. L. Melton, R. C. Benner and H. P. Kirchner, U. S. P. 2,011,181, Aug. 13, 1935, to Carborundum Co.

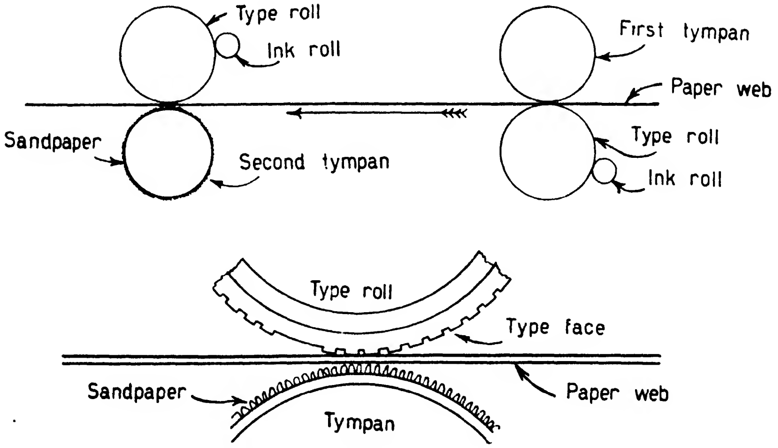
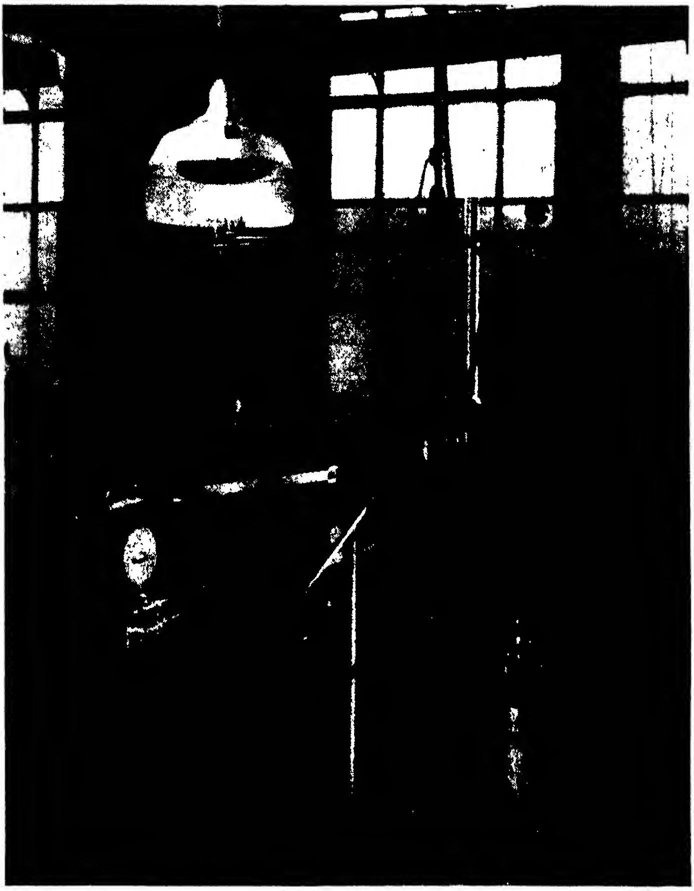


FIGURE 77. Diagrammatic Sketch of Printing Apparatus with Grained Tympan to Prevent Offset of Printed Material (R. L. Melton, R. C. Benner and H. P. Kirchner).



Courtesy Paasche Airbrush

Figure 78. Installation of Paasche No-Offset Equipment.

above the web or sheet as it passes out of the press serves this purpose as well as heating the ink to some degree. By impregnating a felt-covered impression roll or tympan with an oily medium such as glycerin, the static charge on the surface of the paper is removed, thus allowing contact of air with the sheet.[28]

By adding a compound composed of mutton fat, varnish, cornstarch, paraffin oil, and citronella oil to the ink, smudging of the printed sheet is reported to be materially lessened.[29]

The ink film on a web of paper may be set very quickly by the inclusion of an inflammable vehicle in the ink. "Butyl Carbitol," a volatile,

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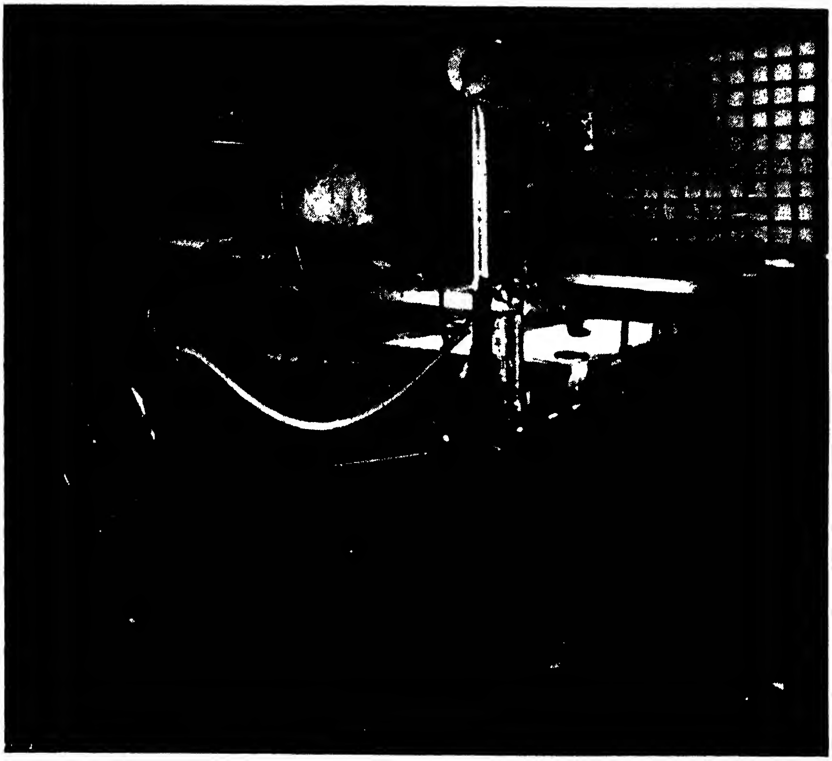
[28] A. B. Beck, U. S. P. 1,336,995, April 13, 1920.

[29] C. H. Rackle, U. S. P. 1,272,092, July 9, 1918; *Chem. Abs.*, 1918, 12, 2056.



Courtesy Paasche Airbrush

FIGURE 79. Paasche No-Offset Equipment.

highly inflammable solvent, may be used. The web, after being printed, is heated to volatilize and ignite the vehicle, which burns, thereby setting the ink. The flame is extinguished by the winding of the paper on a roll.[30] There is an appreciable volatilization of lead from the molten type metal. Eighty per cent of the lead in the air of printing plants is due to volatilization, according to Hepler and others.[30a]

Light-fastness of Pigments. A problematical feature of inks is the light-fastness of the pigments contained in them. Any printed material,

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[30] F. J. Jeuck, U. S. P. 2,042,432, May 26, 1936, to International Printing Ink Corp.; *Rev. Paint, Colour, Varnish*, 1936, **9**, 316; *Chem. Abs.*, 1936, **30**, 5062. For general discussions of drying, offset, and problems concerned with them, see: *Paint Manuf.*, 1934, **4** (7), 203; *Rev. Paint, Colour, Varnish*, 1934, **7**, 293. J. D. Cohen, *Paint Manuf.*, 1937, **7** (8), 246; *Rev. Paint, Colour, Varnish*, 1937, **10**, 341; *Chem. Abs.*, 1937, **31**, 7673. *Paint Manuf.*, 1938, **8** (3), 82; *Rev. Paint, Colour, Varnish*, 1938, **11**, 108. C. R. Conquergood, *Printing*, July, 1934; *Am. Ink Maker*, 1934, **12** (8), 15; *Rev. Paint, Colour, Varnish*, 1934, **7**, 376. M. Hartmann, *Klimschs Druckerei-Anzeiger*, 1936, Nos. 9, 10; *Farben-Ztg.*, 1936, **41**, 1168; *Rev. Paint, Colour, Varnish*, 1937, **10**, 24. C. MacArthur, *Paper Trade J.*, 1937, **105**, TAPPI Sect., 219; *Rev. Paint, Colour, Varnish*, 1938, **11**, 109; *Brit. Chem. Abs.* **B**, 1938, 83; *Chem. Abs.*, 1937, **31**, 8956. F. W. Stoyle, *Brit. Color Printer*, Dec. 2, 1937, 550; *Rev. Paint, Colour, Varnish*, 1938, **11**, 25. G. L. Riddell, *Oil Colour Trades J.*, 1937, **91**, 602; *Chem. Abs.*, 1937, **31**, 3308. British P. 427,028, 1935, to Maschinenfabrik Augsburg-Nürnberg A.-G.; *Chem. Abs.*, 1935, **29**, 6428.

[30a] J. M. Hepler, P. F. Regin and R. W. Colina, *J. Ind. Hyg.*, 1938, **20**, 641; *Brit. Chem. Abs.* **B**, 1939, 330.

especially that which is subjected to the action of sunlight and artificial light, such as outdoor posters, depends for its value upon its resistance to fading. Ink containing a mineral pigment such as chrome yellow or Milori Blue, or carbon black, is by its nature light-fast because these pigments cannot be oxidized or reduced easily by external influences. Organic pigments, on the other hand, are susceptible on the whole to rather easy fading because very little alteration in their molecular configuration is necessary to produce a colorless compound. However, mineral or inorganic pigments do cause trouble in fading when two compounds are present in the pigment, because of the double decomposition which may take place through the agency of water and sunlight. Zinc oxide, when present as a filler in ink, accelerates double decomposition because of its action as a sensitizer in molecular electrolysis. A protective film that is wetted easily prevents the action of zinc oxide when the ink is stored. The coating is said to envelop the particles of the pigment and to isolate them from the oxide present.[31]

Other atmospheric factors, such as gas, smoke and heat, exert an influence on the light-fastness of ink, and their presence must be taken into account when ink is prepared. The character of the residue content of paper which is to be printed is of importance. Many impurities show a tendency to react with the ink pigments. Paper prepared from textile fibers protects the ink to a greater degree than material composed of wood or grass fibers. The choice of vehicle is also of considerable import when considering the light-fastness of the ink.[32]

Table 39.—Light-Fastness of Pigments.

Excellent	Good
Chrome yellows	Permanent Red R
Chrome orange	Toluidine Red
English vermilion	Pigment Scarlet 3B (barium lake)
Milori blues	Lithol Rubine B (calcium lake)
Bronze blue	Ultramarine blue
Carbon black	
Chrome green	
Madder lake	

Fair	Fugitive
Tartrazine (barium lake)	Naphthol Yellow S
Lake Red C	Auramine (barium lake)
Lithol Red	Acid Orange II (tin lake)
Para Reds	Acid Orange II (barium lake)
Methyl Violet (tungstic toner)	Methyl Violet (tannin toner)
Alkaline Blue	Peacock Blue (erioglaucine)

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[31] H. J. Wolfe, *Am. Ink Maker*, 1934, 12 (1), 13; *Rev. Paint, Colour, Varnish*, 1934, 7, 22. A. Hancock, *J. Oil Colour Chem. Assoc.*, 1932, 15 (146), 207; *Rev. Paint, Colour, Varnish*, 1932, 5, 245; *Chem. Abs.*, 1932, 26, 5761.

[32] J. Stark, *Mod. Lith. and Offset Printer*, 1930, 26, 78; *Rev. Paint, Colour, Varnish*, 1930, 3, 119. For relation of paper to ink, see Chapter 18.

A table of the relative light-fastness of pigments, based upon research of the Lithographic Technical Foundation,[33] divides the colors into four classifications: "excellent, light-fast even when in reduced form"; "good, light-fast when full strength"; "fair, moderately light-fast"; and "fugitive." The pigments were tested by being exposed to sunlight and artificial light for six-hour periods. At the end of each period the inks were examined and then re-exposed for another six hours. Allowances were made for the bleaching of the varnish and the darkening of the paper upon exposure to light, both daylight and artificial. The results are indicated in Table 39.

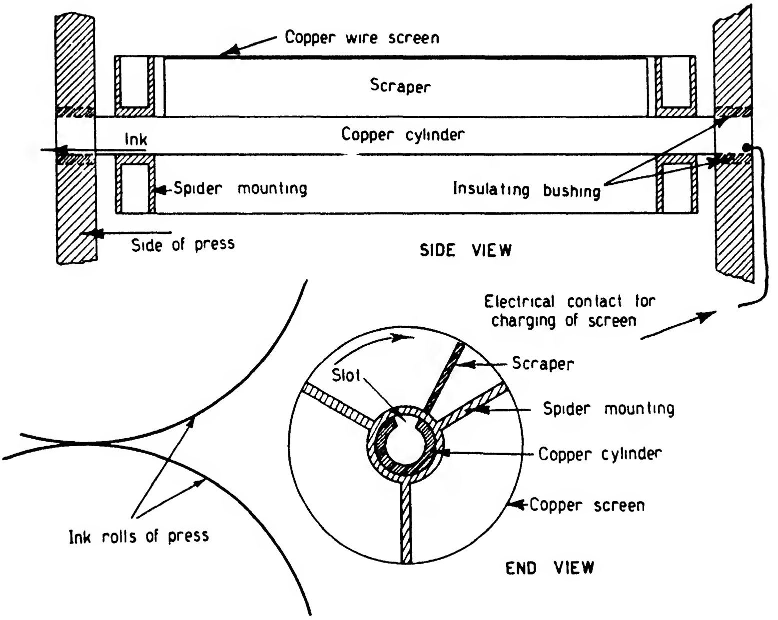

FIGURE 80. Plan of Apparatus for Overcoming Static Electric Charge at Press (W. T. Diefenbach).

Fogging of Ink. The phenomenon of ink clouding or misting is another problem resulting from high-speed printing. The misting is a consequence of the accumulation of a charge of static electricity on the press and paper, and consists of the formation of a fog or mist of ink droplets in the vicinity of the press. The individual drops of ink become similarly charged and repel one another, being caused to remain suspended in the air. The trouble may be overcome by electrically grounding the press and by having charged screens of wire mesh near the press to offset the accumulation of a static charge (Figure 80). The control of the

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[33] *Mod. Lith. and Offset Printer*, 1932, **28** (1), 8; *Rev. Paint, Colour, Varnish*, 1932, **5**, 25. A table containing the results of tests upon forty-two German inks can be found in an article by E. Valenta, *Brit. J. Phot.*, 1910, **56**, Suppl. 92; *Chem. Abs.*, 1910, **4**, 1136.

humidity of the cloth or paper to be printed upon is another means of overcoming the difficulty.[34]

Miscellaneous Problems. The detrimental effect of an ink vehicle upon a lacquered surface has been noted. Posters were printed and allowed to dry for five hours. Subsequently they were glued (printed side up) to doors coated with a nitrocellulose lacquer varnish. Three months after their application the posters were removed and the printed portions of the paper were very adherent to the lacquer beneath. The lacquer surface on the doors, which was damaged with respect to its strength and adherence, was about 2½ years old.[35]

To inhibit the mixing of ink with water, the addition of substances such as magnesia, starch, machine oil, paraffin, beeswax, or a mixture of linseed oil and paraffin wax is advised.[36]

TOXICITY OF SOLVENTS AND PIGMENTS

One of the more important problems in both the ink manufacturing plant and in the print shop is the question of toxicity of pigments and solvents. Such substances as lead, chromium, arsenic, mercury,[37] and some organic pigments are toxic to varying degrees and care must be exerted when their handling is necessary. Since the introduction of high-speed rotary printing processes, the wide use of highly volatile and toxic solvents has become prevalent. Benzene, toluene, xylene, trichlorethylene, and other common solvents are poisonous both in the liquid and vapor phase. When liquid they may be absorbed through the skin, and when in the vapor state they may be inhaled. Many organic solvents, as well as being toxic, are highly inflammable, and have been the cause of disastrous explosions and fires when precautions as to storage and handling were not observed.

Certain laws require the proper ventilation of plants employing dangerous volatile materials, and prescribe the maximum percentage of vapors allowed for safety. The ventilation system used depends upon the density of the vapors present: an up-draft system for lighter-than-air fumes, and a down-draft type for those heavier than air.[38]

Benzene and its homologs, xylene and toluene, and derivatives of these, are especially volatile and toxic. Nitrobenzene and aniline, both derivatives of benzene, have been known to be the cause of poisoning when these substances were present in stamping inks.[39]

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[34] W. T. Diefenbach, *Am. Ink Maker*, 1935, 13 (9), 21; *Rev. Paint, Colour, Varnish*, 1935, 8, 401. F. Fritz, *Paint, Varnish Production Mgr.*, 1931, 6 (2), 12; *Rev. Paint, Colour, Varnish*, 1931, 4, 250. W. T. Diefenbach, U. S. P. 2,096,164, Oct. 19, 1937; *Chem. Abs.*, 1938, 32, 60.

[35] *Ink.-Lack-Betrieb.*, 1934 (9/10), 71; *Rev. Paint, Colour, Varnish*, 1934, 7, 194.

[36] *Mod. Lith. and Offset Printer*, 1937, 33 (7), 140; *Rev. Paint, Colour, Varnish*, 1937, 10, 341.

[37] For discussion of mercury inks, see Chapter 15.

[38] H. N. Morris, *Brit. Printer*, 1935, 48 (285), 125; *Rev. Paint, Colour, Varnish*, 1935, 8, 585; *Brit. Printer*, 1936, 48 (286), 193; *Rev. Paint, Colour, Varnish*, 1936, 9, 65. P. W. Gumaer, *Trans. Nat. Safety Council (Advance Printing)*; *A. P. V. M. Abs.*, No. 14, 351; *Rev. Paint, Colour, Varnish*, 1931, 4, 165. A. P. Stassins, *Ind. chim. belge*, 1937, 8, 383; 1938, 9, 3; *Chem. Abs.*, 1938, 32, 4244; *Usselzew, 15me Congr. chim. ind.*, 1936, 1040; *Chem. Abs.*, 1936, 30, 5817.

[39] H. Temming, *Deut. med. Wochschr.*, 1928, 54, 105; *Chem. Abs.*, 1928, 22, 1200.

Benzene is one of the most toxic of usual organic solvents, especially as a vapor. Its inhalation results in two types of poisoning, acute and chronic. In acute poisoning, this aromatic acts as a convulsive neurotoxin and later as an asphyxiant narcotic. When benzene is inhaled by workers over a considerable period of time, chronic symptoms make their appearance. A feeling of lassitude and the occurrence of headaches and nausea, among other symptoms, usually are the result of continual exposure to the vapors.[40]

The toxic effects of various concentrations of benzene vapor are listed in Table 40.

Table 40.—Toxic Effects of Benzene.

Effects	Concentration of Benzene Vapor in Air (p.p.m.)
Fatal in a short time.	19,000
Dangerous in ½ to 1 hour.	3,000
Slight symptoms in several hours.	1,570-3,130
Maximum concentration allowable.	100

Many cases of poisoning have been reported concerning workers in the printing industries as a result of the use of benzene as a solvent. Four instances of aplastic anemia were observed in intaglio printers by Gerbis.[41] The chief solvent employed was benzene, although from 10 to 30 per cent of toluene and xylene were occasionally mixed with the benzene which, alone, was considered the most dangerous. Mass poisoning of workers was reported by Ehrhardt[42] where 48 per cent of benzene and 50 per cent of xylene and toluene were used as a washing solution in printing.

Toluene is not as toxic as benzene, although the symptoms produced in both the acute and chronic conditions are practically identical with the latter. Instances of unconsciousness are comparatively rare, mostly because of the lower volatility of toluene. Moreover, the oxidation products (chiefly benzoic acid), which are formed very readily in the body, are comparatively non-toxic and are eliminated with ease, thereby removing the cause of the discomfort.[43]

Cases of toluene poisoning have been observed by Litzner and Edlich.[44] Hypersensitivity to alcohol was noted, as well as the usual headache, indigestion and other symptoms after the worker had been exposed to toluene vapors anywhere from a month to 2½ years.

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[40] J. J. Batchelor, *Am. J. Hyg.*, 1927, **7**, 276; *Chem. Abs.*, 1928, **22**, 273. *Mechanical Engineering*, 1935, **57**, 232. See also E. Browning, "Toxicity of Industrial Organic Solvents," Report No. 80, Medical Research Council, Industrial Health Research Board, London, His Majesty's Stationery Office, 1937.

[41] H. Gerbis. *Arbeitsschutz*, 1935, 279; *J. Ind. Hyg. Abs.*, 1936, **18** (3), 38; *Rev. Paint. Colour. Varnish*, 1936, **9**, 142.

[42] W. Ehrhardt, *Zentr. Gewerbehyg.*, 1936, **23**, 10; *J. Ind. Hyg. Abs.*, 1936, **18** (5), 65; *Rev. Paint, Colour, Varnish*, 1936, **9**, 287.

[43] E. Würm, *Arch. Gewerbepath. Gewerbehyg.*, 1931, **2**, 766. W. E. Engelhardt and W. Estler, *Arch. Hyg. Bakt.*, 1935, **114**, 249. J. Brachmann, *Arch. Hyg. Bakt.*, 1937, **118**, 329; *Chem. Abs.*, 1938, **32**, 673.

[44] S. Litzner and W. Edlich, *Farben-Chem.*, 1934, **5**, 473; *Rev. Paint, Colour, Varnish*, 1935, **8**, 78; *Sammlg. v. Vergiftungsfällen*, 1934, Abt. A, **5**, 9; *Chem. Zentr.*, 1934, **105** (1), 3631; *Rev. Paint, Colour, Varnish*, 1934, **7**, 350.

Xylene is lower than benzene in toxicity; but its exact degree is not definitely known. No fatal cases as a result of its inhalation have been reported. It produces similar results to toluene with the addition of circulatory and cardiac injury, such as palpitation.[45]

A mixture of xylene and toluene seems to produce altogether different symptoms than either solvent alone. Panse and Bender[46] report cases of endogenous psychosis in intaglio process workers. Physic disturbance was exhibited, including such symptoms as restlessness, disorientation, loss of memory, auditory hallucinations, and irritability. Recovery followed a change of occupation.

Trichloroethylene is not quite as toxic as are the aromatic solvents, but its danger is enough to warrant special precautions. A concentration of 10,000 parts per million is considered narcotic, and 2½ times this amount is fatal in its results. It is especially dangerous since one cubic centimeter of liquid equals 271 cc. of vapor. Chronic eczema is produced by continued exposure to the material, as well as gastric disturbances and anemia. The plant where trichloroethylene is employed should be ventilated by introducing pure air near the floor and exhausting the old air near the top.[47]

Two cases of poisoning by this solvent are reported by Persson,[48] in which symptoms of a neuromyelitic complex were exhibited. The patients became giddy while working, had a feeling of intoxication, and their gait became staggering. The symptoms passed off as soon as the period of exposure ended, but gradually the effects began to last for a longer time after their work ended, and they had a feeling of being exhausted. Headache, loss of appetite and nausea were complained of. After a cessation of work for about six months, a sufficient improvement was shown so that work could be resumed under more hygienic conditions.

The presence of arsenic in ink for bread wrappers has been noted. Out of 51 samples of wrappers and labels examined by Eldson,[49] nine contained appreciable quantities of the metal. Eight out of nine inks used in printing were practically free of the poison, but as much as 10 per cent of arsenic was reported to be incorporated in one ink. An arsenic lake was employed in the preparation of violet pigments.

Kappeller[50] made tests on fourteen violet carbon papers, two English typewriter ribbons, four pencils, and two aniline ink powders. Five of the carbon papers contained arsenic; the two ribbons showed the presence of from 5 to 15 mg. of arsenic per meter of ribbon length, and the pencils

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[45] See, however, W. Estler, *Arch. Hyg. Bakt.*, 1935, 114, 249.

[46] F. Panse and W. Bender, *Monatschr. Psychiat. u. Neurol.*, 1934, 99, 249; *J. Ind. Hyg.*, 1935, 17 (2), 24; *Rev. Paint, Colour, Varnish*, 1935, 8, 276.

[47] E. Browning, "Toxicity of Industrial Organic Solvents," Industrial Health Research Board, Report No. 80, 176, H. M. Stationery Office, London, 1937. L. Génévois, *Tech. imprim.*, 1936, 4, 842; *Chim. et ind.*, 1936, 36, 64; *Chem. Abs.*, 1936, 30, 6843.

[48] H. Persson, *Acta. Med. Scand.*, 1934, Suppl. 59, 410; *Bull. Hyg.*, 1935, 10, 364; *J. Ind. Hyg. Abs.*, 1935, 17 (5), 97; *Chem. Abs.*, 1935, 29, 3041.

[49] G. D. Elsdon, *Analyst*, 1924, 49, 336; *Chem. Abs.*, 1924, 18, 2969.

[50] G. G. Kappeller, *Z. Untersuch. Lebensm.*, 1930, 60, 213; *Chem. Abs.*, 1931, 25, 1105.

and ink powders were practically free from the substance. In this case, as above, the metal was used in dyestuff lakes.

Several instances of lead poisoning of printers have been reported. This seems only natural since all alloys used for type metal contain lead. The rarity of the cases is surprising, however; in one report, out of 4000 printers in Copenhagen, only two cases of definite poisoning occurred in a ten-year period (1925-1935).[51] Chromium poisoning has been prevalent in printing, especially in lithography, where chromium-plated printing surfaces often are employed.[52]

Two cases of dermatitis as a consequence of the action of ingredients of ink have been observed. Tulipan [53] cites an example where cardin, or cardol, the principal constituent of cashew shell oil, caused skin eruptions on four men who were exposed to an ink containing the oil as the vehicle. Para Red, used in rotogravure ink, was the irritating agent in another instance. Fifteen cases of dermatitis were reported.[54]

PROBLEMS OF ODOR

The odor of printing inks is unpleasant, particularly that of newspaper, aniline and gravure inks. They dry by evaporation or by absorption, so the vehicle either is volatilized into the air or remains unaffected upon the paper. In the case of drying-oil inks the situation is usually not so undesirable, because after a short time a protective coating has formed upon the ink film retaining the odor in the ink and preventing its escape into the atmosphere. Two expedients are used to rid the air of the odor: first, to ventilate the plant to such a degree that the vapors are dispelled, and second, to include a material which covers or perfumes the ink odor. Paradichlorobenzene, as well as about two per cent of a synthetic perfume, frequently is added to the ink as a deodorant or odor suppressor.[55]

Any odor in drying-oil inks is caused by the presence of intermediate products of oxidation, such as hydroxy- acids and aldehydes. When inks containing vehicles which dry by polymerization rather than by oxidation are used, however, this condition is obviated. Vanillin may be added to disguise the odor.[56] The elimination of pungent-smelling lead driers does away with much of the odor in inks. The problem may also be solved by the use of a pale varnish and natural resins, which are reported to act

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[51] G. Lind, *Hospitalstidende*, 1935, **78**, 769; *Bull. Hyg.*, 1935, **10**, 697; *J. Ind. Hyg. Abs.*, 1936, **18** (2), 22; *Rev. Paint, Colour, Varnish*, 1936, **9**, 142. E. Lederer, *Arch. Gewerbepath. Gewerbehyg.*, 1936, **7**, 331; *Chem. Abs.*, 1938, **32**, 3507.

[52] C. P. McCord and R. F. Reed, *Mod. Lith. and Offset Printer*, 1930, **26**, 238; *Rev. Paint, Colour, Varnish*, 1930, **3**, 262.

[53] L. Tulipan, *Ind. Med.*, 1936, **5**, 626; *Rev. Paint, Colour, Varnish*, 1937, **10**, 232; *Chem. Abs.*, 1937, **31**, 2455.

[54] E. A. Oliver, *J. Am. Med. Assoc.*, 1928, **91**, 870; *Chem. Abs.*, 1929, **23**, 906. For a discussion of cashew shell oil, see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935, 1229.

[55] *Paint, Varnish Production Mgr.*, 1935, **47** (281), 221; *Rev. Paint, Colour, Varnish*, 1935, **8**, 108. Bark, *Farbe u. Lack*, 1930, **35**, 447; *Rev. Paint, Colour, Varnish*, 1930, **3**, 219; *Am. Ink Maker*, 1932, **10** (1), 17; *Rev. Paint, Colour, Varnish*, 1932, **5**, 90.

[56] *Cf. Z. Deutschlands Druckgewerbe*, 1939, **51** (42), 448.

as fixing agents which appear to cover up and conceal the odoriferous material.[57] The inclusion of esters of 9,11-octadecadiene-1-carboxylic acid (dehydrated castor oil) and polyhydric alcohols with an odorless natural resin, such as ester gum and purified rosin, makes for a more pleasing odor in inks.[58]

Roller and Blanket Problems

The printing-ink roller invariably presents problems to the printer. The material used for the roller must be resistant to all ingredients of the ink with which it comes into contact, resilient enough to conform to the type face or plate, and tough and lasting. When employing a regular drying-oil ink, the usual roller composition is made up of gelatin or glue, water, and a plasticizer. Rubber would be dissolved or decomposed or caused to swell by the oil vehicle present in the ink. Frequently the plasticizer is glycerol, but it has many disadvantages; mainly its sensitivity to changes in humidity and temperature. For this reason, rollers must be designated for use in summer or in winter, those for cold weather containing more plasticizer than ones suited for warm weather.

Instead of incorporating glycerol as the softening agent for the glue composition, substitutes obviating the defects caused by glycerol have been suggested. Sorbitol dissolved in diethylene glycol in the proportion of 65 to 85 per cent sorbitol, the remainder being the solvent, has been added to the glue base. Ingredients consisting of about 30 per cent glue, 50 per cent sorbitol solution and 20 per cent water make up the composition for the roller. The glycol, water and sorbitol are placed in a hot-water jacketed kettle and heated to 70° C., the amount of water being held constant. The glue is added and the mixture heated for about two hours at 70 to 80° C., at the end of which time the mass is ready for casting.[59] Sorbitol may replace only part of the glycerol as a plasticizer, thus minimizing, although not actually eliminating, all the objectionable properties of the latter. The range of sorbitol content of the plasticizer is from 30 to 75 per cent, the remainder being glycerol, although the usual amount is about 55 per cent. The roll composition consists of 25 per cent glue, 25 per cent water and 50 per cent sorbitol-glycerol plasticizer.[60]

A mixture of chloroprene,[61] a synthetic rubber, with alkyd resins forms a composition which is used for rollers or offset blankets. The resin is synthesized by the reaction of glycerol phthalate with the ethylene glycol ester of adipic acid. The roller is composed of polychloroprene, sulphur,

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[57] P. J. Thoma, *Am. Pressman*, 1937, **48** (1), 30; *Rev. Paint, Colour, Varnish*, 1938, **11**, 110. See also *Am. Ink Maker*, 1938, **16** (10), 41.

[58] J. Schieber, German P. 522,486, 1930; *Rev. Paint, Colour, Varnish*, 1931, **4**, 288. The rosin is purified by vacuum distillation.

[59] L. H. Harrison, U. S. P. 2,121,126, June 21, 1938, to Atlas Powder Co.; *Chem. Abs.*, 1938, **32**, 6362.

[60] J. T. Power, U. S. P. 2,121,131, June 21, 1938 to Atlas Powder Co.; *Chem. Abs.*, 1938, **32**, 6362. British P. 477,903, 1938; *Chem. Abs.*, 1938, **32**, 5118.

[61] Also called "Neoprene" and "Duprene." See Carleton Ellis, "The Chemistry of Synthetic Resins," New York, Reinhold Publishing Corp., 1935, and Carleton Ellis, "The Chemistry of Petroleum Derivatives," Vol. II, New York, Reinhold Publishing Corp., 1937, Chapter 27.

the above resin, and fillers, such as zinc oxide. An antioxidant for the chloroprene may be included.[62] Another ingredient for rollers said to be resistant to oil and acids is a non-benzenoid polymer of acetylene of the empirical formula C_8H_8. The resin is dissolved in benzene and coated on the roller.[63] A felt material which has been impregnated with a cellulose derivative, such as cellulose acetate or nitrate, forms a coating for another variety of roller.[64]

Offset blankets[65] must have the same qualities as do inking rollers, for they are also subjected to the action of the oil vehicles of ink. Rubber may be used in instances where the ink contains no solvent or vehicle which causes deterioration of rubber. One or more layers of cloth may be employed, between which rubber may be deposited to produce a cushioning effect.[66] A coating of rubber hydrochloride is said to make the blanket impermeable to the effects of the varnish in the ink. A layer of felt is coated with rubber cement and pressed together with a similarly treated layer of cloth. Over this a coating of rubber hydrochloride is applied by means of successive applications of a solution of the material in benzene or chloroform.

The rubber hydrochloride is produced by dissolving 20 lbs. of plasticized crepe rubber in 313 lbs. of benzene and passing hydrogen chloride gas into the solution for about six hours at 10° C. Addition of the gas is stopped when the increase in weight of the solution reaches 11.6 lbs. The cement then is allowed to warm to room temperature and to react until a washed and dried sample is of the required tackiness, showing the chlorination has taken place. The usual time required is approximately 20 hours. This procedure yields a rubber compound about 30 per cent saturated, which is about the desired amount. Fully saturated rubber hydrochloride is too brittle for use as a roller; that chlorinated to an amount less than 27 per cent is reported to be too tacky to be of value. Steam distillation removes the excess hydrogen chloride and solvent. The purified rubber hydrochloride is dissolved in benzene or chloroform and applied to the roller. Hexamethylenetetramine to the extent of ½ per cent of the halogenated rubber may be added as an age resister for the rubber derivative.[67]

An alkyd resin, prepared from glycerol, phthalic anhydride, ethylene glycol, and succinic acid, in a ratio of glycol succinate to glycerol phthalate of about 4:1 by weight, finds application as a roller-forming material. The ingredients are heated in an aluminum vessel at 180 to 200° C. until there is evidence of gelation. The prepared resin is poured into shallow

[62] British P. 479,625, 1938, to Brit. Thomson-Houston Co., Ltd.; *Rev. Paint, Colour, Varnish*, 1938, **11**, 194; *Brit. Chem. Abs.* **B**, 1938, 1330; *Chem. Abs.*, 1938, **32**, 5115.

[63] A. L. Freedlander, Canadian P. 372,423, 1938, to Dayton Rubber Mfg. Co.; *Rev. Paint, Colour, Varnish*, 1938, **11**, 280; *Chem. Abs.*, 1938, **32**, 3523.

[64] F. Tutzschke, German P. 603,550, 1935; *Chem. Zentr.*, 1935, **106** (1), 1131; *Rev. Paint, Colour, Varnish*, 1935, **8**, 109.

[65] For a discussion of offset printing, see Chapter 9.

[66] British P. 481,587, 1938, to Dewey and Almy Chem. Co.; *Chem. Abs.*, 1938, **32**, 6906.

[67] W. C. Calvert, U. S. P. 2,064,780, Dec. 15, 1936, to Wingfoot Corp.; *Brit. Chem. Abs.* **B**, 1938, 1198; *Chem. Abs.*, 1937, **31**, 907.

amalgamated tins and cured at about 150° C. for three to five weeks. The resin sheet then is rolled on metal cones and wrapped with paper and wire to maintain its shape while it is baked to harden it to a sufficient tackiness. When at the right thickness the roll is cooled and machined to the required size on a lathe.[68]

SPECIAL PRINTING SURFACES

Three or four unusual varieties of printing surfaces may be noted. The usual composition, type metal, is composed of lead, tin, antimony and bismuth, although other materials have been used, such as thermosetting, synthetic resins. The face of the type is covered with a layer of rubber 0.5 mm. thick to equalize the pressure when printing.[69] Thermo-

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[68] M. M. Safford, U. S. P. 2,073,528, April 9, 1937, to General Electric Co.; *Brit. Chem. Abs.* **B**, 1938, 1329; *Chem. Abs.*, 1937, **31**, 3180.

[69] British P. 482,016, 1938, to E. Gundlach A.-G.; *Chem. Abs.*, 1938, **32**, 6774. P. A. Frazier, U. S. P. 2,133,981, Oct. 25, 1938, to Frazier Processes Inc.; *Chem. Abs.*, 1939, **33**, 787.

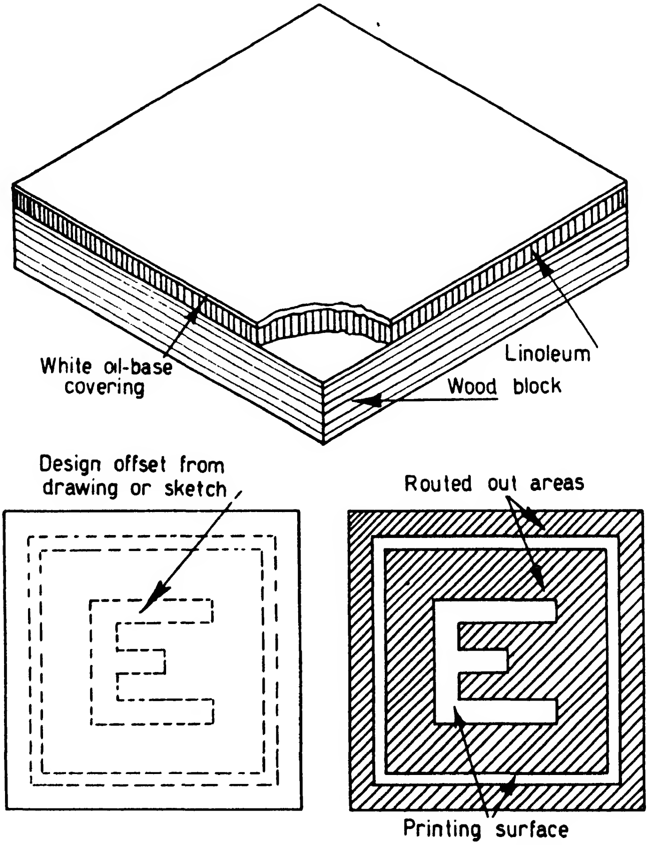

FIGURE 81. Method of Preparing Printing Block from Linoleum (C. E. Gray).

plastics may be used in making type or in the linotype process, where the characters may be cast and then melted after printing for re-use. Cellulosic materials combined with a plasticizer produce one species of type surface. A mixture of nitrocelluloses of different viscosities with sufficient triphenyl phosphate or some other plasticizer, to impart to the compound a viscosity of more than 10 seconds as tested in the falling-ball treatment, may be cast into type.[70] Linoleum, a frequently used substance for making plates of drawings, is employed as a base for the production of a printing block. It is buffed down with pumice and dried. Next, a coat of an oil-base enamel is sprayed on it and allowed from one to two weeks to set. It is then wiped over with alcohol to soften the extreme outer surface to permit transference of designs to the plate by pressing the drawing on paper against the surface of the block. The non-printing areas of the linoleum are then cut away to produce a relief printing block (Figure 81).[71]

INK REMOVAL

Another common problem connected with ink is that of its removal from cleaning cloths and the skin of pressroom workers. The usual method of removal from hands is by the use of a soap containing pumice or fine sand in its body.

However, the problem of ink removal from textiles is more complex, because the fibers absorb the vehicles and sometimes the pigments of ink. More involved methods, therefore, must be resorted to in the cleaning of cloth. A solvent such as toluene, aniline, or benzene often is used as a detergent. A mixture of 65 parts of toluene, 31 parts of anisole, 1.5 parts of aniline and 0.5 part of sassafras oil is reported to serve as an ink remover.[72] Often in the recovery of oily inks from cloths, the vehicle of the ink is a valuable by-product and is separated for re-use. The textile material is treated with various solvents, such as acetone, turpentine, carbon tetrachloride, ether, chloroform, or carbon disulphide, to dissolve the ink. The resulting liquor is passed through infusorial earth, clay, or activated carbon to remove the pigment, and the oil filtrate is freed of impurities by distillation when possible.[73]

Another preparation for the removal of ink from textiles, glass and other materials consists of soft soap, quartz sand, borax, and oil of bitter almonds (benzaldehyde).[74]

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[70] R. H. McKee, U. S. P. 2,116,536, May 10, 1938, to Cellu-Type Plate Co.; *Chem. Abs.*, 1938, 32, 5209. See also W. B. Wescott, U. S. P. 2,134,165, Oct. 25, 1938, to Addressograph-Multigraph Corp.

[71] C. E. Gray, U. S. P. 2,124,294, July 19, 1938, to M. Hurt and McLaughlin and Wallenstein Co.; *Chem. Abs.*, 1938, 32, 7171.

[72] P. A. Geller, Canadian P. 354,185, 1936; *Rev. Paint, Colour, Varnish*, 1936, 9, 170; *Chem. Abs.*, 1936, 30, 1908.

[73] M. S. Hopkins, U. S. P. 1,021,737 and U. S. P. 1,021,738, March 26, 1912, to the Separate Recovery Co. of America; *Chem. Abs.*, 1912, 6, 1370. M. S. Hopkins and C. R. Barnett, U. S. P. 932,470; 932,548; and 932,549, Aug. 31, 1909; *Chem. Abs.*, 1909, 3, 2632. For a discussion of ink removal see W. Wilburn, *Natl. Cleaner & Dyer*, 1936, 27 (8), 36; *Chem. Abs.*, 1937, 31, 6893.

[74] E. Frier, Swiss P. 161,520, 1934; *Chem. Zentr.*, 1934, 105 (1), 150; *Rev. Paint, Colour, Varnish*, 1934, 7, 102.

Chapter 17

The Testing of Printing Inks

Testing of both raw materials and finished inks is of importance in order to secure uniformity and standard quality. For this purpose a large number of physical and chemical tests are available. Not only have the properties of the vehicles, pigments and the inks to be investigated, but the knowledge of all factors is essential; relations of paper and temperature, press speed, adhesive power and other properties are necessary for correct judgments of printing inks.[1, 2]

Specific Gravity. Specific gravity is the comparison of the weight of a given volume of material with the weight of an equal volume of water under given conditions, the latter liquid having the specific gravity of 1. This test is of value for the estimation of covering power of an ink;[3] for calculation of ink losses while grinding, since the loss of weight is proportional to the density of an ink;[4] and for the consumption of pigments, because their specific weight and oil absorption are closely related,[5] heavy pigments having lower oil absorption.[6]

The specific gravity of a liquid is ordinarily determined by means of such common devices as the Westphal balance and the pycnometer. Usually the measurements are made at a temperature of 15.5° C. or 60° F. If, as is often the case, an accuracy of only 2 to 3 per cent is all that is required the following method may be used:[7] a piece of clean glass tubing of about 4 mm. bore and 4 cm. in length is weighed and the internal radius of the tube accurately measured. Ink is then forced into the tube by vertically submerging the end slowly beneath the surface of the ink. It is not difficult with a little care to exclude air bubbles. When the tube is nearly full it is withdrawn from the ink, carefully wiped, reweighed, and the length of the ink column measured. From the length of the ink column (L) radius of bore (R) and the weights of the tube

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[1] R. Beuerle, *Chem.-Ztg.*, 1932, **56,** 669; *Chem. Abs.*, 1932, **26,** 5438; *Brit. Chem. Abs.* **B,** 1932, 1040.

[2] For reviews on testing of printing inks, dyes and pigments see: *Am. Ink Maker*, 1936, **14** (12) 23; 1937, **15** (1), 21. W. Kühn, *Farben-Chem.*, 1936, **7,** 219; *Chem. Abs.*, 1936, **30,** 8425. B. Evton *Oil Col. Trades J.*, 1935, **87,** 1605; *Chem. Abs.*, 1935, **29,** 5289; *Brit. Chem. Abs.* **B,** 1935, 684. R. F Reed, *Off. Digest*, 1934, **138,** 245; *Chem. Abs.*, 1934. **28,** 7558; *Brit. Chem. Abs.* **B,** 1934, 1069. *Farbe u. Lack*, 1931 (11), 125; (12), 137; (14), 161; (17), 196; (18), 209. S. Levinson, *Ind. Eng. Chem.*, 1912, **4,** 661; *Chem. Abs.*, 1913, **7,** 1621. B. Walther, *Chem.-Ztg.*, 1921, **45,** 430; *Chem. Abs.*, 1921, **15,** 2088.

[3] S. T. Kantor, *Am. Ink Maker*, 1936, **14** (2), 19.

[4] K. H. Bettner, *Am. Ink Maker*, 1936, **14** (3), 23; *Chem. Abs.*, 1937, **31,** 6035; *Brit. Chem. Abs.* **B,** 1936, 1217.

[5] E. Stock, *Farben-Ztg.*, 1936, **41,** 959; *Chem. Abs.*, 1937, **31,** 4512; *Brit. Chem. Abs.* **B,** 1936, 1108.

[6] H. Hebberling, *Farbe u.- Lack*, 1935, 435; *Chem. Abs.*, 1935, **29,** 8364.

[7] J. A. V. Fairbrother and R. G. W. Croney, *Patra J.*, 1937, 1 (3), 104; *Am. Ink Maker*, 1938, **16** (1), 18; *Chem. Abs.*, 1938, **32,** 2375.

empty (W_1) and full (W_2) the density (D) may be calculated from the formula

$$D=\frac{W_2-W_1}{R^2L}$$

Viscosity. This is the internal friction of the material under investigation and depends upon the temperature and pressure. Hence, viscosity measurements should be made at a specified temperature. Regulation of viscosity permits adjustment of distribution, penetration, tack and other properties of the ink to suit the particular pigment, paper and process used.[8] There are many kinds of viscosimeters available[9] which can be divided into three classes: falling weight, efflux (capillary tube) and torsion.[10] A very good method for varnishes is that of the falling ball, giving absolute values. The unit for viscosity is the "poise." A substance is said to have the viscosity of 1 poise when a force of 1 dyne is required to move a plane surface of 1 sq. cm. at the speed of 1 cm. per second relative to another plane surface, when these two surfaces are separated from one another by a layer 1 cm. thick of the substance under investigation.

Actually, the measurement of viscosity by the falling ball method is made by allowing a metal ball to fall down a cylinder filled with the material. The time required to fall down a definite length is observed by means of a stopwatch. Stokes' law,

$$V=\frac{Gr^2\times d_s-d_l}{n}\,\frac{2}{9}$$

does not take into account two factors, wall effect and end effect, which are encountered when rather narrow cylinders are employed. For this reason Gibson and Jacobs[11] suggest that the narrowness of the cylinder and the end effect (at the bottom of the vessel) be corrected by extending the original formula to:

$$n=\frac{2}{9}\,\frac{Gr^2(d_s-d_l)T}{(1+2.4x)(1+3.3r/hs)}$$

V = Velocity of sphere
G = Acceleration of gravity
r = Radius of sphere
d_s = Density of sphere
d_l = Density of liquid
n = Viscosity of liquid
T = Time in seconds for sphere to fall through distance s
x = Ratio of radius of sphere to that of cylinder
h = Height of liquid

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[8] R. F. Bowles, *Penrose's Ann.*, 1937; *Am. Ink Maker*, 1937, **15** (4), 25.

[9] *Am. Ink Maker*, 1936, **14** (11), 22, 41. W. Flerus, *Farbe u. Lack*, 1932, 318. J. R. Stewart and G. G. Sward, *A. P. V. M. Circ.*, **393**, **283**; *Chem. Abs.*, 1931, **25**, 5065. *Rev. Gen. Mat. Plast.*, 1930, **6**, 333.

[10] C. J. Opp, *Am. Ink Maker*, 1934, **12** (6), 13; *Chem. Abs.*, 1934, **28**, 4613; *Brit. Chem. Abs.* **B**, 1934, 726.

[11] W. H. Gibson and L. N. Jacobs, *J. C. S.*, 1920, **117**, 473; *Chem. Abs.*, 1920, **14**, 2431; *Brit. Chem. Abs.* **A**, 1920, 558.

Tentative standards, issued by the Standards Committee of Graphic Arts, called for a falling aluminum or brass ball in connection with a Fischer instrument.[12] Very convenient and sufficient for most purposes is the Gardner-Holdt Bubble Viscosimeter.[13] It consists of a set of tubes each of which is filled with an oil of standard viscosity. The oil to be tested is placed in an empty tube of the same caliber. All tubes are not entirely filled, but have an air bubble at the top. By turning the tubes upside down and by comparing the speeds of the ascending bubbles in the oils the viscosity of the sample can be estimated. Viscosimeters designed by Stormer and MacMichael also are suitable for varnishes,[14] although more complicated to handle.

An international comparison has been made of Redwood, Engler and Saybolt viscosimeters, used in England, Germany and the United States, respectively, and it has been suggested that these three countries agree to conversion tables for the apparatus mentioned.[15]

Viscosities of pigmented vehicles and finished inks are determined the same way as those of varnishes. The consistency of an ink naturally is influenced by the pigment and its dispersion in the vehicle. Pigments which have not been ground into the vehicle with the necessary care give misleading results.[16] Flow,[17] tack,[18] stickiness [19] and thixotropy are dependent upon viscosity. Thixotropy [20] can be measured in absolute units by means of a special device constructed by Goodeve and Whitfield.[21]

A simple type of thixotrometer (Figure 82) was described by Gamble.[22] This instrument is essentially a torsion pendulum. It consists of a hollow metal cylinder coaxially suspended from a steel wire of known rigidity and partially immersed in the liquid under examination. The other end of the wire is attached to a torsion head. The angular rotation is measured by a mirror and light beam. In the case of a sol possessing yield value the cylinder will rotate through an angle smaller than the angular displacement of the torsion head. From the difference of these two angles the torque remaining in the wire may be calculated and the yield value of the sol (*e.g.*, ink or paint) determined from the dimensions of the cylinder. In operating the instrument the torsion head is displaced

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[12] *Farben-Ztg.*, 1922, **27**, 2491; *Chem. Abs.*, 1922, **16**, 3404.

[13] J. R. Stewart, *A. P. V. M. Circ.*, **434**, 219; *Chem. Abs.*, 1933, **27**, 4426; *Brit. Chem. Abs.* **B**, 1933, 1068. *Inst. Paint, Varnish Research, Sci. Circ.* No. 325.

[14] S. N. Glarum, *Am. Dyestuff Rep.*, 1934, 23, 175; *Chem. Zentr.*, 1934, **105** (2), 517; *Chem. Abs.*, 1934, **28**, 4911; *Brit. Chem. Abs.* **B**, 1934, 495.

[15] S. Erk, *J. Rheol.*, 1931, **2**, 163; *Rev. Paint, Colour, Varnish*, 1931, **4**, 155.

[16] H. Wolff, *Farben-Ztg.*, 1929, **34**, 2990; *Chem. Abs.*, 1929, **23**, 5598; *Brit. Chem. Abs.* **B**, 1929, 947.

[17] *Farbe u. Lack*, 1931, **36**, 501.

[18] R. Bulkley & F. G. Bitner, *J. Rheol.*, 1930, **1**, 269; *Chem. Abs.*, 1930, **24**, 5183; *Brit. Chem. Abs.* **B**, 1930, 674, 844.

[19] A. V. Pamfilov and E. N. Roslyakova, *Zh. Prikl. Khim.*, 1936, **9**, 1057; *Brit. Chem. Abs.* **B**, 1936, 911.

[20] Thixotropy is the isothermal reversible decrease of viscosity with shear. (C. F. Goodeve and G. W. Whitfield, *Trans. Faraday Soc.*, 1938, **34**, 511.)

[21] C. F. Goodeve and G. W. Whitfield, *loc. cit.* G. W. Whitfield, *Paint Manuf.*, 1939, **9** (3), 80; *Rev. Paint, Colour, Varnish*, 1939, **12**, 181; *Chem. Abs.*, 1939, **33**, 4442.

[22] D. L. Gamble, *Ind. Eng. Chem.*, 1936, **28**, 1205; *Chem. Abs.*, 1936, **30**, 8649.

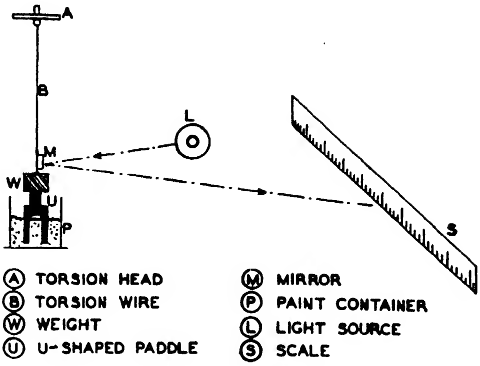
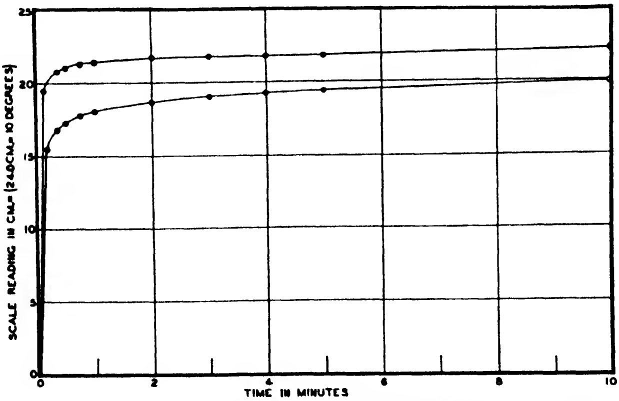


FIGURE 82.

Diagram of Torsion Pendulum (D. L. Gamble).

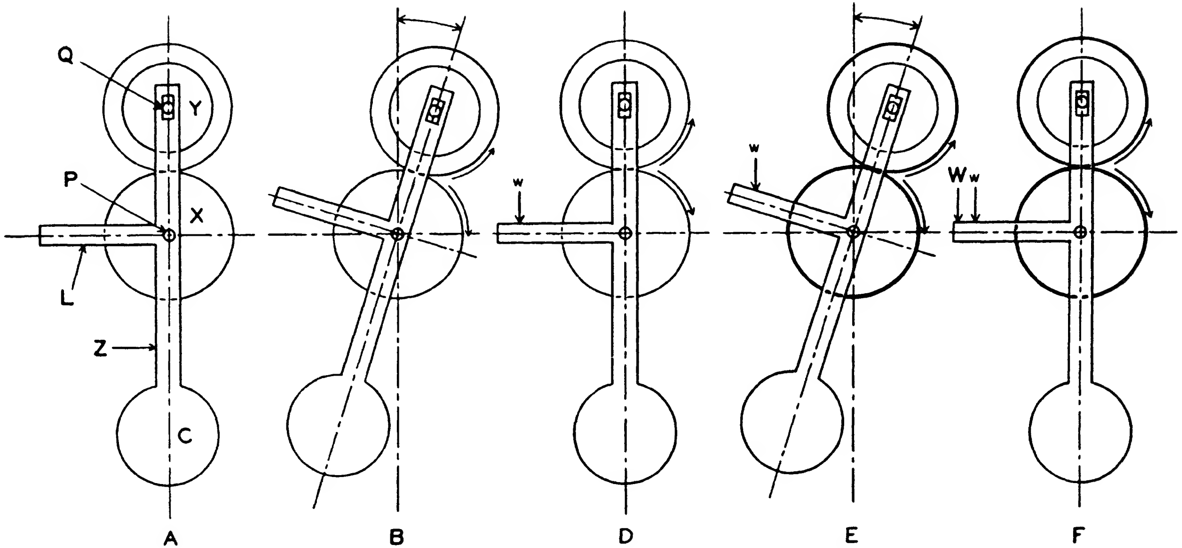
Courtesy Industrial and Engineering Chemistry

through a given angle and the rate of relaxation and its ultimate position of equilibrium are determined by recording the position of the light beam on the scale at definite time intervals. If displacement is plotted against time, curves of the type shown in Figure 83 are obtained. The curve flattens out and becomes essentially horizontal. The point at which the curve becomes apparently horizontal is taken as a measure of the rigidity of the sol. By decreasing the initial displacement of the torsion head the approach to equilibrium may be made so slow as to leave the ink virtually undisturbed and thus obtain a measure of its consistency, sufficiently accurate for most purposes. Flow is measured by comparing the time required for the liquid to travel a specified distance down a smooth surface inclined at 45° and comparing it with the time needed for the same quantity of oil of known flow to cover the same distance.



Courtesy Industrial and Engineering Chemistry

FIGURE 83. Relaxation Curves Obtained with Torsion Pendulum (D. L. Gamble).



Courtesy Lithographic Technical Foundation, Inc.

FIGURE 84. Diagrammatic Illustration of Inkometer Principle (R. F. Reed).

A. Swinging frame in static balance with the rollers free from ink and at rest
B. Angular displacement of swinging frame Z which results from rotating rollers by driving metal roller X
D. Static balance restored by application of force W
E. Angular displacement of swinging frame Z when ink is applied to rollers after balance is restored
F. Balance again restored by application of force W
C. Fixed counterweight
L. Side arm

P. Journal
Q. Journal
W. Force to overcome angular displacement of Z caused by applying ink to rollers
w. Force to overcome angular displacement of Z caused by driving X
X. Metal roller
Y. Composition covered roller
Z. Swinging frame

A special apparatus for indicating the consistency in terms of the frictional torque of inks between rollers wet with ink[23] is illustrated in Figures 84 and 85. This device is called an "Inkometer." It provides the inkmaker with a quick and accurate method of evaluating tack and mobility according to the temperature and film thickness, and is of especial importance because it most nearly duplicates actual operating conditions. The instrument consists of a metal roller, X, and a composition roller, Y. The latter is supported by and permitted to swing freely on the shaft of the lower roller. All bearings are practically frictionless. The lower roller is driven by an electric motor capable of three different speeds, 200, 400 and 600 r.p.m. The upper roller is driven only by contact with the lower roller against which it rests. The upper roller thus functions as a brake on the lower. A graduated balance arm (L) with a sliding weight (W) is attached to the frame in such a way that the torque acting on the steel frame may be balanced by moving the weight along the balance arm. The frame and the rollers are so balanced that the center of gravity of the steel frame and upper roller is a little below the axis of the lower roller. This arrangement forms a dynamometer capable of indicating the frictional torque between the rollers at their point of contact. The friction, it may be noted, is found to be virtually independent of the speed when no ink is present on the rollers. This frictional force is overcome by the side-arm (Z) which carries a counterweight (C) The torque produced by an ink film does change with speed of the rollers, and this force is balanced by weight (W), thus permitting measurement of tack of the ink under actual operating conditions.

Consistency, plasticity and viscosity can also be observed, in a general way, with the aid of a microscope.[24]

Penetration. The rate of penetration of an ink into the paper is interesting particularly for news inks, since they dry by absorption. Other inks, however, are also absorbed by the paper to a certain extent. This depends in the first place upon the paper itself and its finish. Unsized papers allow the ink to penetrate better than sized; papers which have been sized by various methods behave differently, too.[25] Smoothness of the paper and viscosity of the ink are the important properties. An arrangement for detecting the absorption power of the paper and for following the course of the impression has been made by Bekk[26] and is known as the "smoothness tester." Viscosity of the ink and penetration into the paper are, of course, very closely related,[27] and upon these proper-

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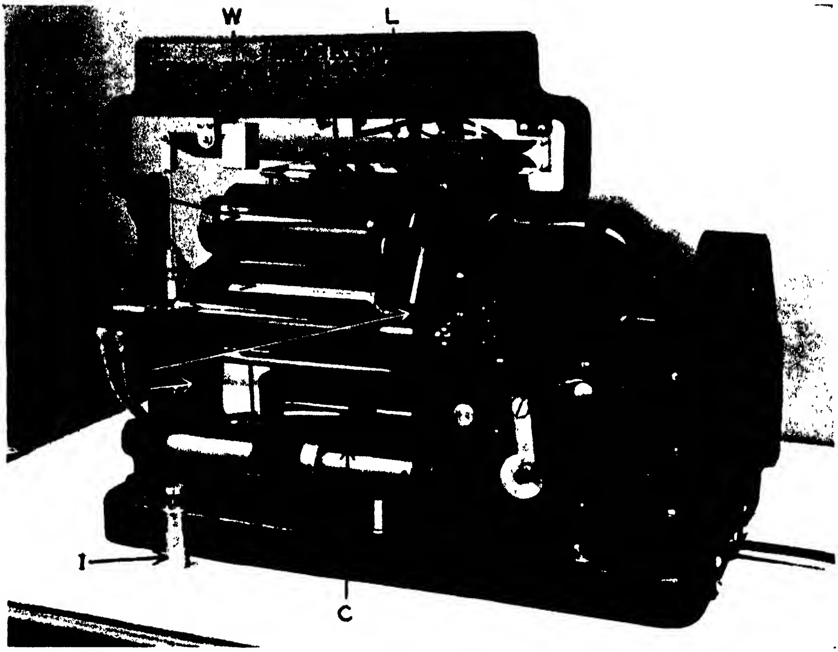
[23] J. Opp, *Am. Ink Maker*, 1934, 12 (2), 9, **12**, (3), 9; *Chem. Abs.*, 1934, **28**, 4919. *Am. Ink Maker*, 1935, **13** (3), 17; *Chem. Abs.*, 1935, **29**, 4607; *Brit. Chem. Abs.* **B**, 1935, 287, 370. R. F. Reed, U. S. P. 2,101,322, Dec. 7, 1937, to Lithographic Technical Foundation, Inc.; *Am. Ink Maker*, 1938, **16** (2), 37. *Lithographic Technical Foundation, Inc.*, *Technical Bulletin* No. 2, Research Series No. 4, 1939.

[24] J. R. Stewart, *Paint Varn. Prod. Mgr.*, 1936, **15**, 32; *Chem. Abs.*, 1936, **30**, 6218.

[25] J. Strachan, *Paper Mill*, 1929, **52** (3), 24; *Chem. Abs.*, 1929, **23**, 3095; *Brit. Chem. Abs.* **B**, 1930, 97.

[26] J. Bekk, *Papier-Fabr.*, **31**, *Tech.-wiss. Teil*, 1933, 485; *Chem. Abs.*, 1934, **28**, 1530.

[27] I. H. Andrews, *Paper Trade J.*, 1930, **90** (16), 59; *Chem. Abs.*, 1930, **24**, 4154.



Courtesy Lithographic Technical Foundation, Inc.

FIGURE 85. Inkometer (R. F. Reed).

C. Fixed counterweight
I. Ink pipette
L. Scale beam (side arm)
V. Composition-covered vibrating roller to provide lateral ink distribution
W. Sliding weight
X. Metal roller
Y. Composition-covered roller
Z. Side members (swinging frame)

ties opacity of the ink or its transparency will depend.[28] Unsized white paper should be used for penetration tests. The rate of penetration is proportional to the quotient of surface tension to viscosity and follows known laws governing capillary flow of liquids through porous bodies. Standard temperatures (preferably 21.1° C.) and a relative humidity of 50 per cent should be chosen.[29]

Several methods for estimating penetration are used. The "oil-flotation method" consists in dropping a two-inch square of paper on the surface of highly refined castor oil and noting the time required for complete absorption or saturation. The "oil-drop method" is carried out by

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[28] W. M. Nash, *Paper Mill*, 1930, **53** (22), 14; *World's Paper Trade Rev.*, 1930, **94**, 149; *Chem. Abs.*, 1930, **24**, 5494. J. Albrecht, *Farben.-Ztg.*, 1938, **43**, 1011; *Brit. Chem. Abs.* **B**, 1938, 1326.

[29] G. L. Larocque, *Pulp Paper Mag. Can.*, 1937, **38**, 77; *Tech. Sect. P. M. A.*, 1937, **14**, 44; *Chem. Abs.*, 1937, **31**, 3268. G. L. Larocque, *Paper Ind. and Paper World*, 1938, 460.

placing one drop of a No. 0000 linseed varnish [30] on paper and noting the time required for complete penetration, at which the oil spot assumes uniform translucency when observed against an illuminated ground glass.[31] The latter test is considered very sensitive for indicating variations due to calendering and to papers of different fiber composition. The castor oil test is not capable of indicating these variations, and with regard to the fiber compositions gives contradictory results.[32] The photoelectric cell has been used to measure the time for a definite degree of penetration to take place.[33] A diagram of one such instrument is shown in Figure 86. Typical results of the penetration tests are shown in Figure

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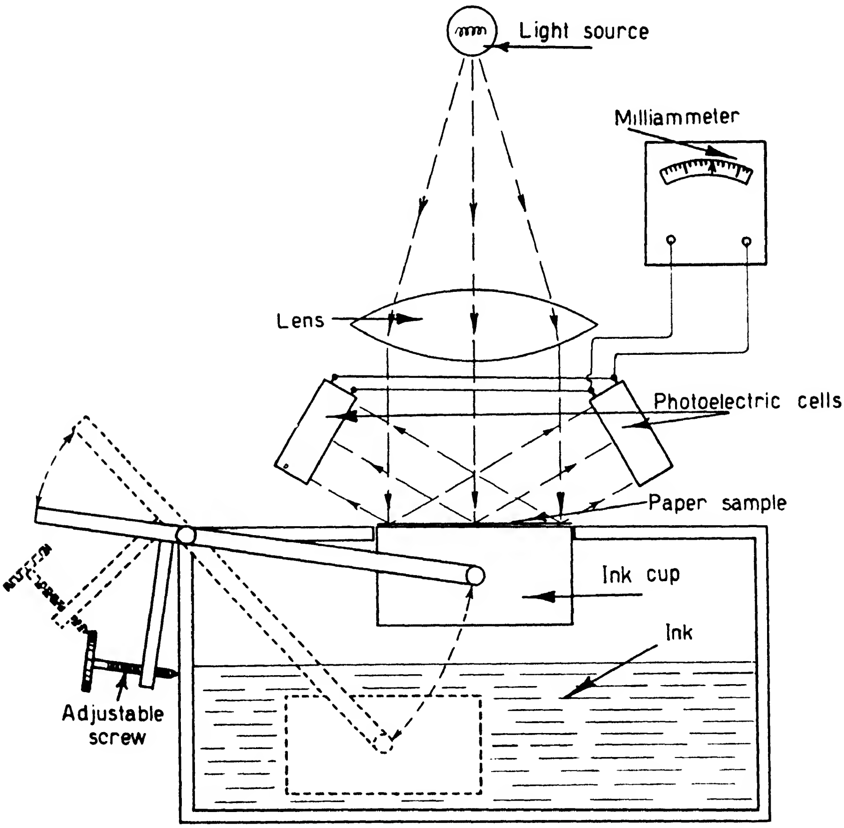
[30] The number designates the consistency of the linseed oil. For the viscosities corresponding to these numbers see Chapter 7.

[31] E. O. Reed, *Paper Trade J.*, 1928, **86** (12), 54; *Chem. Abs.*, 1928, **22**, 1853.

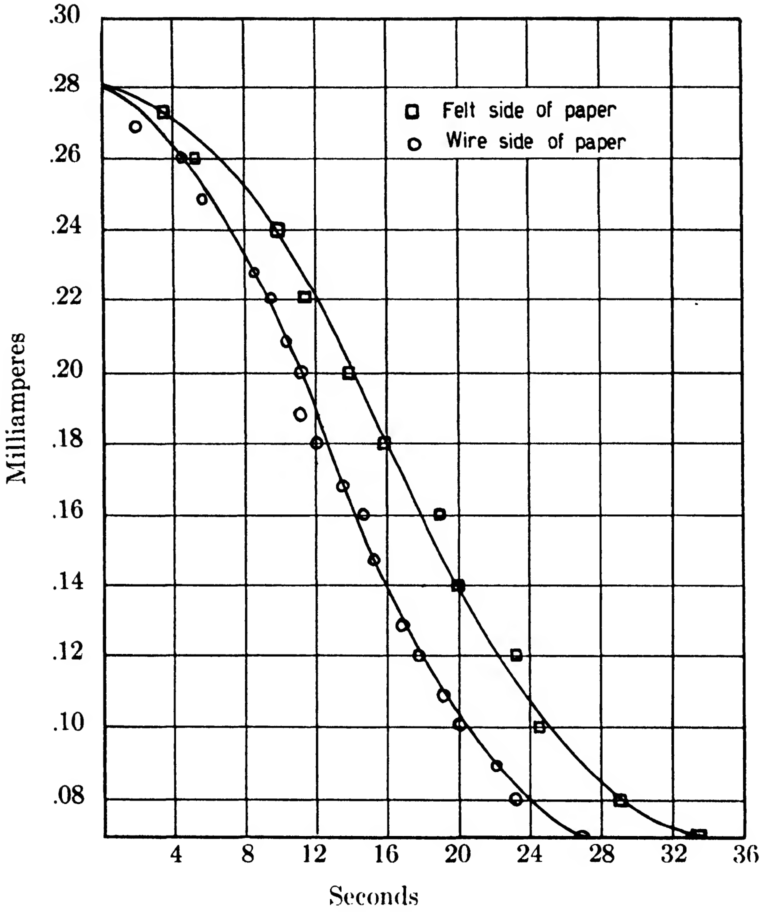
[32] H. H. Grantham and W. Ure, *Paper Trade J.*, 1935, **101**, T. A. P. P. I. Sect., 143; *Brit. Chem. Abs.* **B**, 1935, 1039; *Chem. Abs.*, 1935, **29**, 7654.

[33] W. G. Dodge and C. E. Tarvin, *Paper Trade J.*, 1935, **100** (5), 38; *Chem. Abs.*, 1935, **29**, 2834; *Brit. Chem. Abs.* **B**, 1935, 400.



Courtesy Paper Trade Journal

FIGURE 86. Diagrammatic Sketch of Photoelectric Penetration Tester (W. G. Dodge and C. E. Tarvin).



Courtesy Paper Trade Journal

FIGURE 87. Typical Results Secured with Photoelectric Penetration Tester (W. G. Dodge and C. E. Tarvin).

87. When testing newspaper inks for penetration, a series of at least 10, better 20, tests should be made in order to obtain a good average value, thus overcoming the lack in uniformity of these inks.[34] Oil absorption into paper is not related to water absorption.[35] While printing, the press accelerates penetration.[36] A special apparatus is available for testing properties of printing ink films on different papers (Figure 88).[37]

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[34] L. C. Anderson, *Pulp Paper Mag. Can.*, 1934, **35**, 85; *Chem. Abs.*, 1934, **28**, 2901.

[35] G. A. Albert, *Paper Trade J.*, 1935, **101**, T. A. P. P. I. Sect., 127; *Brit. Chem. Abs.* **B**, 1935, 1040; *Chem. Abs.*, 1935, **29**, 7654.

[36] P. H. Prior, *Paper Makers' Assoc. Gt. Brit. & Ireland*, **15**, 335; *World's Paper Trade Rev.*, 1934, **102**, 1874; 1935, **103**, 60; *Chem. Abs.*, 1935, **29**, 4579.

[37] F. W. Hoch, U. S. P. 1,939,814. Dec. 18, 1933; *Chem. Abs.*, 1934, **28**, 1556; *Brit. Chem. Abs.* **B**, 1934, 735.

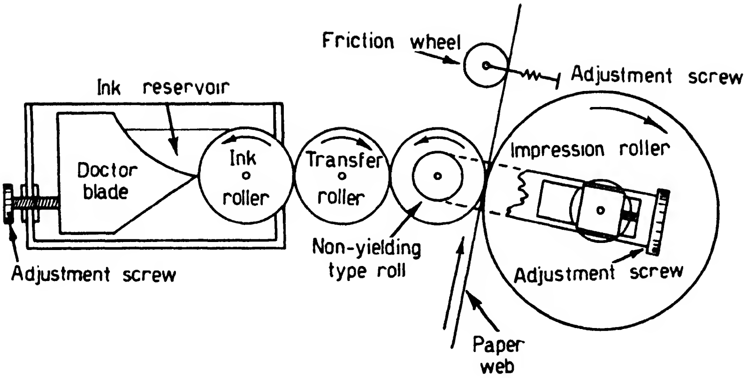

FIGURE 88. Diagrammatic Sketch of Apparatus for Testing Printing Ink and Paper (F. W. Hoch).

With this apparatus, it was said to be possible to measure the thickness of the film of ink that is applied to the paper. Also, the pressure necessary to transfer a good film of ink to any paper may be determined at the same time. The use of castor oil fatty acids instead of oleic acid as toner solvent is reported to reduce penetration.[38] Relations between ink and paper may be observed also with the aid of microscopy [39] or micrography.[40] Fluorescence microscopy is reported to be especially useful for this purpose.[41]

Molecular Refraction. The total reflection of light going from one medium into another can be measured by means of a refractometer. The refractive index, n, is the ratio of the sines of the angles formed by the incident and the reflected beams with the ordinate. From the refractive index, n, the molecular refraction can be calculated according to the formula

$$n_D = \frac{n^2-1}{n^2+1}\,\frac{M}{d}$$

M standing for the molecular weight and d for the density of the liquid. Since the molecular refraction (n_D) is proportional to the temperature, most of the data available refer to 20° C. and the D-line of a sodium light. Very convenient refractometers have been constructed, the better known being those designed by Pulfrich and Abbé. The molecular refraction is not simply the sum of the atomic refractions but is greatly influenced by the molecular arrangement, certain groups, double and triple bonds. Hence, the molecular refraction of a drying oil is a very

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[38] B. L. Wehmhoff, D. P. Clark and H. D. Boyce, *U. S. Govt. Print. Office Tech. Bull.*, 1933, No. 18.

[39] W. Kühn, *Farben.-Chem.*, 1935, **6**, 417; *Chem. Abs.*, 1936, **30**, 2409.

[40] H. Kienast, *Bl. Unters.- & Forsch.-Instr.*, 1937, **11**, 33; *Chem. Zentr.*, 1937, **108** (2), 3534.

[41] J. Grant, *Chem. & Ind.*, 1937, **56**, 237.

well established value and in many instances may be used as a specific test for such an oil. For the exact determination of all properties of a drying oil, however, it is necessary to make several other tests as described in this chapter.

Covering Power and Gloss. Covering power and spread of inks [42] can be measured, the former by printing a known volume of ink on a paper and ascertaining the area which has been covered.[43] Prior and Bekk [44] suggest applying the ink to the paper, determining the quantity applied and the degree of blackening with a Zeiss-Pulfrich step-photometer. Quantity of ink applied plotted against degree of blackening gives measure of the "coloring power." With colored filters this method can be employed for colored inks also. Closely connected with the covering and coloring power is the gloss of the print. The latter is caused by a high index of refraction and increases with the reflection of light. The specular reflection is measured from a certain angle, mostly between 55° and 57°. Many devices have been constructed facilitating these measurements, using photoelectric cells [45] and various other improvements. Pfund's glossmeter [46] and the Oxford glossmeter are widely in use, the latter having been modified to eliminate certain defects.[47] A diagram of the Pfund glossmeter as modified by Haslam and Grady [48] is shown in Figure 89.

The principle of its operation is briefly as follows:

To a vertical post (A) of the apparatus are attached a movable collar (E) and a fixed pivot (D) which supports two hollow arms (B and C) which make equal angles with the panel surface. The printed surface under test is placed upon the panel, which is rotated in order to integrate the gloss over a considerable area of the panel. By adjusting the collar the angle of the arms with the panel may be changed. A beam of light from a single filament lamp is directed down one arm onto the panel. All specularly reflected light passes up the second arm where it is focused onto the filament of an optical pyrometer. The current in the filament can be adjusted so that the filament in the brightest portion of the light will just disappear.

Calibration of the milliammeter in terms of reflected light intensity may be accomplished by measuring the current as known fractions of the full illumination are reflected from a surface which may be taken as having a 100 per cent gloss, *e.g.*, glass.

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[42] M. O. Schur, U. S. P. 1,691,739, Nov. 13, 1928, to Brown Co.; *Chem. Abs.*, 1929, 23, 532.

[43] *Am. Ink Maker*, 1933, 11 (8), 15.

[44] P. H. Prior, *World Paper Trade Rev.*, 1934, 102, 1874; 1935, 103, 60; *Chem. Zentr.*, 1935, 106 (1), 1623; *Rev. Paint, Colour, Varnish*, 1935, 8, 109. J. Bekk, *Am. Ink Maker*, 1932, 10 (4), 25; *Chem. Abs.*, 1932, 26, 5438; *Brit. Chem. Abs.* B, 1932, 1076.

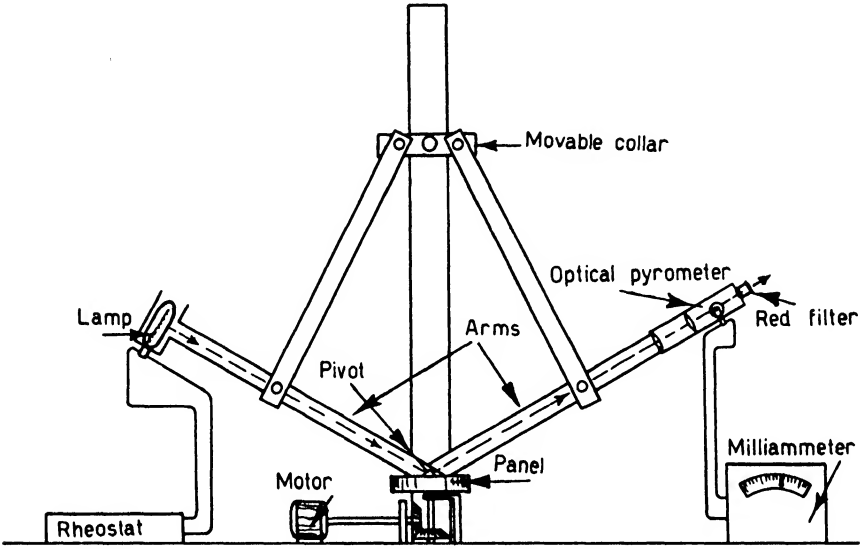
[45] R. F. Hanstock, *J. Oil Col. Chem. Ass.*, 1937, 20, 91; *Chem. Abs.*, 1937, 31, 7271.

[46] R. C. Chandler, *Am. Ink Maker*, 1937, 15 (9), 39.

[47] O. Kress and H. W. Morgan, *Paper Trade J.*, 1935, 100 (26), 41, *Tech. Assoc. Papers*, 18, 409; *Brit. Chem. Abs.* B, 1935, 753; *Chem. Abs.*, 1935, 29, 7126.

[48] G. S. Haslam and L. D. Grady, Jr., *Ind. Eng. Chem., Anal. Ed.*, 1930, 2, 346.

Glossmeters in general follow the same principles as the Pfund glossmeter.[49] Filters give the possibility of measurements in different colors.[50] Slater[51] built a photometer which is said to record the measurings graphically.



Courtesy Industrial and Engineering Chemistry

FIGURE 89. Diagram of Pfund Glossmeter (G. S. Haslam and L. D. Grady, Jr.)

Color. The color measurement of oils and varnishes is important especially for light inks. Dark vehicles naturally yield darker inks than light ones. The use of the common devices such as the Zeiss step-photometer or Lovibond tintometer is limited on account of their cost. Color values can be determined, according to Greitemann,[52] by comparison with a potassium iodide solution of iodine. The color value of the oil is given as the mg. of free iodine in 10 cc. of an aqueous iodine-potassium iodide solution viewed through a 25-mm. layer. Other workers state that a thickness of 10 mm. is most suitable and recommend the employment of potassium bichromate for clear pale oils.[53] For use on tintometers color scales have been drawn containing 10 main and 10 intermediate steps resulting from trichromatic measurements on a large number of oils and

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[49] R. S. Hunter, *J. Opt. Soc. Am.*, 1935, **25**, 47. H. Wolff and G. Zeidler, *Paint, Var. Prod. Mgr.*, 1937, **17** (4), 7. R. Fritz, *Chim. Ind.*, 1935, **33**, 541; *Chem. Abs.*, 1935, **29**, 3859; *Brit. Chem. Abs.* **B**, 1935, 510.

[50] J. W. Ayers and D. H. Clewell, *Paint, Oil, Chem. Rev.*, 1938, **100** (3), 7; *Am. Paint J.*, 1938, **22** (21), 15.

[51] J. M. Slater, *J. Opt. Soc. Am.*, 1935, **25**, 218.

[52] G. Greitemann, *Chem. Umschau*, 1929, **36**, 167; *Chem. Abs.*, 1929, **23**, 4358; *Brit. Chem. Abs.* **B**, 1929, 564.

[53] F. Pallauf, *Chem. Umschau*, 1930, **37**, 21; *Chem. Abs.*, 1930, **24**, 1531; *Brit. Chem. Abs.* **B**, 1930, 466.

one varnish.[54] This method is considered applicable for absolute measurements despite some sources of error. The three-filter spectrophotometer is good for comparative measurements.[55] Tentative standards for tintometers have been recommended by the American Oil Chemists' Society.[56]

Odor. The odor of a varnish can be detected by warming a sample gently or rubbing a trace on the hand. Tung oil has a characteristic odor and is sometimes rejected for food wrappers. There are no standards as to the determination of odors. Some modifiers are perfumed today in order to cover any disagreeable smell of inks.

Evaporation Rate. Inks containing a thinner should be tested with regard to the evaporation of the solvent.[56a] The evaporation rates of organic liquids are not always proportional to their boiling points. Compounds containing a hydroxyl group evaporate more slowly than those of the same boiling point without this group. The most practical method is to allow the solvent to evaporate under given conditions and determine loss of weight with time. The quantity of liquid evaporating in a given time is proportional to the product of vapor pressure and molecular weight. *n*-Butyl acetate is suggested as a standard.[57] Measuring devices based on the same principles [58] have been constructed, in some cases with slight variations.[59]

Acid Number. The acid number is defined as the number of milligrams of potassium hydroxide required to neutralize one gram of oil or varnish. Two or three grams of the oil to be tested are weighed and dissolved in 40 cc. of a benzene-alcohol mixture (2:1) containing 1 per cent of phenolphthalein. If necessary, especially with heavy-bodied varnishes, the mixture may be warmed, or even heated under reflux, to secure dissolution of the acidic bodies. The solution is then titrated with $0.1N$ potassium hydroxide. A blank test is made in the same manner to determine the alkali consumption of the solvent mixture. The change in color of the indicator is sometimes very difficult to recognize when titrating dark oils. In this case the best method is electrometrical titration.[59a]

Saponification Number. The consumption of milligrams of potassium hydroxide for one gram of oil is defined as its saponification number. Two to three grams of the oil are refluxed with 25 cc. of $0.5N$ alcoholic potassium hydroxide for an hour. After this the excess of alkali is titrated with $0.5N$ hydrochloric acid, using phenolphthalein as indicator. A blank test is run in the same manner. The difference (expressed

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[54] D. L. Tilleard, *J. Oil Chem. Ass.*, 1937, **20**, 124; *Chem. Abs.*, 1937, **31**, 7269.

[55] F. Lindmayer, *Akad. Wissensch., Wien, Ber.*, 1936, **145**, 2a, 611; *Sci. Abs. A.*, 1938, **41**, 150; *Rev. Paint, Colour, Varnish*, 1938, **11**, 152.

[56] W. D. Hutchins, *J. Oil Fat Ind.*, 1931, **8** (8), 303; *Chem. Abs.*, 1931, **25**, 5053.

[56a] *Am. Ink Maker*, 1937, **15** (12), 23.

[57] H. E. Hofmann, *Ind. Eng. Chem.*, 1932, **24**, 135; *Chem. Abs.*, 1932, **26**, 1490; *Brit. Chem. Abs.* **B**, 1932, 331.

[58] L. A. Wetlaufer and J. B. Gregor, *Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 290; *Chem. Abs.*, 1936, **30**, 52; *Brit. Chem. Abs.* **B**, 1935, 1025.

[59] L. Ivanovsky, *Farbe u. Lack*, 1932, **37**, 231; *Chem. Abs.*, 1932, **26**, 3411; *Brit. Chem. Abs.* **B**, 1932, 590. German P. 615,333, 1935, to Maschinenfabrik Augsburg-Nurnberg A.-G.; *Chem. Abs.*, 1935, **29**, 6112.

[59a] B. P. Caldwell, *Ind. Eng. Chem. Anal Ed.*, 1932, **4**, 52.

in milligrams per gram of oil) in alkali consumption represents the saponification value. By subtracting the acid number from the saponification number, one finds the "ester number." A comparatively low saponification number indicates that the oil is blended with unsaponifiable matter, *e.g.*, mineral oil.

The saponification velocity may be used to estimate the resin content of a varnish.[60] The velocity coefficient for the saponification of boiled linseed and a mixture of linseed and tung stand oils (0.0013/40° and 0.03/80°) in benzene under specified conditions differs considerably from that for glyceryl resin esters (*viz.*, 0.000045/40° and 0.00047/80° for rosin ester and 0.00007/40° for copal ester). The resin content of a varnish may be estimated from the determination of the partial saponification value and acid value in benzene.

Iodine Number. This value is the number of centigrams of halogen, calculated as iodine, which react with 1 gram of the material. Under specified conditions, this value indicates the proportion of unsaturated linkages present in the material. There are three methods of determination according to Wijs, Hanus and Kaufmann, the two latter being practically alike, but the former requires more time. If the duration of any method is unduly extended, great variations in results will be observed.[61] Interesting is the behavior of tung oil in this test. Normally only one of the three double bonds will be saturated. If the halogen is added in the form of a solution in carbon tetrachloride, two double bonds will react. If the latter method is applied in the presence of ultraviolet rays, all three double bonds will be halogenated.[62] Triple bonds, although considered very reactive, normally add only one mole of halogen.

The method of Hanus, which apparently is employed most frequently, is as follows: The quantity of the material to be used depends upon the expected iodine number; if the latter is above 120, 0.1-0.2 g. should be employed; for an iodine number of 60-120, 0.2-0.4 g. is required; and for a value below 60, a sample of 0.4-0.8 g. The substance is placed in a glass-stoppered bottle with 10 cc. of chloroform. Subsequently 25 cc. of a solution of 10 g. monobromide of iodine in 500 g. of glacial acetic acid are added and the mixture allowed to react in the closed bottle for 30 to 60 minutes. After addition of 15 cc. of 10-per cent aqueous potassium iodide and 50 cc. of water, the excess of halogen is titrated with 0.1*N* sodium thiosulphate, using starch as an indicator. A blank test (as a means of standardizing the iodine bromide solution) has to be made in exactly the same manner. From the difference in consumption of thiosulphate, the iodine number can be calculated.

If besides the iodine number the thiocyanate number[63] is determined,

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[60] H. Wolff and G. Zeidler, *Öle, Fette, Wachse*, 1938, No. 5, 1; *Brit. Chem. Abs.* **B**, 1938, 1329.

[61] von Reibnitz, *Farben-Ztg.*, 1929, **34**, 1782; *Chem. Abs.*, 1929, **23**, 3358.

[62] H. E. Mestern, *Inaug-Diss.*, Münster, Germany, 1936.

[63] This value is based on the selective addition of thiocyanogen $(SCN)_2$, which saturates only a part of all double bonds present in oils. H. P. Kaufmann and M. Keller, *Z. Ang. Chem.*, 1929, **42**, 20; *Chem. Abs.*, 1929, **23**, 2051; *Brit. Chem. Abs.* **B**, 1929, 135, 401. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," Vol. II, New York, Reinhold Publishing Corp., 1937.

an almost complete quantitative analysis of the oil can be made by calculation. The diene number[64] indicates the proportion of conjugated double linkages. The hexabromide value for the determination of linolenic acid gives but a partial result due to steric rearrangements.[65] However, these tests are not of immediate importance to the printing ink chemist.

Detection of Rosins and Resins. The presence of rosins is easily proved by the Storch-Morawsky-Liebermann method. A small sample is placed in a test tube and gently warmed with 1 cc. of acetic anhydride. After cooling, a drop of concentrated sulphuric acid is allowed to flow down the wall of the test tube. In the presence of rosins the mixture acquires a violet color which soon changes to brown. This test is not fully reliable as certain other substances, *e.g.*, stearins, cause the same effect. However, absence of color indicates that the oil contains no rosins.

Synthetic resins may be detected by various properties of their ingredients. Wagner and Schirmer[66] devised procedures for the qualitative determination of synthetic resins in oils, including solubilities and compatibilities. They recommend tests of fluorescence for molten or heated resins, the Storch-Morawsky-Liebermann test, and numerous individual reactions for each group of resins. A quantitative determination of phthalics has been worked out by other investigators[67] based on the substitution of one mole of phthalic acid by one mole of lead sulphate.[68]

Livering Tests. As previously mentioned, heavy-bodied varnishes tend to react with certain pigments, yielding a solid cake which cannot be converted into a useful ink. This reaction sometimes requires years to take place. An accelerated livering test consists in placing the ink in an oven and exposing it to a constant temperature of 150-180° F. An exposure of 72 hours is said to be equivalent to 1 year, and if the ink has not livered after 96 hours in the oven, it is unlikely ever to do so.

Fluorescence Analyses. Ultraviolet light as developed by a mercury lamp is used for analyses of printing inks. The fluorescence of a known ink is compared with that of the test sample. Penetration of inks, as stated above, can be observed by this method; moreover, mineral oils, fluorescing brilliantly blue, can be detected. Linseed oil is easily distinguished from other vegetable oils by its characteristic yellow color. Driers may be identified as well as resins, since different kinds of resins differ greatly in fluorescence. Most solvents, however, fluoresce blue; hence the use of the method is limited in this respect. Use of ultraviolet light.

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[64] Quantitative addition of maleic anhydride to conjugated double bonds is the basis of this method. H. P. Kaufmann and J. Baltes, *Fette & Seifen*, 1936, **43**, 93; *Chem. Abs.*, 1936, **30**, 7885; *Brit. Chem. Abs.* **A**, 1936, 966. See also Carleton Ellis, "The Chemistry of Synthetic Resins," New York, Reinhold Publishing Corp., 1935.

[65] H. E. Mestern, *Inaug. Diss.*, Münster, 1936. See also H. P. Kaufmann and H. E. Mestern, *Ber.*, 1936, **69**, 2684; *Chem. Abs.*, 1937, **31**, 2033.

[66] H. Wagner and H. Schirmer, *Farben-Ztg.*, 1938, **43**, 131.

[67] E. Fonrobert and A. Muenchmeyer, *Farbe u. Lack*, 1938, 451; *Am. Ink Maker*, 1938, **16** (5), 35.

[68] See Carleton Ellis, "The Chemistry of Synthetic Resins," New York, Reinhold Publishing Corp., 1935.

however, does not give reliable results in fading tests.[69] Nevertheless, different kinds of inks can be recognized, and it is maintained that even the age of an ink may be determined.[70] Small amounts of oils, inks or resins can be found by fluorescence, even if present only in traces.[71] Invisible or sympathetic inks and those obliterated by coats of other inks may be discovered,[72] also forgeries, such as counterfeits.[73] Trapp [74] as early as 1870 described the discrimination of charred banknotes and detection of fake documents, also removal of ink stains in order to recover letters under them. Modern science, naturally, takes advantage of microscope and ultraviolet light for these purposes in connection with these improved methods and devices and special treatment for the material to be investigated.[75] Infrared rays also have been applied to these cases.[76]

Miscellaneous Tests. A large number of devices and methods have been developed to test properties of varnishes and inks.[77] One procedure for estimating the drying time of an oil involves applying the liquid to a strip of metal, glass, wood or paper onto which a band of corrugated material is applied at regular intervals of time, thus producing markings on the layer under test until it dries.[78] Drying of oils has been investigated by determining increases in the weights of samples exposed to pure oxygen.[79] A measurement of oxidation is accomplished by following photochemical changes that occur in methylene blue admixed with the oil. When illuminated by a constant source of light the admixture will bleach due to reduction. This is taken as a degree of susceptibility of the fat to oxidation and is measured by the decrease of optical density observed with the aid of a potassium hydride photoelectric cell.[80] The mechanism of drying on paper has been studied, using micrographs of various kinds of printed papers.[81] Antioxidants may be tested by means of exposure to oxygen of linseed oil in various substrates and measuring the rate of disappearance of the gas. The efficiency of the antioxidant is determined by the speed with which absorption of oxygen occurs.[82] Resistance of printing inks to soap,[83] cheese [84] or other substances of alkaline

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[69] *Manuf. Chem.*, Dec., 1937; *Am. Ink Maker*, 1938, **16** (1), 19; *Oil Col. Trades J.*, 1932, **82,** 230.

[70] C. A. Mitchell, *Analyst*, 1930, **55,** 736; *Chem. Abs.*, 1931, **25,** 3851; *Brit. Chem. Abs.* **B,** 1931, 212.

[71] Stockis, *Bull. Acad. Roy. Med. Belg.*, 1922, **2** (5), 513; *Chem. Abs.*, 1923, **17,** 1256.

[72] W. Urban, *Jahrb. Photo.*, 1906, 650; *Chem. Abs.*, 1907, **1,** 19.

[73] J. Grant, *Analyst*, 1933, **58,** 603; *Chem. Abs.*, 1934, **28,** 73; *Brit. Chem. Abs.* **B,** 1933, 1050.

[74] J. Trapp, *Pharm. Zeitschr. Russl.*, **IX,** 77; *Chem. Zentr.*, 1870, **1,** 244.

[75] L. Amy and J. Melissinos, *Ann. méd. légale, criminol., police sci.*, 1936, **16,** 14; *Chem. Abs.*, 1936, **30,** 5905.

[76] C. A. Mitchell, *Analyst*, 1935, **60,** 454; *Chem. Abs.*, 1935, **29,** 6533; *Brit. Chem. Abs.* **B,** 1935, 774.

[77] Some methods are described by P. H. Walker (*U. S. Dept. Agr., Bur. Chem.*, 1908, **109;** *Chem. Abs.*, 1908, **2,** 1943; **109** *Rev.*, 1910; *Chem. Abs.*, 1910, **4,** 1144; *J. S. C. I.*, 1910, **29,** 460) and J. B. Tuttle and W. H. Smith (*Bur. Standards, Tech. Paper*, 1914, **39;** *Ind. Eng. Chem.*, 1914, **6,** 659; *Chem. Abs.*, 1914, **8,** 3632; *Bur. Standards, Cir.*, 1914, **45;** *Chem. Abs.*, 1914, **8,** 556; *Bur. Standards, Circ.*, 1915, **53;** *Chem. Abs.*, 1915, **9,** 2155). *Bur. Standards J. Research*, 1931, **7,** 73.

[78] A. M. Parks, U. S. P. 1,938,975, Dec. 12, 1933; *Chem. Abs.*, 1934, **28,** 1557; *Brit. Chem. Abs.* **B,** 1934, 736.

[79] D. G. Nicholson and C. E. Holley, *Ind. Eng. Chem.*, 1938, **30,** 114.

[80] G. R. Greenbank and G. E. Holm, *Ind. Eng. Chem., Anal. Ed.*, 1930, **2,** 9; *Chem. Abs.*, 1930, **24,** 1237; *Brit. Chem. Abs.* **B,** 1930, 248.

[81] R. Rau, *Papier*, 1934, **27,** 903; *Chem. Abs.*, 1935, **29,** 340. J. D. Cohen, *Paint Manuf.*, 1939, **9,** 73; *Chem. Abs.*, 1939, **33,** 4442.

[82] H. J. Stern and W. Puffelt, *Inst. Rubber Ind. Trans.*, 1932, **8,** 216; *Chem. Abs.*, 1933, **27,** 2060; *Brit. Chem. Abs.* **B,** 1933, 79.

[83] L. F. Hoyt, *Oil and Soap*, 1935, **12,** 48; *Chem. Abs.*, 1935, **29,** 2768.

[84] W. Kühn, *Farben-Chem.*, 1934, **5,** 205; *Chem. Abs.*, 1934, **28,** 5258; *Brit. Chem. Abs.* **B,** 1934, 636.

reaction is essentially a test of alkali-fastness. Soap contains but little free alkali, unlike cheese which with increasing age and ripening develops substantial quantities of ammonia. But hydrogen sulphide, volatile fatty acids, amino-acids, lactic acid, butter fat and other materials present in cheese also may affect the ink. For testing, the ink is printed on paper and the latter is wrapped around the cheese or soap so that the ink comes into close contact with the alkaline material and reaction allowed to continue for one to two weeks. Accelerated tests are reported as not reliable. Detection of arsenic in printing ink is important because of restrictions on its use by the Public Health authorities. Many pigments contain appreciable amounts of this element [85] and should not be used for printing on food wrappers. Some investigators state, however, that very small quantities of arsenic are harmless.[86] Aluminum and magnesium can be identified by printing on aluminum-free paper; after drying, the paper is cut into strips, and the strips are boiled with hydrochloric acid (2*N*). Afterwards the extracts are treated with aluminon for aluminum and with Benzopurpurine 4B for magnesium. A colored precipitate in either case indicates the presence of the corresponding metal.[87]

A qualitative test for the presence of fish oil in linseed oil may be carried out as follows:[88] dissolve 3 drops of sample in 5 cc. of acetone, add 0.05 g. lithium carbonate, shake and add 10 cc. distilled water. Then remove any insoluble material by filtration and dilute the filtrate with distilled water to a volume of 100 cc. If the solution is so clear that one can read letters through it, then the oil contains less than 20 per cent fish oil. The lithium soap of linolic acid formed produces a slight opalescence which must not be confused with the insoluble suspension formed in the presence of fish oil.

Testing of Pigments

Earlier methods, mostly comparisons with arbitrarily chosen standards, are still used. However, these procedures have been improved and now include the use of the Fade-Ometer, microscope and many other instruments.

If pigments dispersed in a vehicle are to be investigated, they have to be isolated first. This may be done by treating the dispersion with a mixture of benzene and alcohol [89] or other solvents and centrifuging or filtering. A very convenient method is extraction by means of a Soxhlet apparatus. After removal of the solvent these pigments can be investigated in the same manner as unused ones.

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[85] T. H. Barry, *Analyst*, 1927, **52**, 217; *Chem. Abs.*, 1927, **21**, 2156; *Brit. Chem. Abs.* **B**, 1927, 371.

[86] R. S. Morrell and C. I. Smith, *Analyst*, 1927, **52**, 330; *Chem. Abs.*, 1927, **21**, 2747; *Brit. Chem. Abs.* **B**, 1927, 971.

[87] L. M. Larson, *Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 416; *Chem. Abs.*, 1930, **24**, 6038; *Brit. Chem. Abs.* **B**, 1931, 260.

[88] Ernö Peres, *Ber. ungar. pharm. Ges.*, 1938, **14**, 183; *Chem. Abs.*, 1938, **32**, 5645.

[89] H. J. Wolfe, *Am. Ink Maker*, 1933, **11** (6), 9; *Chem. Abs.*, 1933, **27**, 3625; 1934, **12** (5), 19; *Chem. Abs.*, 1934, **28**, 4920; *Brit. Chem. Abs.* **B**, 1934, 589.

Strength. To determine the coloring strength of a pigment, it is usually compared with a standard pigment of the same kind. Comparison may be effected in the following manner: A mixing stone consisting of a lithographic stone or a marble or glass plate is covered with linseed oil and the excess then wiped off. This is done to prevent the stone from absorbing oil from the test sample. One-half of a gram of the pigment is weighed and put on the stone together with three-fourths of a gram of a No. 0 linseed varnish containing an appropriate amount of drier. However, some pigments have a very high oil-absorption power and hence require a larger quantity of vehicle. Varnish and pigment are then mixed thoroughly by means of a muller which is conducted over the mixture in long, even strokes. This is continued until the pigment is very finely dispersed in the vehicle. The strokes are counted, and the standard sample receives as many strokes as the test sample. The ground ink must not contain particles large enough to be visible to the eye. Samples of the ink thus prepared are put on unsized white paper, and a "pulldown" is made.[90] This pulldown is compared in appearance to one of the standard sample. Of equal value is the observation on glass slides; the unevenness of the surface is thus avoided by looking at the back side of the slide. If the degree of dispersion is to be investigated more correctly, a sample of the ink is diluted and examined under a microscope.

Tinctorial strength can be measured in the same manner. For this purpose the pigment is reduced in strength by mixing it with zinc oxide in the proportion of 1 part to 50 of the oxide. Proportions of 1:100 are sometimes used for testing the tinctorial strength of black pigments. After incorporation with linseed oil, as described above, pulldowns will show clearly the difference in tinctorial strength between the standard and the test sample.[91] Other methods have been suggested, *e.g.*, to prepare a standard sample of 1 g. standard white and 0.78 g. standard tinting material (Foam "A" barytes 6 pts. and ultramarine 1 pt.) with 0.50 cc. light-bodied linseed oil (acid number 1-3). This operation is repeated with the test sample and, if necessary, oil is added to the resulting composition until the color of the latter matches that of the standard.[92] The Hunter reflectometer may be used to advantage in making these measurements.[93] It has been recommended that as a tentative standard for white pigments there be used the finest grade of lampblack ground with 6 parts of precipitated calcium carbonate and bleached linseed oil to produce pastes of about 20 per cent light reflection.[94] Munk [95]

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[90] A pulldown is made in the following manner: A small amount of the ink is placed on paper and is spread over it with a fast stroke of a special knife. The thickness of the film thus formed depends on the stress applied.

[91] See also *Am. Ink Maker*, 1938, **16** (9), 55.

[92] C. E. Reynolds, *Am. Ink Maker*, 1936, **14** (11), 21; *Chem. Abs.*, 1937, **31**, 7266.

[93] F. Scofield and L. P. Hart, *Sci. Sect. Nat. Paint, Varnish Assoc.*, Mar. 1938. *Circ.* **549**, 17; R. S. Hunter, *Tech. Assoc. Papers*, 1935, **18**, 405; *Paper Trade J.*, 1935, **100** (26), 37; *Chem. Abs.*, 1935, **29**, 7642. *Nat. Paint, Varnish & Lacquer Assoc. Circ.*, 1935, **480**, 268. U. S. P. 1,988,556, Jan. 22, 1935, to H. A. Gardner; *Chem. Abs.*, 1935, **29**, 1294.

[94] Committee on Preservative Coatings, Brooklyn, N. Y., *British Ind. Fin.*, 1932, **3** (26), 41; *Chem. Abs.*, 1932, **26**, 4391.

[95] F. Munk, *Z. ang. Chem.*, 1929, **42**, 737; *Chem. Abs.*, 1929, **23**, 4833; *Brit. Chem. Abs.* **B**, 1929, 690.

states that much time and care are required to determine coloring power and tinting strength with adequate accuracy. Skilled operators can come as close as ±2 per cent, although errors up to 30 per cent are not uncommon. However, coloring power is not proportional to tinting strength, and it is doubtful if the former case be taken as even an approximate value for the latter. According to Bruce [96] tinting strength can be determined by drawing spectral reflection curves and by calculating the brightness. Logarithmic relationship is indicated (for mixtures of low pigment content) between pigment concentration and both purity and brightness. Easier is the determination of tinting strength by means of the trichromatic system of color analysis using the Guild Colorimeter, as described by Allen.[97] "Printing strength" [98] is defined as a relative value indicating how much ink is required to give an equal depth of tint to a definite amount of white ink as compared with the same amount of a standard ink of the same consistency; *i.e.*, printing strength is deduced from the relative tinting strength of the ink when mixed with a standard white ink.

Carbon blacks and lampblacks are tested similarly by mixing them with white pigments and comparing the resulting gray shade with standards.[99]

Tinctorial strength and color intensity of Prussian Blue are not easily determined by the usual methods. As one method, it has been suggested to dilute the blue with aqueous oxalic acid and to shake the mixture with a determined amount of white pigment until the blue is completely hidden by the white pigment. After filtering and drying, the paste is ground into a varnish and the tinctorial strength determined as mentioned above.[100]

All these comparisons, as discussed here, are subject, of course, to the human eye, and different observers will often find different results.[101] Many a method and apparatus have been invented for exact color measurements, and these are able to distinguish the finest shades and hues. Tinting strength of carbon blacks appears to be lower than the respective color strength, according to observations made with the nigrometer.[102]

Color Measurement. The desire to have correct measurements for colors, hues and shades is an old one. Standardization is necessary for this purpose. Each industry usually has some specific method of color

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[96] H. D. Bruce, *Bur. of Standards, Res. Paper*, 1928, **7**; *Chem. Abs.*, 1929, **23**, 291; *Brit. Chem. Abs.* **B**, 1929, 64.

[97] E. R. Allen, *Off. Dig.*, 1931, **104**, 409.

[98] S. L. Karpeles, *Am. Ink Maker*, 1936, **14** (3), 15; *Chem. Abs.*, 1937, **31**, 6035; *Brit. Chem. Abs.* **B**, 1936, 1217.

[99] *Am. Ink Maker*, 1932, **10** (5), 11. T. Hamburger, *Chem.-Ztg.*, 1931, **55**, 962; *Chem. Abs.*, 1932, **26**, 1457; *Brit. Chem. Abs.* **B**, 1932, 271. For coloring strength of carbon blacks see also Carleton Ellis, "The Chemistry of Petroleum Derivatives," Vol. 1, New York, The Chemical Catalog Co. (Reinhold Publishing Corp.), 1934, 250, 252. G. L. Roberts, *Am. Ink Maker*, 1938, **16** (3), 18; *Rev. Paint, Colour, Varnish*, 1938, **11**, 172.

[100] G. Zerr. *Farbe u. Lack*, 1932, **53**, 640; *Chem. Abs.*, 1933, **27**, 1525; *Brit. Chem. Abs.* **B**, 1933, 157.

[101] W. O'D. Pierce, *J. Oil Col. Chem. Assoc.*, 1931, **14**, 90; *Chem. Abs.*, 1931, **25**, 3179.

[102] W. B. Wiegand and J. W. Snyder, *Ind. Eng. Chem.*, 1934, **26**, 413; also *Paint Manuf.*, 1934, **4**, 156; *Chem. Abs.*, 1934, **28**, 3531; *Brit. Chem. Abs.* **B**, 1934, 485.

measurement, conditions varying with the material employed. For instance, in the petroleum industry color of lubricating oil is frequently given in terms of Robinson units and that of gasoline or kerosene in Saybolt units.[103]

As early as 1886 Lovibond[104] had developed means for measuring intensity of colors in transparent bodies, and soon afterwards his well known "Tintometer" became available.[105] The latter is a color-measuring device by means of which the depth of colors may be investigated in degrees, consisting of a standard scale made of numbered colored glasses. These tintometers are still in use, although a large number of newer methods and apparatus have been invented. Many of them are of great value to the printing ink chemist.

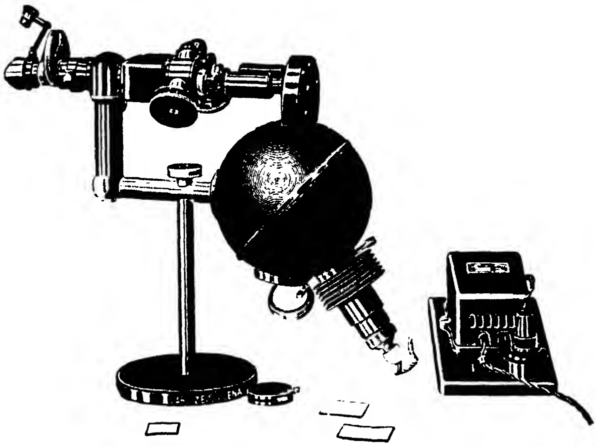

FIGURE 89A.
Sphere Reflectometer.

Courtesy Carl Zeiss, Inc.

Ostwald's well-known color system has been thoroughly investigated, and its validity and application to the industry have been described extensively by Krüger[106] and by Cunliffe and Lambert.[107] This color system is subdivided into twenty-four chief members differing in hue, and these are arranged in a circle that constitutes the common base of two cones representing mixtures of the pure hue with black and white, respectively.[108] All colors have a black content which for blue, green, yellow and other hues is reported to be about half the Ostwald color circle.[109] Klughardt and Richter[110] stress the limits of validity, particularly psy-

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[103] Tag Manual, C. J. Taglinbue Mfg. Co., Brooklyn, New York, 1930.

[104] J. W. Lovibond, British P. 12,867, 1886; *J. S. C. I.*, 1887, **6**, 522.

[105] J. W. Lovibond, *J. Dyers & Col.*, 1887, 186; *J. S. C. I.*, 1887, **6**, 628.

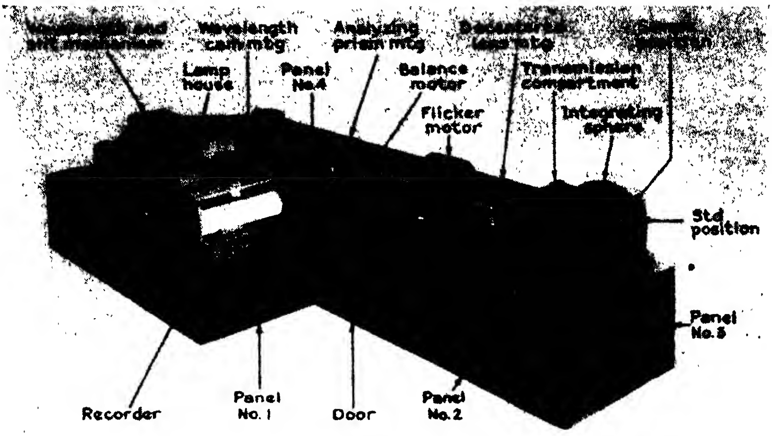
[106] F. A. O. Krüger, *Paint, Var. Prod. Mgr.*, 1934, **11** (5), 10; *Rev. Paint, Colour, Varnish*, 1934, **7**, 495; *Farben-Ztg.*, 1927, **32**, 682; *Chem. Abs.*, 1927, **21**, 1034; *Z. Ver. deut. Ing.*, 1929, **73**, 465; *Chem. Abs.*, 1929, **23**, 3609.

[107] P. W. Cunliffe and P. N. Lambert, *J. Soc. Dyers Col.*, 1930, **46**, 297; *Chem. Abs.*, 1930, **24**, 6024; *Brit. Chem. Abs.* **B**, 1931, 670.

[108] F. Scholefield, *J. Soc. Dyers Col.*, 1930, **46**, 5; *Chem. Abs.*, 1930, **24**, 3408; *Brit. Chem. Abs.* **B**, 1930, 222.

[109] P. J. M. Preston, *Oil Col. Trades J.*, 1933, **83**, 101. R. Fischer, *Z. Angew. Chem.*, 1920, **33**, 299; *Chem. Abs.*, 1921, **15**, 1080.

[110] A. Klughardt and M. Richter, *Farben-Chem.*, 1932, **3**, 205; *Chem. Abs.*, 1933, **27**, 638.



Courtesy General Electric Co.

FIGURE 89B. General Electric Recording Photoelectric Spectrophotometer.

chological effects involved in color perception. The Ostwald color scheme was accepted by the German Committee on Standardization for color tones in printing inks as early as 1922.[111] Baker and others have established a set of standards for the Netherlands.[111a] Other supporters of color standardization recommend Munsell's Book of Color.[112] Although some investigators consider color standardization highly problematical,[113] they recommend it nevertheless. Standardization of printing inks means really standardization of their pigments, according to Anstead.[114] However, in order to obtain standards for printing inks, not only their color is to be borne in mind, but also the relation to paper,[115] and also lightfastness, water resistance, acid and alkali resistance, heat,[116] hiding power,[117] overtone and undertone,[118] which properties will be discussed later in this chapter.

In addition to the two prevailing methods of color determination, namely, by dominant wave-length and by the percentage of the red, green and blue components in the matching mixture, Rosch [119] describes a third method based upon the principle that every light may be matched in color and intensity by a continuous part of the spectrum of equal intensity

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[111] *Color Trade J.*, 1922, **11**, 114; *Chem. Abs.*, 1923, **17**, 476.

[111a] G. I. Baker, et al., *Verfkroniek*, 1936, **9**, 256; *Chem. Abs.*, 1936, **30**, 7851.

[112] P. B. Millar, *Ind. Fin.*, 1931, **7** (4), 18. E. W. Melson, *Paint, Oil, Chem. Rev.*, 1934, **96** (20), 12.

[113] F. A. Wertz, *J. Oil Col. Chem. Ass.*, 1928, **11**, 180; also *Am. Paint Var. Mfgs. Ass. Circ.*, 1928, **341**, 874; *Chem. Abs.*, 1929, **23**, 1290.

[114] T. W. Anstead, *Print. Industries (A. S. M. E. Trans.)*, 1928, **50**, 1; *Chem. Abs.*, 1929, **23**, 4087; also *Modern Lithographer & Offs. Printer*, 1929, **25**, 70.

[115] G. Rübencamp, *Farben-Ztg.*, 1929, **34**, 2883.

[116] O. Sänberlich, *Farben-Ztg.*, 1922, **27**, 2624; *Chem. Abs.*, 1922, **16**, 3403.

[117] H. Hadert, *Farben-Chem.*, 1932, **3**, 246; *Chem. Abs.*, 1932, **26**, 5438.

[118] A. B. Portman, *Am. Ink Maker*, 1931, **9** (5), 35; *Chem. Abs.*, 1931, **25**, 3851. *Am. Ink Maker*, 1932, **10** (6), 11; **10** (7), 17; *Chem. Abs.*, 1932, **26**, 4483.

[119] S. Rosch, *Physikal Z.*, 1928, **29**, 83; *Sci. Abs.*, 1928, **31**, 1219.

throughout, or by an equal intensity spectrum from which a continuous part has been removed. In the latter case, the wave-lengths of the ends of the removed parts give two parameters for the determination of the color. These two parameters furnish a complete description of color and intensity together with the value of the spectral intensity. Rosch describes the practical application of this method and also an instrument which may be employed.

A great many optical measurements for color and tinting strength have been suggested. The Zeiss-Pulfrich step-photometer, used for finished inks, as described by Bekk,[120] is also advocated for color matching.[121] The T. C. B. photo-colorimeter uses the light reflection measured by means of a photoelectric cell and recorded by a galvanometer.[122] The "colorscope" acts in a similar way in recording the radiation of pigments.[123] Also several other automatic color analyzers have been proposed for this purpose.[124] One of these devices is portable and is reported to record automatically.[125] Another records photographically.[126] Slight modifications, *e.g.*, special filters, are necessary for the determination of white colors in order to obviate difficulties in obtaining standard scales of whiteness. With these pigments, too, the Pulfrich photometer is useful.[127] The blancometer measures nearly white colors, employing a photoelectric cell the response of which is measured by an electrometer.[128] Munk and Weigl [129] suggest their method of testing white pigments as standard. They measure brightness, color, tone and covering power by trichromatic photometry and employ a calibrated "hollow cone multiplicator" in order to overcome errors in comparing the standard surface with that of a powdered pigment.

For the measurement of "blackness," the nigrometer is recommended, being based on the principle of the photometer.[130] General outlines on the application of trichromatic colorimetry for pigments are given by Tilleard. [131]

X-ray examinations of pigments have been made for the purpose of investigating coloring and covering power, and also light-fastness.[132]

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[120] J. Bekk, *Am. Ink Maker,* 1932, **10** (4), 31; *Rev. Paint, Colour, Varnish,* 1932, **5,** 177; *Chem. Abs.,* 1932, **26,** 5438.

[121] W. Van Wüllen-Scholten, *Farben-Ztg.,* 1930, **35,** 1824; *Chem. Abs.,* 1931, **25,** 2579; *Brit. Chem. Abs.* **B,** 1930, 827.

[122] J. Pinte, *Rev. Gen. Mat. Plast.,* 1928, **4,** 323; also *Tiba,* 1927, **5,** 955; *Chem. Abs.,* 1927, **21,** 3492.

[123] H. H. Sheldon, *Paint, Var. Prod. Mgr.,* 1930, **36** (7), 18; *Chem. Abs.,* 1930, **24,** 5596.

[124] *Chem. Age,* 1932, **27,** 365. See also D. K. Donovan, *Paper Ind.,* 1936, **17,** 663. Carl E. Foss, *J. Opt. Soc. Am.,* 1938, **28,** 386; A. C. Hardy, *J. Opt. Soc. Am.,* 1935, **25,** 305.

[125] J. Razek and P. J. Mulder, *J. Opt. Soc. Am.,* 1930, **20,** 155; also U. S. P. 1,964,365, June 26, 1934; *Chem. Abs.,* 1934, **28,** 4947. British P. 349,565, 1929; *Brit. Chem. Abs.* **B,** 1931, 726.

[126] *Paint Col. Record,* 1931, **1** (1), 17.

[127] F. A. O. Krüger, *Farben-Chem.,* 1931, **2,** 559. E. Becker, *Farben-Chem.,* 1932, **2,** 533; **3,** 11; *Chem. Abs.,* 1932, **26,** 2068.

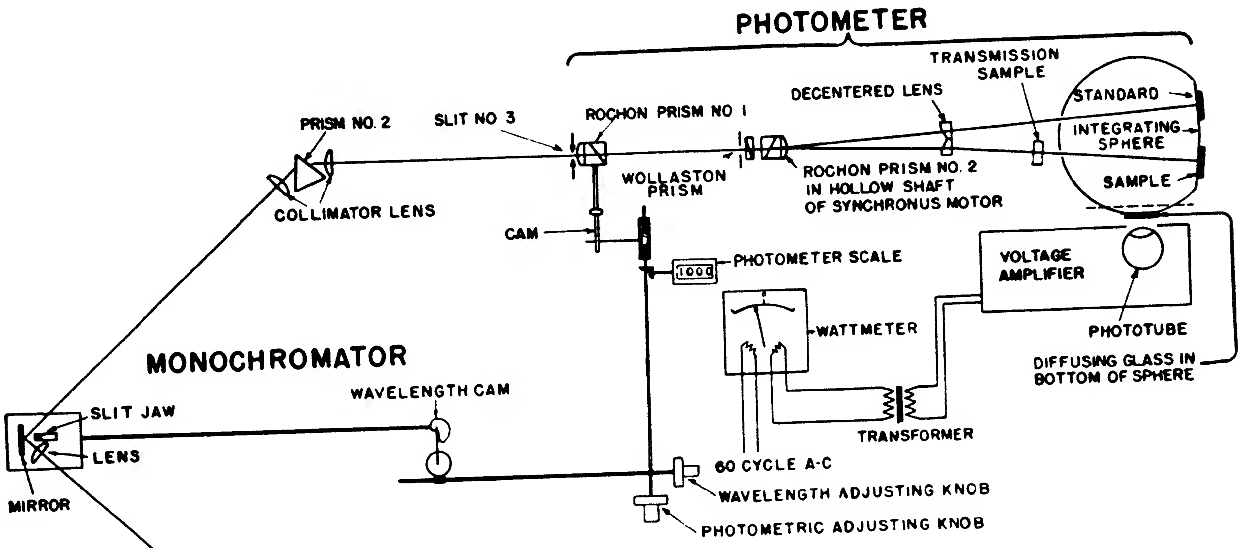
[128] J. B. Charters, *J. Soc. Dyers Col.,* 1932, **48** (6), 160; *Chem. Abs.,* 1932, **26,** 2331; *Brit. Chem. Abs.* **B,** 1932, 314, 713.

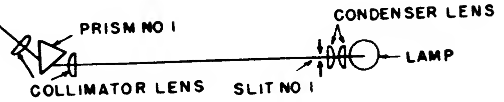
[129] F. Munk and A. Weigl, *Z. ang. Chem.,* 1931, **44,** 941; *Chem. Abs.,* 1932, **26,** 1139; *Brit. Chem. Abs.* **B,** 1932, 117.

[130] *The Laboratory,* 1929, **2,** 21.

[131] D. L. Tilleard, *J. Oil Col. Chem. Ass.,* 1937, **20,** 151; *Chem. Abs.,* 1937, **31,** 7267.

[132] A. Fonlon, *Farbe u. Lack,* 1932, **37** (3), 33.





Courtesy General Electric Co.

FIGURE 89C. Schematic Diagram of General Electric Recording Photoelectric Spectrophotometer.

Müller-Skjold[133] made an extensive study of numerous types of pigments with respect to their behavior toward x-rays in order to answer the question whether this method has any deleterious effects. They found that only pigments containing white lead are darkened to a very slight extent on prolonged exposure (48 hours) to the rays.

Particle Size. Covering and coloring power, and also light-fastness (which property will be discussed later in this chapter) are closely related to the particle size of the pigment. In earlier years, printing ink makers simply rubbed the ink between the fingers to find out whether the pigment was ground finely enough. It is unnecessary to say that this crude method could not always give satisfactory results. To secure a good knowledge of particle fineness, the use of a microscope is compulsory.[134] One method consists in projection of the microscopic image on a screen where the particles can be measured and classified.[135] By means of an ultramicroscope the average particle size of different brands of carbon black has been found to be 0.061 to 2.22 μ and for zinc pigments to be 0.076 to 0.57 μ.[136] A Chinese black ink consisting of an aqueous suspension of sumi, which is a vegetable oil lampblack, is reported to have a particle size of less than 1 μ and to average 0.12 μ.[137] The results of the ultramicroscopic investigation have been used for calibrating a turbidimeter. Turbidities of suspensions of pigments vary with average particle size, concentration and wave-length of the light used and may be also employed for the measurement of particle fineness.[138]

Particle size, structure and optical properties of zinc whites have been determined with the microscope and the polariscope.[139] A variety of black pigments also have been examined microscopically for their particle sizes.[140] By using microscopic photography for carbon blacks, Hadert[141] found that addition of certain aniline dyes to black printing inks causes hazy reproductions.[142]

Light-Fastness. Many printing inks tend to fade in the course of time. This property depends on the pigment, the structure of which is largely responsible for its stability. While inorganic pigments, except Ultramarines, usually are resistant to light, dye pigments often do not stand prolonged exposure because of their tendency to turn into the more

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[133] F. Müller-Skjold, *Z. ang. Chem.*, 1936, **49**, 161; 1937, **50**, 321; *Chem. Abs.*, 1936, **30**, 3665; 1937, **31**, 6033.

[134] *Farbe u. Lack*, 1933, **44**, 527.

[135] E. J. Dunn, Jr., *Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 59; *Chem. Abs.*, 1930, **24**, 1554; *Brit. Chem. Abs.* **B**, 1930, 613.

[136] S. D. Gehman and T. C. Morris, *Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 157; *Chem. Abs.*, 1932, **26**, 3122; *Brit. Chem. Abs.* **B**, 1932, 613.

[137] I. T. Terada, R. Yamamoto and T. Watanabe, *Sci. Papers Inst. Phys. and Chem. Res. (Tokyo)*, 1934, **23**, 173; *Chem. Abs.*, 1934, **28**, 2924; *Brit. Chem. Abs.* **B**, 1934, 370.

[138] S. D. Gehman and T. C. Morris, *loc. cit.*

[139] W. Taute, *Farbe u. Lack*, 1932, **37**, 57; *Chem. Abs.*, 1932, **26**, 2331; *Brit. Chem. Abs.* **B**, 1932, 314.

[140] H. Wagner and G. Hoffman, *Farben-Ztg.*, 1934, **39**, 549; *Brit. Chem. Abs.* **B**, 1934, 636.

[141] H. Hadert, *Farbe u. Lack*, 1928, **33**, 118.

[142] For additional discussions on measurements of particle size, see L. T. Work, *New Intern. Ass. for Testg. Materials, Zurich*, 1931; *Build. Sci. Abs.*, 1931, **4**, 356; *Chem. Abs.*, 1932, **26**, 2629; *Brit. Chem. Abs.* **B**, 1931, 950.

stable leuco form.[143] This may be influenced by the position of the lake-forming group within the molecule, the precipitating agent or the type of substrate used. Other factors influencing the stability are the atmospheric conditions, particularly humidity.[144] Probably the first thorough investigations were made by Lovibond,[145] who exposed printing inks and other colored materials to different conditions, such as north and south daylight and north daylight in an artificial damp atmosphere. He classifies colors into (1) those which are stable, (2) those which increase in density after exposure, (3) those which fade partly while the density of the vehicle increases, and (4) those which fade entirely. A similar division for printing inks is given by Krais [146] and has been extended by Hartmann.[147] Standardization of samples of lakes exposed to sunlight by comparison with a lake of known fastness, *e.g.*, eosin or Victoria Blue, is said to be unsuccessful. The same holds true for the use of photographic actinometers or of chemical solutions susceptible to radiation, since none of these methods seems to measure the specific destructive action on any particular lake.[148] However, other workers report satisfactory results with Victoria Blue B as the standard to be compared with other materials exposed to sunlight.[149]

Fading occurs only after a long period of time, and tests are accelerated by using artificial light sources of several types. A 750-watt tungsten lamp, the light of which is concentrated by use of a lens and several filters, is considered to have an action fifty times as fast as daylight.[150] Muller discusses lightproof inks. Testing by sunlight and ultraviolet are compared. Causes of fading of printed matter and the methods of preventing fading are given.[150a] Carbon arc lamps also serve as light sources for fading tests. Exposure of colors to them for 2⅓ hours is reported equivalent to 6 hours' exposure to sunlight between 9 A.M. and 3 P.M. during summer and autumn at Washington, D. C.[151] The time for these tests can be reduced, according to Arend,[152] by thinning the ink with thin litho varnish. Apparatus have been constructed maintaining definite humidity and temperature.[153] Ultraviolet light as provided by a mercury lamp is said to be inferior to the carbon arc lamp, although quicker in action, because of the decreasing activity of the former in the course of time.[154] A convenient instrument, much used now, is the Fade-Ometer

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[143] J. L. Deeney, *Am. Ink Maker*, 1933, 11 (2), 9; (3), 13; *Chem. Abs.*, 1933, 27, 5557.

[144] H. Rein, *Z. ang. Chem.*, 1934, 47, 157; *Chem. Abs.*, 1934, 28, 3235; *Brit. Chem. Abs.* **B**, 1934, 444.

[145] J. W. Lovibond, *J. S. C. I.*, 1905, 24, 262.

[146] P. Krais, *Z. ang. Chem.*, 1917, 30, 298.

[147] M. Hartmann, *Farben-Ztg.*, 1923, 28, 558; *Chem. Abs.*, 1923, 17, 1339.

[148] H. J. Stern, *J. Oil Col. Chem. Ass.*, 1930, 13, 184; *Chem. Abs.*, 1930, 24, 5170; *Brit. Chem. Abs.* **B**, 1930, 957.

[149] P. Krais, *Kolloid-Z.*, 1930, 52, 173; *Chem. Abs.*, 1930, 24, 5162; *Brit. Chem. Abs.* **A**, 1930, 1260.

[150] C. A. L. De Bruyn, *Verfkroniek*, 1934, 7, 309; *Brit. Chem. Abs.* **B**, 1935, 1.

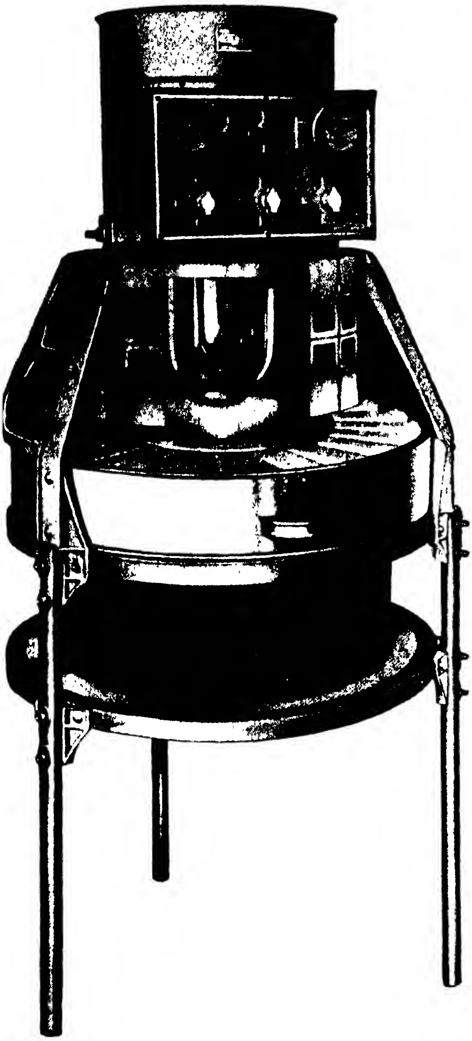
[150a] K. A. Muller, *Druck-u. Werbek*, 1939, 2, 44; *Rev. Paint, Colour, Varnish*, 1939, 12, 180.

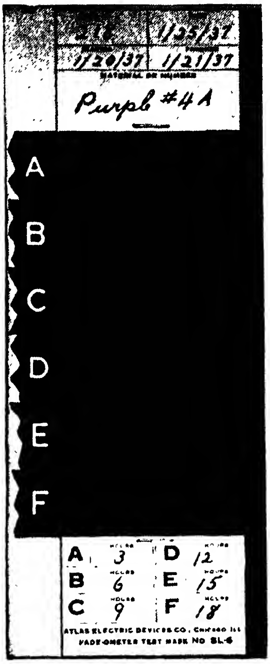
[151] W. D. Appel and R. F. Reed, *Bureau of Standards J. Research*, 1929, 3, 359; *Chem. Abs.*, 1930, 24, 1526; *Brit. Chem. Abs.* **B**, 1929, 1046. See also *Lith. Tech. Foundation, Res. Series* 4.

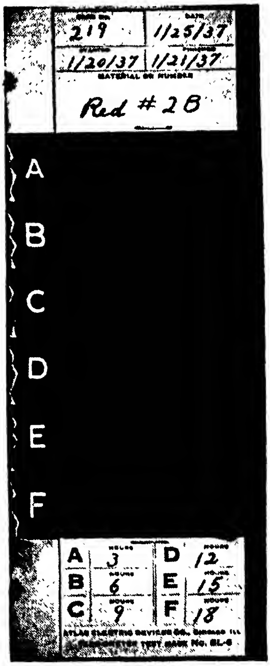
[152] A. G. Arend, *Proc. Engr. Mthly.*, 1937, 44, 173; *Chem. Abs.*, 1937, 31, 8221.

[153] British P. 390,731, 1933, to Ontario Research Found.; *Chem. Abs.*, 1933, 27, 5552; *Brit. Chem. Abs.* **B**, 1933, 458. R. O. Hall, U. S. P. 1,969,606, Aug. 7, 1934, to Ontario Res. Found.; *Chem. Abs.*, 1934, 28, 6323; *Brit. Chem. Abs.* **B**, 1935, 533.

[154] H. Rein, *Z. ang. Chem.*, 1934, 47, 157; *Chem. Abs.*, 1934, 28, 3235; *Brit. Chem. Abs.* **B**, 1934, 444.







FIGURES 90 and 91.

Fade-Ometer, Showing Results Secured. At Top, a Very Fugitive Color. At Bottom, a Fairly Permanent Color.

Courtesy Atlas Electric Devices Co.

(see Figure 90). It provides constant humidity and temperature and has an intensive action. Fifty hours of exposure to it are equivalent to thirty days of daylight.[155] An example of a test secured with the Fade-Ometer is illustrated in Figure 91. It has been stated that light-fastness depends to a certain extent also upon the printing ink vehicle, and it is advisable to subject this, too, to fading tests.[156]

Wettability and Absorption. In grinding pigments into vehicles one will observe that some pigments are easily dispersed while others show much resistance. This phenomenon is known as the "wettability" of the pigment. According to De Waele [157] the dispersion of one phase s in another l is dependent upon the interfacial tension. The relation between the surface tensions of the various phases and the change in free energy may be represented by the formula

$$T_s - T_l - T_{ls} = E,\ 0 \text{ or } -E$$

E is the change in energy per unit of surface and T the surface tension. If E is positive, the particles repel one another, being surrounded by a polymolecular layer of the dispersing agent. If $E=0$, the layer is only in loose contact with the particle, and if E is negative, the particles attract one another, having no layer surrounding them. Usually the interfacial tension acts on the boundaries of the layer surrounding the particles, and the molecules of the free continuous phase are oriented to the interphase. However, on tangential shear, *i.e.*, while grinding, this transverse orientation is changed to a direction tangential to the surface of the particles varying according to the applied stress. This is true physical wetting in contrast to some other phenomena to which this term sometimes is erroneously applied.[158] Aggregates of pigments are broken down during wetting, and each pigment molecule becomes surrounded with a layer of the liquid.[159] There is close relation between wettability of a pigment and its oil absorption. Wetting can be facilitated and oil absorption reduced by adding a small percentage of fatty acids, aluminum stearate or other modifying agents [160] as outlined in Chapter 5. Heats of absorption and wetting of zinc oxide have been investigated by Ewing.[161] He states that heat of absorption is directly proportional to the surface of the pigments and not related to their particle size.[162] Oil absorp-

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[155] C. W. Jameson, *Am. Ink Maker*, 1932, 10 (12), 13; *Chem. Abs.*, 1933, 27, 2589. R. Lonchart, *Papier*, 1936, 39, 129; *Chem. Abs.*, 1936, 30, 3642. *Cf. Ind. Eng. Chem., News Ed.*, 1932, 10 (11), 154; A. Grunder, *Am. Pressman*, Dec., 1937, 35.

[156] M. Hartmann and R. Rau, *Farben-Ztg.*, 1936, 41, 1010. For a review on testing methods of light-fastness, see H. Sommer, *Mitt. deutsch. Materialprüfgs. anst.*, 1934, Sonderheft, 24, 11; *Verfkroniek*, 1934, 7, 309; *Chem. Abs.*, 1934, 28, 5243.

[157] A. De Waele, *J. A. C. S.*, 1926, 48, 2760; *Chem. Abs.*, 1927, 21, 845; *Brit. Chem. Abs.* **A**, 1927, 16.

[158] L. W. Shuger, *Nat. Paint Bull.*, 1937, 1 (11), 14; 1938, 2 (1), 19.

[159] J. C. Smith, *Paint Man.*, 1935, 5 (2), 37; 5 (3), 63.

[160] W. Van Wüllen-Scholten, *Farben-Chem.*, 1932, 3, (3), 91; 3 (4), 130; *Chem. Abs.*, 1932, 26, 3123; *Brit. Chem. Abs.* **B**, 1932, 613.

[161] W. W. Ewing, *Ind. Eng. Chem.*, 1931, 23, 427; *Chem. Abs.*, 1931, 25, 2616; *Brit. Chem. Abs.* **A**, 1931, 559.

[162] For discussions on methods of determining oil absorption see I. Traube, *Z. ang. Chem.*, 1931, 44, 73; *Chem. Abs.*, 1931, 25, 2616; *Brit. Chem. Abs.* **B**, 1931, 277. G. Tröger, *Farbe u. Lack*, 1933, 40; *Chem. Abs.*, 1933, 27, 1771.

tion of carbon black is particularly high. It can be determined by measuring the volume of vehicle absorbed by a known quantity of pigment and thereby giving a paste of a definite viscosity as compared with a standard sample.[163] The "oil absorption" is expressed as the weight in grams of oil per 100 gm. of pigment[164] required to secure such a paste.

With fluffy pigments of high oil absorption value and heavier-bodied litho varnishes such as are used in the printing ink industry, another method[165] is to grind a known weight of pigment into a known weight of varnish and compare the results with those obtained with the standard pigment which has received identical treatment. The influence of carbon black on the fluidity[166] and viscosity[167] of an ink has been the subject of investigations, and it has been found that change in concentration of the pigment alters the viscosity widely, while influence on the fluidity is somewhat smaller.

Determination of Moisture. Moisture is determined quantitatively either by drying the material in an oven or by refluxing it with xylol. In the latter instance it is desirable to use a special calibrated device which collects the water and facilitates direct determination of its amount. A special method for carbon black[168] consists in heating it with xylol and mineral oil to 150-175° C. in a current of nitrogen. The distillate is then heated on a water bath and the vapor passed through vessels packed with calcium chloride. Finally nitrogen is passed through in order to remove xylol until constant weight is secured. This method is reported to indicate higher moisture contents than are found by drying for five hours at 105° C.[169]

Miscellaneous Tests. Bleeding tests are made to determine the resistance of pigments to such materials as water,[170] alcohol or other organic solvents, oil, and synthetic, natural or paraffin wax, depending on the purpose intended for the ink. To test an ink, unsized white paper is partly covered with it, and, after drying, a drop of the liquid is allowed to fall on the surface so that it (the liquid) partly covers the printed area. If the unprinted paper acquires the color of the pigment, the latter is soluble in the material. It is also possible to put strips of the printed paper in test tubes filled with the liquid. Wax and paraffin are heated to a liquid state for testing.

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[163] D. F. Cranor and L. J. Venuto, *Am. Ink Maker*, 1932, **10** (12), 17; *Chem. Abs.*, 1933, **27**, 2589.

[164] A. S. T. M. Standards, D281-31, American Society for Testing Materials, Philadelphia, 1933, Part II, 561.

[165] *Am. Ink Maker*, 1938, **16** (9), 55.

[166] E. P. W. Kearsley and G. L. Roberts, *Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 310; *Chem. Abs.*, 1931, **25**, 5302; *Brit. Chem. Abs.* **B**, 1931, 851.

[167] M. P. Volarovich and V. S. Borinevich, *Kolloid-Z.*, 1936, **77**, 93; *Chem. Abs.*, 1937, **31**, 560; *Brit. Chem. Abs.* **B**, 1936, 1217.

[168] C. M. Carson, *Ind. Eng. Chem., Anal. Ed.*, 1929, **1**, 225; *Chem. Abs.*, 1929, **23**, 5438; *Brit. Chem. Abs.* **B**, 1929, 1003.

[169] Methods of testing carbon black are also described by Anchor Chem. Co., Ltd., Brochure No. 2, 1933; *Rubber. Res. Abs.*, 1935, **13**, 79.

[170] Especially zinc pigments tend to bleed as described by R. Schwarz, *Farbe u. Lack*, 1934, 342.

Resistance of pigments to acids, alkalies[171] and heat also are determined; in the last-named instance a temperature of about 270° F. is recommended.

Settling of pigments can be determined by accelerated tests.[172] These involve observing the rate of penetration through a body of ink by a steel ball attached to the end of a rod to which pressure is applied. The pressure is increased as the ball travels downward through the ink. Figure 92 is a diagram of a recording penetrometer. In Figure 93 are represented penetrometer graphs of equivalent mathematical value, each of which represents a different type of settling.

Analyses of mineral pigments are accomplished by determination of their specific chemical properties.[173] For instance, for the detection of white lead, employment of a 10-per cent solution of sodium sulphide is recommended by Schlegel.[174] If lead is present, the pigment will turn black due to the formation of lead sulphide.

Many procedures are available for indicating the presence of the various types of dyes. For example, a precipitating agent for acid dyes

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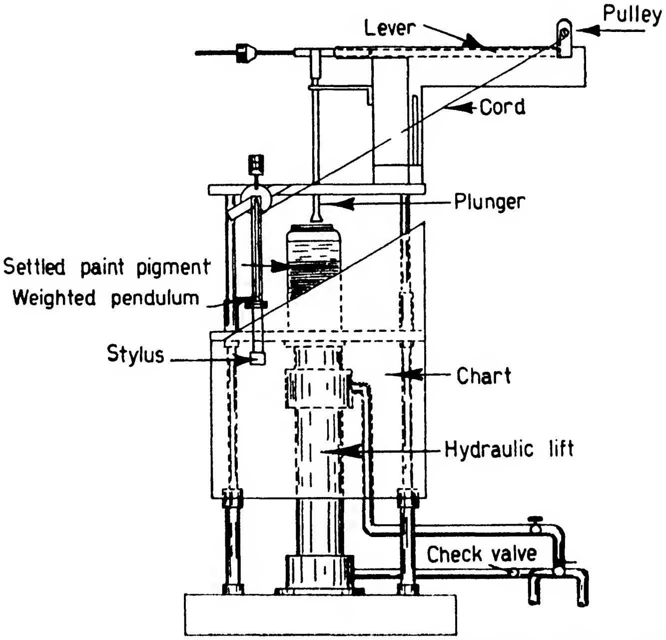
[171] *Am. Ink Maker*, 1938, 16 (9), 55.

[172] S. Werthan, R. H. Wien and E. A. Fatzinger, *Ind. Eng. Chem.*, 1933, 25, 1288; *Chem. Abs.*, 1934, 28, 347; *Brit. Chem. Abs.* B, 1934, 27.

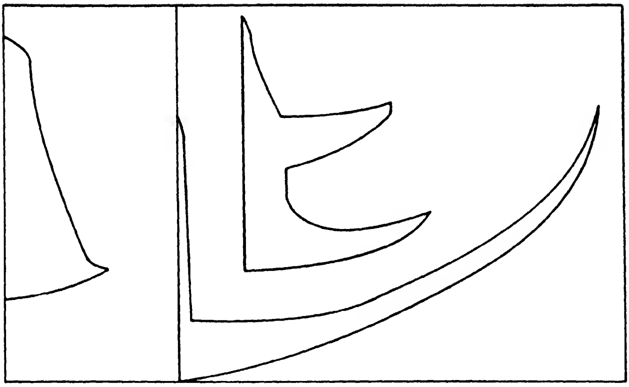
[173] H. Wilson, *Ind. Min. Rocks*, 1937, 493; *Chem. Zentr.*, 1938, 109 (I), 1465.

[174] O. H. Schlegel, *Chem.-Ztg.*, 1908, 32, 608; *Chem. Abs.*, 1908, 2, 2630.



Courtesy Industrial and Engineering Chemistry

FIGURE 92. Diagram of Recording Penetrometer (S. Werthan, R. H. Wien, and E. A. Fatzinger).



Courtesy Industrial and Engineering Chemistry

FIGURE 93. Penetrometer Graphs of Equivalent Mathematical Value, but Representing Radically Different Types of Settling (S. Werthan, R. H. Wien, and E. A. Fatzinger).

is a product known as "Solidogen," which can be applied to the detection of such dyes in printing inks.[175] Separation of substrate from dye is sometimes necessary in analyzing lakes.[176] Sulphated oils employed for printing inks may contain free water, oil or sulphuric acid or other undesirable constituents. A qualitative test is accomplished by acidification of 4 g. of the oil with acetic acid, followed by addition of 40 cc. of absolute alcohol. After filtering, the filtrate is diluted with 50 cc. of water and refluxed with 50 cc. of concentrated hydrochloric acid until the mixture becomes clear. After cooling, the latter then separates into two layers, and the aqueous layer may be tested for sulphuric acid. The oil layer can be neutralized, treated with a fusion mixture and the resulting mass tested for sulphates.[177]

Sulphonic acids may be detected by means of pyridine.[178] These acids condense with pyridine to yield products which, on hydrolysis with alkali and condensation with an aromatic amine, give colored compounds. Chlorinated compounds interfere with this test, however.

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[175] E. Ullrich, *Spinner & Weber*, 1934, 52 (41), 8; *Chem. Abs.*, 1935, 29, 8337.

[176] A. G. Green, *J. Oil Col. Chem. Ass.*, 1928, 11, 38; *Chem. Abs.*, 1928, 22, 3539; *Brit. Chem. Abs.* B, 1928, 647.

[177] D. Burton and G. F. Robertshaw, *J. Soc. Leather Chem.*, 1931, 15, 308; *Oil, Col. Trades J.*, 1931, 80, 86; *Chem. Abs.*, 1931, 25, 5782; *Brit. Chem. Abs.* B, 1931, 935.

[178] H. Freytag, *Z. anal. Chem.*, 1938, 111, 385; *Analyst*, 1938, 63 (745), 290.

Chapter 18

Paper for Printing

A consideration of the various properties of paper surfaces, heretofore mentioned only incidentally in connection with special types of inks and unusual surfaces, such as glassine, is necessary to comprehend completely the action of inks when used in printing. Obviously, any ink cannot be used with all types of paper, whether it be soft and absorbent, such as blotting paper (to cite an example of one extreme), or hard and heavily coated, such as a super-sized bond or ledger paper (to illustrate the other extreme of absorptivity). Not only the type of paper, but also the speed of the printing operation must be taken into account.

Many different varieties of paper are available, such as newsprint, calendered, supercalendered, sized, heavily loaded, and lithographic. Newsprint, for example, is very loosely and openly fibered, and an ink that is applicable on such paper may be very liquid because it can be absorbed readily and does not need to dry by the usual oxidation and polymerization reactions. It must be easily absorbed because of the speed at which newspapers are printed. An ink for calendered or supercalendered stock must be rather viscous and tacky, so it will not offset before it has had a chance to dry. It cannot penetrate to any great degree because of the compressed state in which the fibers lie. The calendering process consists of passing the still wet paper between hot rollers at great pressure to form a smooth, hard surface on the sheet. This pressure flattens out the fibers and fills up all the interstices which naturally occur as the paper is made. On the printing of such surfaces, and more especially when heavily-sized paper is used, a considerable amount of drier must be added to the ink to accelerate its oxidation. A more complete discussion of each type of paper will be found later in this chapter.

Paper to be used in printing must be carefully freed of all injurious residues which might affect the color, durability and other qualities of the ink. Among the undesirable residues are sulphur and its compounds, acids, such as sulphuric, alkalies, bleach residues, such as hypochlorites, organic deposits from the wood pulp, and excess alum.

Some of the physical properties of the paper are also important when they affect the printability and durability of the sheet. Its opacity must be considered when the material is to be printed on both sides; tensile strength and resistance to changes in size due to humidity are important when multicolor printing is to be done, to insure perfect register. The

Courtesy Pfaltz & Bauer, Inc.
Courtesy Campbell-Lampee, Inc.

FIGURE 94. Reflectometer.

thickness variation and smoothness of the paper are important factors aiding in the production of a good-looking piece of work. If the paper were to be thinner in one place than in another, the type would not make the same impression in different parts, and the result would be a light register in one area and an over-heavy impression in another. In halftone[1] printing especially, the smoothness of the surface determines the appearance of the finished product: whether it be clear and well printed, or mottled and cloudy in appearance.

Much experimentation has been done in the field of paper-making with a view to the improvement of the paper so as to aid in the perfection of printed matter, insofar as it can be affected by change in paper quality. Many instruments have been devised to test paper quantitatively for such qualities as opacity, oil absorption, smoothness, folding resistance, dusting, picking and softness. Many of the tests and the

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[1] See Chapter 1.

instruments for making them have been the result of the work of Julius Bekk, a prolific worker in this field of the relationships of paper and ink. He has also done much research on the improvement of the printing qualities of ink.[2]

The color of the paper has a pronounced effect upon the appearance of the ink when printed. A gray or muddy-colored stock will change the color of an ink, especially a light-colored one, and even an opaque ink. A neutral-colored paper should be used, therefore, as nearly as possible a pure white.[3]

An excess of filler in paper, while serving the purpose of evening the texture, is objectionable for two reasons. First, it tends to weaken the structure of the paper, and, second, it decreases the absorptive power of the sheet for the vehicles used in printing inks. Another factor affecting the permeability of the paper is the composition and quality of the sizing used. The paper must contain some sizing, otherwise it would be soft and absorbent like filter or blotting paper, but when a heavy sizing is applied, especially a mineral size, the permeability is reduced almost to zero. A gelatin size is almost non-absorptive. A rosin coating increases the penetration of oil, which is one of the principal binder constituents of ink. As mentioned above, the degree of calendering has a strong influence upon the rate at which the ink will be absorbed into the texture of the paper. The complete absence of calendering would leave the paper too rough to effect a good printing, but the other extreme, that of a high calender, decreases the absorption to such a degree that a quick-drying ink must be used, such as the type required for ceramic and metallic surfaces. Therefore, the optimum amount of calendering seems to be somewhere in between, where the surface is sufficiently smooth for good impression and absorptive enough to insure good working qualities.

The presence of some interfibrous spaces is desirable in order to obtain more area upon which the ink can spread, and also to include some air in the paper to effect a quicker drying of the ink. Thus, when a paper has considerable filler included in it, the appearance and opacity are greatly improved, but the absorptivity and affinity for ink, as well as the drying rate of the ink used on it, are decreased. In a like manner, the surface of the paper has disadvantages when either completely uncalendered and unsized or when highly calendered and covered with a thick layer of sizing. As mentioned above, the surface when untreated is too uneven for register, but when highly finished, it tends to cause offset[4] to a higher degree as well as not being absorptive. A slight

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[2] J. Bekk, *Papier-Fabr.*, 1933, **31**, *Tech.-Wiss. Teil*, 485; *Chem.-Ztg.*, 1933, **57** (76), 756; *Rev. Paint, Colour, Varnish*, 1933, **6**, 265; 1934, **7**, 195; *Chem. Abs.*, 1934, **28**, 1530. *Paper Maker*, 1935, **89** (5), T. S. 71; (6), T. S. 88; *Proc. Tech. Sect. Paper Makers' Assoc. Gt. Brit. & Ireland*, 1935, **16**, 9; *Chem. Abs.*, 1935, **29**, 7653; 1936, **30**, 2755. *Paper Market & Printing Technique*, 1937, **102** (New Series), (12), 227; 1938, **103** (2), 59; *Rev. Paint, Colour, Varnish*, 1938, **11**, 107. *Svensk Papperstidn.*, 1934, **37** (14), 442; *Chim. et ind.*, 1935, **33** (2), 433; *Rev. Paint, Colour, Varnish*, 1935, **8**, 108.

[3] H. J. Wolfe, *Am. Ink Maker*, 1933, **11** (4), 9; *Rev. Paint, Colour, Varnish*, 1933, **6**, 136; *Chem. Abs.*, 1933, **27**, 3092.

[4] See Chapter 16.

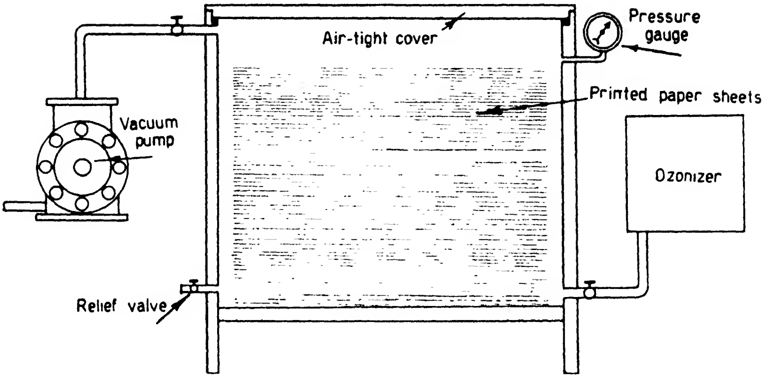

FIGURE 95. Diagrammatic Sketch of Apparatus for Drying Printed Sheets by Ozonation (P. Aitchison, F. T. Wood, and A. A. Wittnebel).

amount of unevenness in the surface acts as a cushion and separates the sheets so that air can circulate and dry the ink, and also so that the layers of ink on one sheet will not come into contact with the surface of the adjacent sheet of paper. This circulation of air is one of the most important aspects of the drying process, and methods have been devised to accelerate the latter operation, one of which is the use of ozone as an oxidizing agent. The sheets of printed paper are piled in an air-tight container and the air is evacuated and replaced by ozone, which will dry the ink overnight (Figure 95).[5]

The low absorptivity of a paper surface, whether because of excess calendering or thick sizing, has another effect upon the appearance of the printed material. When the plate presses upon the paper, the ink must either be forced into the interstices of the fibers, or in their absence squeezed out around the raised portions of the plate, which results in what is known as the "halo" effect. The film of ink is too thin in the center of the character and the periphery has a heavy excess. The remedy for the "halo" is to use a more absorbent paper, a slightly less viscous ink, and less printing pressure.

The temperature at which printing is done is one of the important factors in the production of a pleasing result. The viscosity of the vehicle in the ink becomes less as the temperature rises, and as a result an increased penetration of the fibers by the liquid is accomplished. When the temperature is too high the vehicle is absorbed to such a degree that the pigments and fillers are left unprotected on the surface and are easily rubbed off. Since the degree of humidity affects the hygroscopic fibers of the paper and a large proportion of moisture causes them to swell as

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[5] A. Aitcheson, F. T. Wood and A. A. Wittnebel, U. S. P. 1,925,429, Sept. 5, 1933, to American Banknote Co.; *Rev. Paint, Colour, Varnish*, 1934, 7, 293; *Brit. Chem. Abs.* **B**, 1934, 571. British P. 415,261, 1934; *Chem. Abs.*, 1935, 29, 861. For further discussion of the use of ozone as a drying agent, see Chapters 8 and 16.

the percentage of moisture in the air increases, the control of the moisture content of the air is essential to the production of good printing. Many printing establishments, especially where multicolored work is done, use air-conditioning to maintain the size of the paper constant.[6]

The mineral content of a paper, as before mentioned, greatly affects the printability because of its effect upon the absorptivity of the surface, upon the oils used for the ink vehicle, and upon the pigment in the ink. Sulphuric and other acids and excess alum in the paper are harmful because they destroy the color of basic dyes of inks and tend to saponify the oil vehicles. Hypochlorite bleach residues have a decolorizing effect upon some of the colored pigments of inks and also tend to weaken and blacken the paper. Any iron compounds in the paper react with colored pigments to cause black or brown spots to develop, especially in the lithographing[7] process. Sulphur and sulphur compounds are particularly harmful to lead pigments, as they tend to form black lead sulphide. Bronze powders are also attacked by sulphur compounds. The alkali residues present in some coated papers destroy acid pigments and react with Prussian Blue, changing its color. The color of inks is also affected by the presence of organic materials which are derived from mechanical wood pulp and glue.[8]

The printing qualities of paper are equalled in importance by the characteristics of ink that make for its good adhesion, fast drying, suitable stability and penetration. The ink must be fitted to the particular stock used and to the process employed in the operation. A good rule to follow is to use the most tacky ink which the paper will allow.

The pigment content of the ink must be fixed in order to obtain the highest penetration and adhesion. When a loose-fibered paper is to be printed upon, the percentage of pigment may be higher than when glossy stock is used. A high proportion of pigment makes for less adhesion and consequently more of a tendency for offset and smudging. The dyestuff must be opaque and must have what is called good covering power, that is, its capacity for hiding the material beneath and producing a uniform and opaque surface. The finer the particle size and the more complete the dispersion of the pigment, the greater will be its opacity and covering power.

The vehicle of the ink is largely determined by the process of printing and by the stock used. In ordinary letterpress work, the ink may be

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[6] For general notes on paper in relation to printing, see the following: Michiyo Yano, *J. Chem. Ind. Tokyo*, 1917, **20** (229); *Chem. Abs.*, 1917, **11**, 2406. B. Thomas, *Mod. Lith. and Offset Printer*, 1932, **28** (4), 74; *Rev. Paint, Colour, Varnish*, 1932, **5**, 174. J. Strachan, *Paper Maker*, 1934, **88** (5), TS 193; *Chem. Abs.*, 1935, **29**, 3834. *Brit. Printer*, 1933, **46** (273), 114; *Rev. Paint, Colour, Varnish*, 1933, **6**, 336. V. S. Smith, *Paper Ind.*, 1934, **16**, 626; *Chem. Abs.*, 1935, **29**, 1633. Rübencamp, *Farben.-Ztg.*, 1923, **28**, 1389; *Chem. Abs.*, 1923, **17**, 3423. J. G. Patrick, *Am. Ink Maker*, 1938, **16** (2), 18; (3), 27; *Rev. Paint, Colour, Varnish*, 1938, **11**, 109. J. Niemczyk, *Paper Trade J.*, 1936, **102** (18), 31; *Brit. Chem. Abs.*, **B**, 1936, 587; *Chem. Abs.*, 1936, **30**, 5034. P. Klemm, *Wochbl. Papierfabr.*, 1914, **45**, 2306; *Chem. Abs.*, 1914, **8**, 3118. E. A. Dawe, *World's Paper Trade Rev.*, 1929, **92**, 1736, 1842; *Chem. Abs.*, 1930, **24**, 958. C. R. Conquergood, *Am. Ink Maker*, 1939, **17** (3), 27. H. H. T. Alway, *World's Paper Trade Rev.*, 1936, **105**, 1443, 1484; *Chem. Abs.*, 1936, **30**, 7337. W. T. Diefenbach, *Paper Mill*, 1935, **58** (24), 13; *Chem. Zentr.*, 1935, **106** (2) (15), 2455; *Rev. Paint, Colour, Varnish*, 1935, **8**, 516; *Brit. Chem. Abs.* **B**, 1935, 798; *Chem. Abs.*, 1935, **29**, 7654.

[7] See Chapter 1.

[8] H. A. Maddox, *Pulp Paper Mag. Can.*, 1913, **11**, 126; *Chem. Abs.*, 1913, **7**, 1415.

of the oxidation-drying type, capable of but little absorption and slight evaporation. Because of the speed maintained and because of the looseness of the fibers in the paper, as stated, newsprint printing requires a non-drying ink which will penetrate at the greatest speed into the paper. When printing glassine and other cellulosic material of this type, the vehicle usually contains a solvent for the surface to be printed, so as to obtain a better adhesion. A high proportion of volatile solvent must be added to the vehicle to make the drying time as short as possible. Aniline inks usually contain a vehicle which dries solely by evaporation, thus establishing the main advantage of this ink for high-speed carton work. The length of the ink must be controlled so as to produce the best results with particular surfaces.

The drier content of inks is largely determined by the degree of finish possessed by the surface to be printed. When a highly absorbent material is used, little or no drier is needed in the ink, but a large proportion is required when hard and calendered stocks are to be printed.[9]

Wolfe[10] gives the following general formulas (Table 41) for inks to be used on the various types of stock. The proportions of oil in the vehicle as well as the inclusion of different quantities of other ingredients are given merely to point out that the several varieties of paper require a rather specialized type of ink.

Table 41.—Inks for Various Paper Stocks.

Weight (lbs.)	Bond Bronze Blue
16	No. 0 lithographic varnish
24	No. 1 lithographic varnish
4	No. 3 lithographic varnish
1	melted beeswax
3	paste drier
44	Bronze blue, dry
8	Alkaline Reflex Blue, red shade, ink
100	

Weight (lbs.)	Bond Black
25	No. 3 lithographic varnish
10	No. 5 lithographic varnish
5	boiled linseed oil
10	long gum varnish
10	cobalt drier, 3%
18	Bronze blue, ink
22	high-grade carbon black, dry
100	

Weight (lbs.)	Coated Paper Red
35	No. 1 lithographic varnish
12	No. 00 lithographic varnish
4	soft wax compound
4	paste drier
22	gloss white, dry
23	barium Lake for Red C, dry
100	

Weight (lbs.)	Coated Paper Yellow Lake
23	No. 00 lithographic varnish
6	No. 0 lithographic varnish
6	No. 1 lithographic varnish
5	paste drier
5	soft wax compound
50	Tartrazine Yellow Lake, dry
5	alumina hydrate, dry
100	

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[9] J. Bekk, *Svensk Papperstidn.*, 1934, **37** (14), 422; *Chim. et ind.*, 1935, **33** (2), 433; *Rev. Paint, Colour, Varnish*, 1935, **8**, 108. *Chem.-Ztg.*, 1933, **57** (76), 756; *Rev. Paint, Colour, Varnish*, 1933, **6**, 265. *Papier-Fabr.*, 1933, **31**, *Tech.-Wiss Teil*, 485; *Chem. Abs.*, 1934, **28**, 1530. J. Strachan, *Paper Maker*, 1934, **87** (5), TS 97; *Chem. Abs.*, 1934, **28**, 7011. J. Bekk, *Zellstoff u. Papier*, 1937, **17**, 294; *Rev. Paint, Colour, Varnish*, 1937, **10**, 260; *Brit. Chem. Abs.* **B**, 1937, 1322; *Chem. Abs.*, 1937, **31**, 6878.

[10] H. J. Wolfe, *Am. Ink Maker*, 1933, **11** (4), 9; *Rev. Paint, Colour, Varnish*, 1933, **6**, 135; *Chem. Abs.*, 1933, **27**, 3092.

Table 41.—*(contd.)*

Weight (lbs.)	Supercalendered Paper Red
26	No. 1 lithographic varnish
4	No. 33 mineral ink oil
8	soft wax compound
4	paste drier
14	gloss white, dry
14	barium Lithol Toner, dry
30	AAA Orange mineral, dry
100	

Weight (lbs.)	Parchment Black
12	No. 1 lithographic varnish
25	No. 3 lithographic varnish
12	hard-drying gum varnish
12	cobalt drier
1	melted beeswax
15	Bronze blue, ink
23	carbon black, dry
100	

Weight (lbs.)	Carton Yellow
20	No. 0 lithographic varnish
5	No. 3 lithographic varnish
1	heavy gum varnish
4	wax offset compound
4	paste drier
21	lemon chrome yellow, dry
30	medium chrome yellow, dry
15	gloss white, dry
100	

Weight (lbs.)	Machine-finished Red
20	No. 33 mineral ink oil
20	No. 1 lithographic varnish
5	No. 3 lithographic varnish
4	soft cup grease
6	paste drier
15	gloss white, dry
30	barium Lithol Toner, dry
100	

Weight (lbs.)	Glassine Violet
50	hard-drying gum varnish (lithographic varnish and Amberol)
5	wax compound
10	cobalt drier
10	AAA Orange mineral, dry
25	phosphotungstated Methyl Violet Toner, dry
100	

Weight (lbs.)	Supercalendered Paper Blue
32	No. 0 lithographic varnish
10	No. 1 lithographic varnish
8	No. 33 mineral ink oil
6	soft wax compound
2	paste drier
8	alumina hydrate, dry
34	Bronze blue, dry
100	

Weight (lbs.)	Parchment Red
10	No. 0 lithographic varnish
12	No. 3 lithographic varnish
8	dammar varnish
3	paste drier
15	gloss white
25	English vermilion, dry
22	AAA Orange mineral, dry
5	Madder Lake, dry
100	

Weight (lbs.)	Carton Red
28	No. 0 lithographic varnish
8	No. 3 lithographic varnish
3	wax offset compound
4	paste drier
12	alumina hydrate, dry
36	blanc fixe, dry
9	calcium Lithol Toner, dry
100	

Weight (lbs.)	Machine-finished Blue
15	No. 33 mineral ink oil
20	No. 0 lithographic varnish
6	No. 3 lithographic varnish
3	cobalt drier
6	soft cup grease
10	gloss white, dry
40	Bronze blue, dry
100	

Weight (lbs.)	Glassine Green
35	hard-drying gum varnish
4	wax compound
4	paste drier
46	lemon chrome yellow, dry
11	green shade Milori Blue, dry
100	

The development of high-speed printing processes has necessitated the formulation of inks that are fast-drying and papers that can stand the mechanical strain of the presses and that allow inks to be absorbed faster in order to inhibit smudging and offset.[11] John Walter in 1814 proudly announced that he was able, by a faster method of printing, to produce 1,100 copies of the London *Times* per hour![12] That seems to be snail-paced printing compared with the thousands of copies printed hourly by modern presses. A different type of ink must be used on platen presses than on rotary machines, and the composition of the ink must be varied, as will be more fully discussed later, according to the method of printing employed, whether it be typographic, lithographic, or rotary photogravure.[13]

Newsprint is a non-enduring type of paper which is lightly calendered to lower the penetration of the ink. Such paper is composed of groundwood and sulphite pulp, and about 60 per cent of its volume is composed of air spaces. Groundwood is mechanically macerated pulp which contains all the original impurities (*e.g.*, calcium oxalate, lignin, rosin, etc.) that were present in the wood. Sulphite pulp is a material produced by the action of calcium bisulphite on wood and is freer of impurities than is groundwood. Most newsprint in use is composed of from 75 to 82 per cent groundwood and the remainder sulphite pulp.

Sulphite fibers are of uniform size and are not fibrillated, or broken into smaller bits of fibers, whereas groundwood, because of the abrasive process of manufacture, is of non-uniform size and is split or fibrillated. Therefore the latter make a stronger paper because of the enmeshing of these small fibrills. The rate of absorption of ink is dependent upon the capillary forces of the fibers and upon the area of fiber surfaces exposed to the oil vehicle of the ink. The amount of "show-through," or transparency, caused by the action of the oil can be expected to be low in newspapers because of the high groundwood content. The calendering process, however, counterbalances the effect by decreasing the absorptive area and by decreasing the oil resistance of the fibers. Penetration would be least if the paper were composed of 100 per cent groundwood and would increase with an increase in sulphite content. Groundwood paper has higher opacity and less "strike-through," or running through, of the ink oil than sulphite paper. The gloss is also lower and the printing more uniform.

The inclusion of sulphite pulp, however, increases the tensile strength of the paper, a factor very important in the high-speed printing processes. Sulphite pulp increases the gloss of the paper, increases the ink absorp-

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[11] See Chapter 17.

[12] "Encyclopaedia Britannica," 1937, 16, 337.

[13] J. Bekk, *Zellstoff u. Papier*, 1937, 17, 294; *Rev. Paint, Colour, Varnish*, 1937, 10, 260; *Brit. Chem. Abs.* B, 1937, 1322; *Chem. Abs.*, 1937, 31, 6878. J. Strachan, *Paper Maker*, 1934, 87 (5), TS 97; *Chem. Abs.*, 1934. 28, 7011. J. Bekk, *Papier-Fabr.*, 1933, 31, *Tech.-Wiss Teil*, 485; *Rev. Paint, Colour, Varnish*, 1934, 7, 195; *Chem. Abs.*, 1934, 28, 1530. For description of these three processes, see Chapter 1.

tion, and decreases the opacity. Groundwood paper has the highest opacity, unbleached sulphite next, and bleached sulphite least of all.

Spruce is considered to be one of the best woods for the production of newsprint because of its low rosin content. Pine is often used, although special alkali treatment must be followed to free it from the rosin, present in a large proportion, with the production of "tall oil" as a by-product.

Because newsprint is so unenduring, most newspapers print a few copies of each issue on a better grade of paper for record purposes, or they employ photography (miniature films) to obtain copies of their paper for filing purposes.[14]

News ink is one of the most fluid of the printing inks. It is non-hardening and its drying, as stated above, depends upon absorption into the fibers of the paper. Carbon black is used as the pigment, and toners [15] are added with the aid of rosin oil. The whole is ground into an oil which is chiefly or entirely mineral in character, and which varies from a light green to a very dark brown. The higher the proportion of pigment content, the less ink can be used; consequently less strike-through and show-through will result. The temperature of the ink and the paper is an important factor in this printing as in others, because the viscosity of the oil is lowered with an increase in temperature.[16]

Because news ink is of the non-drying type, it is rather easy to remove from the paper when new pulp is to be made from the waste material. Drying inks form a hard film when they dry, but news ink remains as "wet" always as it was when printed; all that occurs is that the vehicle penetrates into the fibrous structure of the paper, leaving the pigment stranded, so to speak, on or among the surface fibers. Removal is effected, therefore, by employing some solvent for the vehicle, such as turpentine, with an alkali or soap, and a peptizing agent such as beidellite [17] for the carbon black. The pulp is washed and the carbon black and vehicle are carried through the screen, leaving the fibers behind.[18]

In the removal of other types of ink from waste paper, however, more complicated procedures must be followed, the most important consideration of which is the cost of the process and the chemicals employed, since the products obtained are almost exclusively used for dark mate-

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[14] B. L. Wehmhoff, *Paper Trade J.*, 1932, 94 (13), 39; *Chem. Abs.*, 1932, 26, 3109. G. Thompson, *J. S. C. I.*, 1937, 1052. Official Notices, Liverpool Section. O. Ant-Wuorinen and A. Backman, *Zellstoff u. Papier*, 1938, 18, 470; *Brit. Chem. Abs.* B, 1938, 1279.

[15] See Chapter 6.

[16] H. Andrews, *Can. Chem. Met.*, 1932, 16 (3) 64; *Am. Ink Maker*, 1932, 10 (4), 33; *Rev. Paint, Colour, Varnish*, 1932, 5, 90, 173.

[17] A variety of bentonite with a 1:3 ratio of Al_2O_3 to SiO_2, from Biedell, Col.; E. S. Larsen and E. T. Whewy, *J. Wash. Acad. Sci.*, 1925, 15, 465; C. S. Ross and E. V. Shannon, *J. Wash. Acad. Sci.*, 1925, 15, 467; *Chem. Abs*, 1926, 20, 885.

[18] Forest Prod. Lab., Madison, Wis.; *Chem. Ind.*, 1938, Jan., p. 47; N. Osawa, U. S. P. 1,833,840 and 1,833,852, Nov. 24, 1931, to Ko Watanabe; *Chem. Abs.*, 1932, 26, 1122.

rials such as pasteboard and wrapping paper. Three common methods of ink removal are the alkali, emulsion and beater processes.[19]

In the alkali treatments, soaps as well as alkalies, such as lye, lime, ammonia, sodium alkaline salts, *e.g.*, sodium carbonate, silicate, and borate are employed. The paper is macerated and mixed with one or more of these materials, whereby the ink is dissolved leaving the pulp behind.[20] The inclusion of bentonite, a colloidal clay material, with an alkali such as sodium carbonate is recommended.[21] Kieselguhr, silica powder, fuller's earth, kaolin, talc, soapstone, casein, gelatin, glue, albumin, gum arabic or tragacanth, starch, or dextrin are sometimes substituted for bentonite as a detergent along with the alkali material.[22] The use of tetralin with dilute sodium hydroxide has been suggested by Berl and Pfannmüller.[23] The tetralin, in which is dissolved the removed ink and its binders, is separated from the cleaned pulp by flotation with water, in which the fibers remain in suspension.

Frequently a bleaching agent, such as calcium hypochlorite, sulphurous acid, or chlorine, is added to whiten the fibers while the ink is being removed, and to bleach any ink left in the pulp.[24] By the use of an alkaline bleach, such as sodium peroxide, barium peroxide, sodium orthoborate, or sodium persulphate, the bleaching action and the alkaline detergent action are performed by the same substance, thus obviat-

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[19] For a discussion of ink removal from waste paper, see T. R. Briggs and F. H. Rhodes, "Fourth Colloid Symposium Monograph," 311, New York, Chemical Catalog Co. (Reinhold Publishing Corp.), 1926; *Chem. Abs.*, 1927, **21**, 3456. A. Bryant, *Paper Mill*, 1926, **49** (23), 56; *Paper Trade J.*, 1926, **82** (23), 63; *Chem. Abs.*, 1926, **20**, 3082. B. Haas, *Chem.-Ztg.*, 1921, **45**, 1187; *Chem. Abs.*, 1922, **16**, 829. P. R. Hines and J. J. Bean, *Paper Trade J.*, 1936, **103** (10), 37; *Chem. Abs.*, 1936, **30**, 8612. C. M. Joyce, *Chem. Met. Eng.*, 1921, **25**, 242; *Chem. Abs.*, 1921, **15**, 3745. E. G. Milham, *Paper Trade J.*, 1931, **93** (14), 40; *Paper Mill*, 1931, **54** (40), 18; *Chem. Abs.*, 1931, **25**, 5989. I. I. Kovalevskii, *Bumazhnaya Prom.*, 1935, **14** (3), 16; *Chem. Abs.*, 1935, **29**, 5267. J. J. O'Connor, *Paper Mill*, 1926, **49** (10), 10; *Chem. Abs.*, 1926, **20**, 3812. W. Schrauth, *Chem.-Ztg.*, 1921, **45**, 1090; *Chem. Abs.*, 1922, **16**, 645.

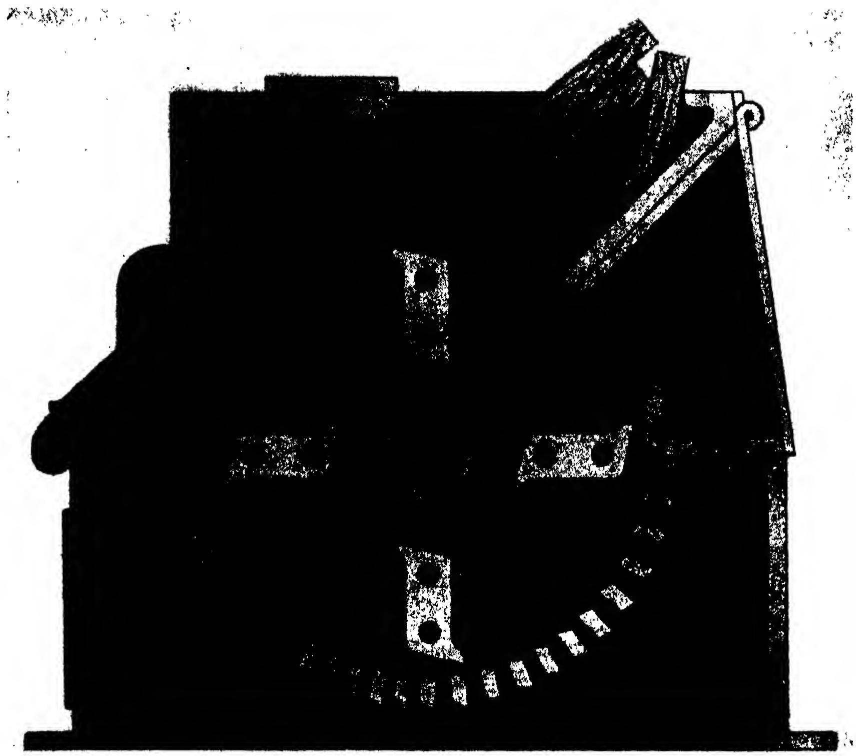
[20] As examples of this procedure, the following are cited: A. F. Allen, A. F. McCoy and R. O. Sternberger, U. S. P. 1,406,322, Feb. 14, 1922; *Chem. Abs.*, 1922, **16**, 1317. F. A. Brown, British P. 375,978, 1932; *Chem. Abs.*, 1933, **27**, 3610; Canadian P. 322,965, 1932; *Chem. Abs.*, 1932, **26**, 4176. N. Davis, *Brit. Printer*, 1934, **46** (276), 279; *Rev. Paint, Colour, Varnish*, 1934, **7**, 195. R. Edmunds, *Papierfabr.*, 1927, **25**, *Tech.-Wiss Teil*, 75; *Chem. Abs.*, 1928, **22**, 4814. G. Hammond, U. S. P. 1,572,479, Feb. 9, 1926; *Chem. Abs.*, 1926, **20**, 1323. L. Herz, British P. 24,131, 1908; German P. 220,424, 1909; *Chem. Abs.*, 1910, **4**, 2203. P. R. Hines, U. S. P. 2,005,742, June 25, 1935; *Chem. Abs.*, 1935, **29**, 5657; U. S. P. 2,042,465, June 2, 1936; *Chem. Abs.*, 1936, **30**, 5040. T. Jesperson, U. S. P. 1,311,563, July 29, 1919; *Chem. Abs.*, 1919, **13**, 2596; U. S. P. 1,424,411, Aug. 1, 1922; *Chem. Abs.*, 1922, **16**, 3394. M. E. and B. W. Kinyon, U. S. P. 1,826,179, Oct 6, 1932; *Chem. Abs.*, 1932, **26**, 600. J. Kircher and E. Ebner, *D. Ing.-Ztg.*, 1870, 88; *Chem. Zentr.*, 1870, **3** (1), 166. W. Lewis, British P. 321,826, 1928; *Chem. Abs.*, 1930, **24**, 2885; Canadian P. 283,130, 1928; *Chem. Abs.*, 1928, **22**, 4248; U. S. P. 1,727,722, Sept. 10, 1929; *Chem. Abs.*, 1929, **23**, 5319. A. R. Lukens, U. S. P. 1,680,949, Aug. 14, 1928, to The Richardson Co.; *Chem. Abs.*, 1928, **22**, 3778. B. W. Petsche, German P. 233,665, 1910; *Chem. Abs.*, 1912, **6**, 1851. F. H. Snyder, U. S. P. 1,988,363, Jan. 15, 1935; *Chem. Abs.*, 1935, **29**, 1637; British P. 441,363, 1936; *Chem. Abs.*, 1936, **30**, 5672, both to Snyder Maclaren Processes, Inc. R. W. G. Stutzke, U. S. P. 1,545,707, July 14, 1925; *Chem. Abs.*, 1925, **19**, 2878. O. C. Winestock, U. S. P. 1,138,596, May 4, 1915; *Chem. Abs.*, 1915, **9**, 1691. S. D. Wells, U. S. P. 2,018,938, Oct. 29, 1935, to Lewis L. Alsted; *Chem. Abs.*, 1936, **30**, 287.

[21] H. R. Eyrich and J. A. Schreiber, British P. 186,372, 1921; *Chem. Abs.*, 1923, **17**, 341; Canadian P. 222,060, 1922; *Chem. Abs.*, 1922, **16**, 3394; U. S. P. 1,421,195, June 27, 1922; *Chem. Abs.*, 1922, **16**, 2990.

[22] M. Cline and C. F. Rhodes, U. S. P. 1,138.085, May 4, 1915; *Chem. Abs.*, 1915, **9**, 1691. L. E. Granton, British P. 222,160, 1923; *Chem. Abs.*, 1925, **19**, 1055.

[23] E. Berl and W. Pfannmüller, *Z. angew. Chem.*, 1925, **39**, 887; *Chem. Abs.*, 1926, **20**, 289.

[24] E. Kellner, U. S. P. 1,555,674, Sept. 29, 1925; *Chem. Abs.*, 1925, **19**, 3594. W. M. Osborne, U. S. P. 1,298,779, April 1, 1919; *Chem. Abs.*, 1919, **13**, 1763. J. E. Plumstead, U. S. P. 1,576,994, March 16, 1926; *Chem. Abs.*, 1926, **20**, 1905. F. H. Snyder, U. S. P. 1,991,823, Feb. 19, 1935, to Snyder Maclaren Processes, Inc.; *Chem. Abs.*, 1935, **29**, 2357. D. Wells, U. S. P. 1,992,977, March 5, 1935, to Lewis L. Alsted; *Chem. Abs.*, 1935, **29**, 2744.



Courtesy Williams Patent Crusher & Pulverizer Company

FIGURE 96. Sectional View of Williams "No-Nife" Hog for Shredding Wood.

ing the use of two ingredients.[25] An alkaline organic material is sometimes used instead of lye or soap as a detergent. Water-soluble derivatives of sulphonic acids, such as the sodium, potassium, or ammonium salts, or those of an organic base, *e.g.*, pyridine, cyclohexylamine or triethanolamine, are ink-removing agents which have been employed. They are used in conjunction with various organic solvents, *e.g.*, chlorinated or hydrogenated hydrocarbons, higher alcohols, or with bentonite or fuller's earth, or such solvents as Turkey-red oil. After the paper has been treated, the solvents may be recovered and used again.[26]

In the emulsoid type of ink remover, the agent employed to emulsify the water-insoluble material with the aqueous phase may be soap, sodium carbonate, rubber, gutta-percha, Turkey-red oil, various gums, or an alkali. The solvents used are numerous; among them are pyridine, kerosene, turpentine, benzene, pine oil, rosin and rosin oil, various chlori-

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[25] H. Henkel and O. Gessler, U. S. P. 988,874, April 4, 1911; *Chem. Abs.*, 1911, 5, 2176. C. Kurtz-Hahnle, British P. 26,019, 1911; *Chem. Abs.*, 1913, 7, 1609.

[26] British P. 438,403, 1935, to Deutsche Hydrierwerke A.-G.; *Chem. Abs.*, 1936, 30, 3237.

nated hydrocarbons and phenols, and organic acids. After being agitated with the paper, the solvents are separated from the aqueous pulp mixture and carry with them the decomposed and dissolved ink vehicles and pigments.[27]

The beater process, as used for the purpose of removing ink from paper, utilizes merely the mechanical action of shredders and abrasion wheels, together with the flushing action of water. The paper is macerated and agitated by any one of various types of toothed wheels and is washed with copious amounts of water to remove the ink. The process is of advantage where water is abundant and cheap, and is economical for the reason that no chemicals are needed for ink removal.[28]

Several processes not included in one of the three classifications given above have been used to remove ink from waste paper. The paper may be mixed with a weak aqueous solution of sodium chloride and the resulting mass, after having been macerated, is electrolyzed to remove the carbon black.[29] As an alternative method, the paper is heated with a solid petroleum (*e.g.*, paraffin wax or petrolatum) and the ink dissolved out and removed. The petroleum is then drained off and the pulp washed with water.[30] The use of two immiscible liquids, such as water and benzene, has been suggested as a solvent. The pulp collects in the water layer and the ink stock in the benzene portion, thus effecting an easy method of separating the two.[31]

A rather loosely constructed paper is needed for lithographic printing, in order to be non-sensitive to changes in temperature and relative humidity. In the preparation of lithographic paper, the pulp is subjected to a minimum of beating and refining, and a paper is produced which has a fairly large directional difference, that is, the properties which it possesses across the grain are not the same as those in the direction of the fibers. In other words, it will swell and expand to a

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[27] F. W. Atack, British P. 299,817, 1927; *Chem. Abs.*, 1929, 23, 3548. J. E. Bouser, U. S. P. 1,008,779, Nov. 14, 1911; *Chem. Abs.*, 1912, 6, 293. German P. 369,468, 1921, to Chemotechnische Gesellschaft; *Chem. Abs.*, 1923, 17, 2362. W. S. Crisp, U. S. P. 1,993,362, March 5, 1935, to Wm. J. Weir; *Chem. Abs.*, 1935, 29, 2744. H. C. Fisher, U. S. P. 1,707,604, April 2, 1929, to Richardson Co.; *Chem. Abs.*, 1929, 23, 2571. H. B. Hass, U. S. P. 1,990,376, Feb. 5, 1935, to Purdue Research Foundation; *Chem. Abs.*, 1935, 29, 1986. H. Scheele, German P. 502,730, 1929; *Chem. Abs.*, 1930, 24, 5497. C. G. Schwalbe, *Z. angew. Chem.*, 1931, 44, 24; *Chem. Abs.*, 1931, 25, 3480. O. Welsh, U. S. P. 1,601,193, Sept. 28, 1926; *Chem. Abs.*, 1926, 20, 3814. I. J. Wright, U. S. P. 1,226,735, May 22, 1917; *Chem. Abs.*, 1917, 11, 2154.

[28] Various mechanical de-inking treatments are described and discussed in the following: P. Bourcet and H. Regnault, British P. 219,311, 1923; *Chem. Abs.*, 1925, 19, 577. J. De Witt, U. S. P. 1,705,907, March 19, 1929; *Chem. Abs.*, 1929, 23, 2294. T. Earle, U. S. P. 2,116,511, May 10, 1938; *Chem. Abs.*, 1938, 32, 5213. G. Hammond, U. S. P. 1,846,683, Feb. 23, 1932, to the Reclamation Co. of America; *Chem. Abs.*, 1932, 26, 2594. P. R. Hines, French P. 793,990, 1936; *Chem. Abs.*, 1936, 30, 4672. B. I. Humble, *Paper Trade J.*, 1930, 91 (1), 49; *Chem. Abs.*, 1930, 24, 5491. W. Lewis, U. S. P. 1,696,639, Dec. 25, 1928; *Chem. Abs.*, 1929, 23, 983. G. G. McArthur, U. S. P. 1,904,066, April 18, 1933; *Chem. Abs.*, 1933, 27, 3333. W. B. Meixel, U. S. P. 989,023, April 11, 1911, to James B. Stalnaker and T. W. Jenkins; *Chem. Abs.*, 1911, 5, 2176. H. A. Morrison, *Paper Trade J.*, 1932, 94 (18), 40; *Chem. Abs.*, 1932, 26, 4717. C. A. Shubert, *Paper Trade J.*, 1931, 93 (13), 31; *Chem. Abs.*, 1931, 25, 5989. B. M. Sorokin, Russian P. 35,550, 1934; *Chem. Abs.*, 1935, 29, 8332. O. C. Weinstock, British P. 262,270, 1925; *Chem. Abs.*, 1927, 21, 3744. S. D. Wells, U. S. P. 1,962,164, June 12, 1934; *Chem. Abs.*, 1934, 28, 4908.

[29] N. A. Kuzin, Russian P. 52,792, 1929; *Chem. Abs.*, 1931, 25, 1085.

[30] A. L. De Stürler, German P. 263,220, 1912; *Chem. Abs.*, 1913, 7, 4069.

[31] J. J. Werst, P. Mar, H. L. Collée, and J. M. Egmond, German P. 265,488, 1911; *Chem. Abs.*, 1914, 8, 573; German P. 279,101, 1913; *Chem. Abs.*, 1915, 9, 1246; U. S. P. 1,083,234, Dec. 30, 1913; *Chem. Abs.*, 1914, 8, 1207; Dutch P. 726, 1912; *Chem. Abs.*, 1913, 7, 3415.

greater degree across the grain than with it, and its tensile strength will be greater across the grain than in the direction of the fiber lengths. The "grain" of a paper is produced in mechanical processes of production on the Fourdrinier machine, and a greater proportion of the fibers tend to lie in the direction of motion of the paper through the machine, rather than across the path. In hand-made papers the properties the sheet possesses are exactly equal in both directions, and there is no "grain." The paper should be surface sized[32] for best results in lithographing, for the paper thus produced has the right amount of absorbency to prevent offset and at the same time to hold the ink near the surface.

In the pressroom, as indicated, the control of humidity is important for attainment of the best results. The paper should be conditioned, that is, allowed to come to equilibrium with the humidity and temperature of the room. Most paper will retain, because of the hygroscopic nature of the cellulose fibers, from 0.5 to 1 per cent more moisture than that required for equilibrium. The heaviest paper, piled in sheets, becomes conditioned in less than 2 hours, while light papers reach a stable state in about 1 hour, when changing from 35 per cent to 65 per cent relative humidity.

Below 80 per cent humidity the moisture content and the dimensions of the paper are directly proportional to the relative humidity, but above that degree, both the moisture content and the size of the paper increase to a greater degree than the humidity. Above 95 per cent, the fibers of the paper become pulpy and are rearranged, causing a slight permanent shrinkage. If the moisture content should rise above 95 per cent between two successive impressions in printing, difficulties of register would occur because the two successive plate impressions would not correspond in position. There is a greater degree of expansion across the grain, because of the swelling of the fibers, than with the grain, but no constant ratio is followed.[33]

The desirable types of papers for half-tones are coated and supercalendered stock, although one of the softest and uncoated papers, Bible paper, shows a fine impression. When an antique or uncoated paper is printed with a half-tone, the roughness of the surface causes an uneven, mottled effect. The surface of a paper might be likened to a mountainous terrain, caused by the interlaced fibers. During the calendering operation, the hills are crushed down almost to valley level; the coating of paper fills the hollows, and even covers the hills, to produce a plane surface above that of the original paper.

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[32] Surface sizing is a process of coating a hardening material on the surface of newly made paper as distinguished from vat sizing, whereby the size is mixed in with the pulp and permeates the entire sheet of paper.

[33] R. F. Reed, *Lithographic Technical Foundation, Research Bulletin* No. 1; Research Series No. 1. G. Aubin, *Papier*, 1938, 41, 297; *Pulp Paper Mag. Can.*, 1938, 39, 647; *Brit. Chem. Abs.* **B**, 1938, 1278; *Chem. Abs.*, 1938, 32, 8141. *Bur. Stand. Tech. News Bull.*, 1932, 201, 7; *Rev. Paint, Colour, Varnish*, 1934, 7, 21. R. F. Reed, *Paper Trade J.*, 1938, 107, TAPPI Sect., 25; *Brit. Chem. Abs.* **B**, 1938, 1141.

The degree of calendering, the amount of hydration of the paper, the kind and amount of sizing, the formation of the sheet, and the type of stock all have an influence on the character of the work obtained. Coated paper produces a more accurate reproduction of the half-tone dot than does the supercalendered type. The "halo" effect is less pronounced.

The surface of the paper should absorb the ink in the fraction of a second between the time when the plate first comes into contact with it, and when the squeezing action of the press begins; otherwise the "halo" effect occurs.[34]

The qualities demanded of papers for color printing are very exacting, although not as essential in letterpress work as in the lithographic process. The paper stock must be a pure white in order not to change the hue of the pigment in the ink. If a pure white is unobtainable, as near as possible a neutral shade should be used, and not a blue or a buff shade of white, as these spoil the effect of the ink. The standard white sheet should reflect 92 per cent of the light at the surface and not below it, and therefore must be very opaque. The paper should not be so absorptive as to imbibe the vehicle and so change the character of the ink remaining on the surface.

The physical properties required are a strength of such an order as to withstand without fluffing the pull of the gripper on the press at the rate of 4 to 5 thousand sheets per hour, and to stand up without buckling with an automatic feeder. The amount of fluff and dust produced by the paper should be of such a small quantity as not to necessitate cleaning the press even after an all-day run.[35]

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[34] H. P. Carruth, *Paper*, 1915, 17 (5), 11; *Chem. Abs.*, 1916, 10, 527.

[35] T. S. Foweraker, *Proc. Tech. Sect. Paper Makers' Assoc. Gt. Brit. & Ireland*, 1933, 13 (2), 419; *Chem. Abs.*, 1933, 27, 5185.

Glossary

If given proper care and attention with each revision and revisions occur frequently enough so that definitions can be improved, a *glossary* becomes a very useful part of a book of this kind.

The assistance is asked of the trade to send in such improved definitions with this object in view.

Absorption.—The act of taking up, or assimilation, of one substance by another.

Acid Dyes.—Organic coloring agents in which the dye-base takes the place of the acid constituent of a salt.

Acid Number.—The number of milligrams of potassium hydroxide required to neutralize one gram of substance.

Adsorption.—Phenomenon consisting in the adhesion, in an extremely thin layer, of molecules of gases, of dissolved substances, or of liquids to the surfaces of solid bodies with which they are in contact.

Adsorption Value (D.P.G.).—The per cent diphenylguanidine removed from a solution of 0.1 g. of diphenylguanidine in 50 cc. of alcohol by 1 g. of carbon black.

Alizarine Oil.—The neutralized product obtained by treating olive oil, castor oil, cottonseed oil or other glycerides of fatty acids with sulphuric acid.

Aniline Inks.—Solutions of a coal-tar dyestuff in an organic solvent, *e.g.*, alcohols, esters, ketones and ethers.

Antioxidants.—Agents retarding the action of oxygen on drying oils and other substances subject to oxidation.

Antique Paper.—Book paper that has not gone through a calender and is without finish.

Antiskinning Agents.—Retardants of skin formation on the surface of a drying oil; usually the action is that of exerting a dispersing effect on the newly formed skin.

Autographic Printing.—A process of making facsimiles.

Autopolymerization.—A polymerization reaction which is catalyzed by the polymers formed.

Autotype.—A printing process in which the metal plate is coated with a light-sensitive resin instead of gelatin.

Autoxidation.—The combination of molecular oxygen with oxidizable substances.

Backing.—A piece of resilient material placed behind the paper to be printed to insure a more even impression.

Basic Dyes.—Organic coloring agents in which the dye-base takes the place of the basic constituent of a salt. Generally marketed as colorless hydrochlorides or colorless double salts with zinc chloride.

Binder.—A material effecting adhesion of ink film to printed surface.

Binding Agents.—See **Binder.**

Blanket Cylinder.—A rubber-surfaced cylinder which receives the inked design from the plate cylinder and "offsets" it onto the surface to be printed.

Bleeding.—The spreading or running of a pigment by the action of a solvent, *e.g.*, water or alcohol.

Blown Oils.—Products obtained by conducting air through a vegetable oil while the latter is heated, *i.e.*, heavily bodied oil.

Bodied Linseed Oil.—Linseed oil which has been thickened by heating until the desired viscosity has been secured.

Bodied Linseed Oil Extract.—See **Tekaols.**

Body.—A term designating the viscosity, consistency, density, or covering power of an ink or a vehicle therefor. Sometimes used to indicate density of a pigment.

Body Color.—The color of an unmoistened pigment before admixture with the vehicle.

Bodying Agent.—Material added to an ink to increase the viscosity of the vehicle.

Breaking.—A sudden and distinct separation of a gelatinous mass from raw linseed or other oils.

Broken-tone Negatives.—Negatives obtained by exposing the subject through a ruled screen placed between the film and the continuous-tone positive.

Buhrstone.—A hard, tough rock, white or creamy in color, consisting of chalcedonic silica with a cellular texture.

Calender.—A system of alternate rollers of metal and paper for polishing the surface of sized and coated papers.

Calendered Paper.—Paper which, in the process of manufacture, has been passed between hot rollers at great pressure to form smooth hard surfaces on the sheet.

Carbon Tissue.—A sheet of paper coated with hardened dichromated gelatin containing carbon or other pigment in suspension.

Cellophane.—Transparent paper made by extruding a viscose solution through long narrow slits into a settling bath.

Clouding.—See **Misting.**

Cold-color Printing.—A process for printing on glass or ceramic surfaces.

Collotype Process.—Printing from a gelatin surface which has been rendered non-uniformly ink-receptive by light transmitted through an unscreened negative.

Color Printing.—A process involving the use of the three primary colors, red, yellow and blue in the correct proportions.

Color Strength.—The intensity of color exhibited by a pigment.

Conté Pencils.—Non-greasy agents used for making temporary drawings or designs on lithographic plates.

Copying Press.—A printing press for duplicating copies.

Copy Relief.—The swollen gelatin form from which an intaglio or relief matrix is cast.

Corrected Negatives.—Negatives for color printing made by using a combination of three-color negatives, their corresponding positives, and the negatives therefrom.

Covering Power.—The capacity of an ink to hide the material beneath and to produce a uniform, opaque surface.

Crawling.—The contraction of ink film into drops. Occurs after printing of ink on a hard surface, *e.g.,* glass.

Crazed Drying.—See **Gas Crazing.**

Creeping.—Flowing of ink beyond the limits of the design.

Crystallization.—See **Gas Crazing.**

Cylinder Press.—A press consisting of an oscillating flat bed or surface of type passing alternately under inking rollers and a rotating cylinder which presses the paper against the moving type.

Dampening.—Moistening non-design areas of lithographic plates by means of water-moistened rollers.

Decalcomania.—Printing or painting of designs, patterns, pictures or textual matter upon a temporary base, and later transferring the printed material to a permanent base.

Diapositive.—A positive made from a photographic negative, especially one on a transparent background.

Diene Number.—The proportion of conjugated double linkages in oil employed in printing inks.

Dilution Ratio.—A measure of amount of non-solvent that can be added to a solution containing nitrocellulose, synthetic resin or other solute before precipitation occurs.

Dilution Tolerance.—See **Dilution Ratio.**

Direct Dyes.—Coloring materials not requiring the use of a mordant for forming a marking on cotton.

Dispersing Agents.—Materials which facilitate the mixing of a solid substance into a liquid medium.

Doctor Blade.—A knife edge which wipes excess ink off the surface of the engraved plate in intaglio printing.

Doping or Doctoring.—Changing in the pressroom of the properties of an ink by incorporation of various modifying agents.

Dot-Etching.—Decreasing the size and shaping the outline of the silver dots on photolithographic screen positives.

Dragon's Blood.—An exudate from *draoema draco* or *calamus draco* trees.

Draw Out.—A small portion of a colored paste spread out in a thin layer on white paper to show color properties.

Driers.—Substances which accelerate the rate of drying of oils. Generally derived from the metals cobalt, manganese, or lead.

Drowning.—Operations comprising the dissolution of a dye in acid, (*e.g.*, sulphuric acid) followed by pouring the resulting solution into water to precipitate the dye in pulp form.

Drying Oils.—Oil possessing the ability to form a tough surface film on standing in contact with the atmosphere.

Drying Time.—The time required for an ink composition to penetrate the surface of the paper or to dry to a hard, permanent film.

Electrotypes.—Copper casts electrolytically deposited on a wax impression of assembled type. The copper shells are reinforced by a soft metal backing and are mounted on wood blocks.

Embossed Printing.—A method of printing whereby the lines of the design, sunk in the die, appear in relief on the printed sheet.

Emulsifying Agents.—Agents facilitating the dispersion of one liquid into another.

Emulsion Ink.—A composition comprising pigments, modifying agents, and an emulsion of two immiscible liquids.

Encaustic Inks.—Inks which penetrate the body of the sheet, rendering erasure much more difficult.

Ester Gums.—The products of esterifying rosins with glycerol or ethylene glycol.

Ester Number.—The difference, expressed in milligrams of potassium hydroxide per gram of oil, between the acid number and the saponification number.

Extenders.—Inorganic compounds which have little opacity or hiding power but when mixed with pigments are considered to increase the covering power of the latter.

Fastness to Light.—The resistance of a colored substance to the action of light.

Fastopake Inks.—Compositions for printing on waxed surfaces.

Fatty Acids.—Monobasic, saturated carboxylic acids of the aliphatic series, many of which are obtained by the hydrolysis of fats.

Feathering.—Printing with irregular edges to the design.

Feculose.—A mixture of esters prepared by treating starch with glacial acetic acid and washing the product free of uncombined acid.

Filling Up.—Covering the non-printing areas (on a lithographic plate) with a partially dried ink film. Effect caused by an excess of drier in the ink.

Fine-etching.—A method of modifying a photomechanically prepared plate by controlled undercutting to change the size of the half-tone dots.

Fish Glue.—A gelactose resulting from hydrolysis of fish gelatin.

Flash Point of Solvents.—The temperature to which a liquid must be heated so that the vapors thereof will ignite when a source of ignition is applied under definite conditions.

Flatbed Cylinder Press.—See **Cylinder Press.**

Flatting.—See **Gas Crazing.**

Fleshing.—See **Flushing.**

Flocculation of the Vehicle.—See **Livering.**

Flooding.—Excess ink on type or form caused by the ink fountain being too wide open. In the case of lithographic or offset work, the use of too little water or the absence of an etching material in the water fountain.

Fluid Resin.—See **Tall Oil.**

Flushing.—A grinding process which converts a water-wet pigment directly to an oil-wet pigment, by displacing water with oil.

Flow.—The ability of an ink to spread over a surface or into a thin film.

Flying Ink.—The fine mist or spray of ink thrown off by rapidly moving inking rollers if an incorrect ink composition is used.

Frosting.—See **Gas Crazing.**

Gas-Checking.—See **Gas Crazing.**

Gas Crazing.—The wrinkling of a tung oil film under certain drying conditions. It is said to be caused by rapid absorption of oxygen on the surface.

Gelation.—Conversion, partially or entirely, to a jelly-like mass, by heat or other means.

Grain of Paper.—Structure of paper resulting from method of manufacture; usually most of the fibers lie in one direction.

Graining.—Process of making surface of a lithographic plate water-receptive by grinding with a muller and sand or. mechanically, with pebbles and sand.

Gravure Tissue.—Sheet of paper coated with dichromated gelatin but containing no pigment.

Greasing.—Undesirable adhesion of ink to the non-printing areas of a lithographic plate.

Groundwood.—Mechanically macerated pulp which contains all the original impurities (*e.g.*, calcium oxalate, lignin, rosin, etc.) that were present in the wood.

Gold Number.—A measure of the protective ability of hydrophilic colloids: Specifically, the number of milligrams of colloid which when added to a standard gold sol is just insufficient to prevent a change in color from red to blue.

Half-tones.—Plates composed of a large number of dots which in the heavily shaded portions are of relatively large size. In the lighter parts of the illustration the dots are proportionately smaller.

Half-tone Screens.—These consist of a transparent plate ruled diagonally with opaque lines at right angles to one another, the distance between them and their thickness being approximately equal.

Halo Effect.—Piling up of ink at the periphery of printed letters with a lack in the center.

Hexabromide Number.—The weight percentage of precipitate obtained by treating fatty acids with bromine. It is said to be an indication of the proportion of acids which contain three double bonds, *e.g.*, in linseed oil.

Hue.—Effect resulting from the admixture of a small proportion of one color with another.

Hydrogen Ion Concentration or pH.—An indication of the acidity or alkalinity of a liquid. Thus pH 6 is acid, pH 7 neutral, and pH 8 alkaline.

Hydrophilic Colloids.—These are also designated as lyophilic or reversible, and will redissolve after removal of solvent at atmospheric temperature.

Hydrophobic Colloids.—These are also designated as lyophobic or irreversible colloids and will not redissolve after removal of solvent at atmospheric temperature.

Impression Cylinder.—The roller of an offset printing press which presses the paper into contact with the blanket cylinder.

Indelible Ink.—Compositions which are made water- and alkali-fast.

India Ink.—Consists essentially of a dispersion of carbon black in water.

Induction Period.—The initial period of drying an oil during which no perceptible physical changes take place in the oil.

Induline Bases.—Substances prepared from amidoazobenzene, aniline and aniline hydrochloride.

Ink Compounds.—Materials added to remedy deficiences in the ink vehicle or pigment.

Ink Fountain.—The container or well which supplies ink to the inking rollers.

Inkometer.—An instrument indicating the consistency of an ink in terms of the frictional torque of the ink between rollers wet with the ink.

Intaglio Printing.—Printing with an engraved plate on which the ink to be transferred is found in the depressed areas of the surface.

Interfacial Tension.—The contractile force existing at the interface of two immiscible liquids.

Iodine Number.—The number of centigrams of halogen, calculated as iodine, which under specified conditions react with one gram of substance.

Isoelectric Point.—The hydrogen ion concentration at which a colloid is unchanged, *i.e.*, will not migrate in the electric field.

Lake.—Organic coloring agent precipitated on a substrate.

Leafing.—The phenomenon of metal flakes, when admixed with oil or varnish, rising to the surface and forming a continuous film resembling that of fallen leaves.

Length.—The property of an ink whereby it will stretch between two surfaces without breaking.

Letter Press.—See **Platen Press.**

Light-fastness.—The resistance of printed or colored material to the action of sunlight or artificial light.

Line-etching.—A print made up of lines or pigmented areas and lighter spaces free from shading.

Linotype Printing.—A process utilizing slugs of metal on which are cast the letters for a whole line of print.

Linseed Oil.—Oil pressed from flax seeds. Surfaces of this oil exposed to air dry to tough films. It is a well-known ingredient of printing inks and paints.

Liquefying Stress.—The ease with which concentrated inks can be liquefied by re-milling after storage.

Liquid Rosin.—See **Tall Oil.**

Lithographic Chalk.—A greasy crayon for drawing designs on a lithographic plate prior to etching and composed of soap, wax. oil and lampblack.

Lithographic Stones.—Slabs of limestone, three or four inches thick, the surfaces of which are smoothed or grained, for use in lithographic printing.

Lithographic Varnish.—Linseed oil which has been bodied by heating until it possesses a definite degree of viscosity.

Lithography.—A printing process involving employment of stone or metal plates whose printing surfaces are partly water-repellent and partly ink-repellent.

Livering.—The flocculation and coagulation of inks as a result of gelatinization of the vehicle.

Mahogany Sulphonates.—Oil-soluble sulphonates obtained in refining certain petroleum distillates with sulphuric acid.

Make-ready.—See **Backing.**

Mass-tone.—The color of an ink in bulk.

Mezzotints.—Prints made from ground (*e.g.*, crossed in several directions with knife-edge cuts) copper plates, the burred surface of which is scraped away to create the design.

Mineral Oils.—Oils of petroleum origin.

Mineral Spirit.—Low-boiling distillates of mineral oils.

Minium. -An old term for litharge.

Misting.—A mist or fog of ink droplets in the vicinity of the printing press.

Monotype Printing.—Process of printing from mechanically assembled pieces of type each of which bears one character.

News Ink.—Inks used for high-speed printing of newspapers.

Newsprint.—The unsized, absorbent paper used in newspaper printing.

Non-drying Oils.—Those oils which do not form tough surface films on standing exposed to the atmosphere in thin layers.

Offsetting of Inks.—The transference or smearing of ink from freshly printed matter to another surface with which the undried prints come into contact.

Offset Paper.—A variety of printing paper especially sized for offset lithography; it is non-curling and absorptive.

Offset Printing.—A modification of lithography in which the ink is transferred from a curved lithographic plate to a rubber pad which in turn contacts the paper.

Oil.—A general term which, when referring to emulsions, signifies that a liquid is immiscible with water.

Opacity.—The property of absolutely stopping the transmission of color or light from another source.

Overprinting.—Application of a varnish or lacquer to printed material from typographic or lithographic processes, by brushing, spraying or by roller-coating.

Oxidation of Lithographic Plates.—Corrosion of plates by atmospheric oxygen, occurring in irregular spots because of the presence of impurities.

Pantone Printing.—Planographic printing process using plates having mercury- or amalgam-coated, non-printing areas.

Pellicle.—A thin skin membrane.

Photoengraving.—Process for producing a design on a sensitized metal plate by placing a transparent negative between the plate and a source of light. The areas not rendered water-insoluble by light are washed and etched with acid solutions.

Photogenic Property.—The tendency of a pigment to darken on exposure to sunlight and to be rebleached on being placed in the dark.

Photogravure.—Process for making prints from photomechanically prepared intaglio plates.

Photolithography.—Process utilizing surfaces which, under the selective action of light, are transformed from a water-receptive to a water-repellent and ink-receptive nature.

Picking.—The adherence of a sheet of paper to the plate, due to the tack of the ink.

Pigment Dyestuff.—Insoluble organic coloring agent with no lake-forming properties.

Pigments.—Substances or mixtures of substances which impart color and opacity to inks.

Pinolein.—See **Tall Oil.**

Planography.—Printing processes which are dependent upon the fact that an oily ink will not adhere to water-moistened, non-design areas of a level plate but will wet design areas treated with a greasy ink or varnish.

Plate Cylinder.—That roller of an offset printing press which bears the printing plate.

Plateless Engraving.—A typographic printing process in which densely pigmented ink on printed sheets is dusted with a powdered resin of low melting point. After surplus powder has been blown from the paper, heat is applied to fuse the resin and yield characters which are raised above the paper.

Platen Press.—A press which prints a single sheet by pressing the latter against an entire frame or "chase" of type at the same moment.

Polimerisado Oil.—A bodied Brazilian liquid oiticica oil.

Polymerization.—The union of like or unlike polyfunctional molecules, with or without the elimination of some simpler substance, *e.g.*, water.

Prepared Linseed Oil.—Linseed oil which has been treated with litharge and other chemicals.

Printing Strength.—A relative value indicating how much ink is required to give an equal depth of tint to a definite amount of white ink as compared with the same amount of a standard ink of the same consistency.

Protective Colloid.—A stable colloid present in excess which protects another colloid, normally unstable, from precipitation by coagulating influences.

Protective Factor of an Antioxidant.—The proportion of millimoles of peroxide per kilogram in untreated oil to that in the oil containing an antioxidant.

Pulldown.—A small amount of ink placed on paper and spread over it with a fast stroke of a special knife.

Purified Stand Oil.—See **Tekaols.**

Reducers.—More or less volatile compounds drying by evaporation and penetration, employed to bring the varnish to the proper tack and consistency for use on the press.

Refractive Index.—The ratio of the sines of the angles formed by the incident and reflected light beams with the ordinate as measured by means of a refractometer.

Releasing Liquid.—A term employed to designate a base for receiving printed matter, which base later can be removed by treatment with a solvent, *e.g.*, water or alcohol.

Relief Printing.—Process utilizing those portions of the matrix which are in relief for taking ink from a supply roller and transferring it to the surface to be printed.

Resist.—The composition used on the non-printing portions of a planographic plate.

Reticulation.—The crepe-like appearance of the surface of the colloid on collotype plates.

Rolling Up.—The application of ink to a plate by means of a roller.

Rosin Oil.—A viscous oil obtained from the destructive distillation of rosin.

Rotary Press.—High-speed presses which pass continuously running webs of paper between an impression cylinder and the curved printing form on the plate cylinder.

Rotogravure Printing.—A form of intaglio printing which employs a curved, etched copper plate on a cylinder press.

Rub-off.—Ink on printed sheets after sufficient drying which smears or comes off on the fingers when handled.

Safety Inks.—Mixtures of a drying oil ink with an aqueous solution of a water-soluble color.

Saponification Number.—The number of milligrams of potassium hydroxide required to saponify one gram of oil.

Screens.—See **Half-tone Screens.**

Scumming.—A film formed over non-printing areas of lithographic plates which will not repel ink.

Sensitizer.—An agent which cleanses the ink-repellent, non-printing areas of lithographic printing plates.

Setting.—The partial drying of an ink film by slight absorption of the vehicle by the paper.

Shade.—A gradation of color resulting from the admixture of a small amount of black.

Shale Oil.—The crude tar from bituminous shale.

Short Ink.—A highly pigmented ink which is stiff and cannot be drawn out to a thread.

Show Through.—The transparency of printed sheets as a result of the penetration of oily materials present in the ink.

Siccatives.—See **Driers.**

Size.—Composition applied to paper to fill up the space between fibers and to produce a smooth surface.

Skinning.—The formation of a dried layer or film on the surface of the ink after a period of standing.

Slip Sheet.—A sheet of paper placed between freshly printed sheets to prevent smearing of the ink.

Soft Ink.—Printing composition exhibiting an almost complete absence of tack.

Solvent Naphtha.—A low-boiling hydrocarbon coal-tar distillate.

Spar Varnish.—Water-resistant varnish consisting mainly of a drying oil (*e.g.*, linseed oil) and resinous bodies such as rosin or the glycerol esters thereof (ester gum).

Specific Gravity.—The comparison of the weight of a given volume of material with the weight of an equal volume of water under the same conditions.

Stand Oil.—A drying oil which has been heated until a desired viscosity has been obtained.

Stereotypes.—Printing plates cast in one piece from a heat-dried papier-maché matrix containing the impression of the assembled type.

Stippling.—Engraving by means of dots in distinction from engraving in lines.

Strike Through.—Penetration of ink to the back side of the paper.

Substrate.—Base on which organic coloring agents are precipitated to form lakes.

Sulphite Pulp.—Material produced by the action of calcium bisulphite on wood.

Sulphite Waste Liquor.—The aqueous residue from treating wood chips with solutions of sulphurous acid and calcium acid sulphite.

Swedish Olein.—See **Tall Oil.**

Sympathetic Ink.—Novelty ink which is invisible.

Tack.—That property of cohesion between particles of an ink that can be described as the pulling power of the ink against another surface.

Tall Oil.—A dark brown, viscous, oily liquid obtained as an alkaline waste-liquor in the sulphate process of making wood pulp.

Tallöl.—See **Tall Oil.**

Tekaols.—Linseed stand oils from which the low-polymerized (saturated), highly dispersed phase has been removed.

Thiocyanate Number.—An indication of only part of the double bonds present in the oil as based on the selective addition of thiocyanogen, $(SCN)_2$.

Thixotropy.—The isothermal reversible decrease of viscosity with shear.

Throwing Out.—See **Gas Crazing.**

Tint.—A gradation of color, lighter in appearance than the normal spectrum color or hue thereof, which is created by mixing the color with white.

Toners.—Organic pigments containing no inorganic pigments or inorganic carrying bases.

Toptone.—The color reflected by the surface of an ink.

Transfer Paper.—The temporary backing employed in decalcomania.

Transfer Printing.—See **Decalcomania.**

Transparency.—The property of an ink which permits color or light from another source to pass through it.

Transparent Inks.—Inks with little covering power, *e.g.*, aniline inks.

Turkey-red Oil.—The reaction product of sulphuric acid and castor oil.

Tusche.—See **India Ink.**

Tympan.—The roller opposite the printing roller on a rotary press over which the paper web passes.

Tympan Sheet.—A sheet of paper or cloth placed between the impression surface (platen or cylinder press) and the paper to be printed.

Typography.—Processes of making an impression using a raised, pigmented surface, from type, line-etchings, half-tones or rubber stamps.

Undercutting.—The action of etching solution on the sides of the resist of photomechanically prepared plates.

Underhue.—See **Undertone.**

Undertone.—The appearance of an ink when present as a thin coat on a white background.

Varnish.—See **Stand Oil.**

Vat Dyes.—Those dyes which are insoluble in water, dilute acids, and alkalies but which, on being reduced, form a "color base" soluble in alkaline solutions. Exposure of material dyed with such a color base produces the original colored compound by oxidation.

Vehicle.—The liquid material holding and carrying the pigment and providing good workability on the press.

Viscosity.—Resistance to flow, *i.e.*, the tangential force on a unit area of either of two horizontal planes at a unit distance apart required to move one plane at unit velocity in reference to the other plane, the space between being filled with the viscous substance.

Washing Out.—The removal of the original greasy ink on the design areas of etched lithographic plates.

Web.—A roll of paper which passes continuously through a printing press.

Wetting Agent.—See **Dispersing Agent.**

White Spirit.—Low-boiling hydrocarbon distillate, usually of petroleum origin.

Winded.—The separation of printed sheets so that they will be ventilated by air.

Winterized Oils.—Oils (*e.g.*, fish oils) which have been stored in a cold place for a long time to allow the solid (*i.e.*, mostly saturated) components to settle out.

Woodcut.—A wooden printing plate the image of which has been left in relief by cutting away the background.

Wrinkling.—See **Gas Crazing.**

Xylography.—The art of printing with wooden blocks.

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