
PAINT AND VARNISH TECHNOLOGY

edited by

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Preface

The technology of organic protective coatings has progressed rapidly in recent years. Very little, however, has appeared in assembled printed form. A Division of Protective Coatings was established at Case Institute of Technology several years ago. A complete laboratory course as well as classroom instruction was started. The information required for the establishment of this type of work had to be obtained from a wide variety of technical journals and trade publications, and no textbook was available.

A lecture series under the title of "Paint and Varnish Technology" was sponsored, in which a rather complete coverage of the field was undertaken: the raw materials used were considered; principles of formulation were developed; specific kinds of formulations were introduced; and special problems were discussed. The lectures were then assembled in mimeographed form and distributed to those interested. Over a period of several years information in regard to the mimeographed compilation has spread, requests for copies are still being received from many sections of the United States as well as from foreign countries.

When it was decided to have a second series of lectures under the same title, it was felt advisable to edit the series and to make it available in printed form. Such is the origin of this book. It is the only one-volume book which covers the field from raw materials on through to formulations. It should be especially valuable to those who are interested in an introduction to the entire field, to those in technical schools who are concerned with coatings work, as well as to manufacturers and users of paints, varnishes, and lacquers.

WILLIAM VON FISCHER

Cleveland, Ohio
October 15, 1948

Contents

Chapter 1

Introduction to the Protective Coatings Industry

EDWARD SCHULTE

The Glidden Company, Cleveland, Ohio

Painting is older than writing. It began twenty thousand years ago, when the Stone Age man drew pictures with earth colors on the walls of caves in northern Spain and southern France. For to paint is to picture in colors. Even at that time there were painters who possessed the adroitness of hand and power of observation which enabled them to paint with amazing fidelity and spirit.

When the Egyptians added lime and glue to their colors, white chalk and charcoal, they made the first so-called water paints, known today as cold-water paints. These should not be confused with emulsion paints.

In a similar manner oil paints originated when the artists of the early centuries added drying oil to their colors. The literature is not definite in regard to date, but possibly painting with colors in oil is most correctly associated with the great painters of the Fifteenth Century. Up to that time pictures showed action and form, but not depth. The old masters, with a few strokes of the pencil, created solid forms with length, breadth and thickness, on flat surfaces; and with a few dabs of paint blended in harmony created sunlight and shadow, or the soft green of a quiet meadow, or made men and women appear realistically.

In brief, paint may be defined as a mixture of pigment with some suitable liquid, such as a drying oil, a varnish, or a water dispersion of glue or protein. When spread in thin films (generally 0.8 to 1.5 mils), these mixtures form a solid, adherent coating for decorative and protective purposes.

The date of the first incorporation of resin with oil is likewise indefinite. There are references to the use of resin with drying oil in the early centuries. Some mention is also made of driers. Even in the Eleventh Century a monk, Theophilus, describes the dissolving of molten resin in hot oil. In the Fifteenth Century, painters seemed to be familiar with both the oil-resin varnish and the spirit-type varnish. The latter consisted of a resin dissolved in solvent instead of oil. Possibly the best example of a spirit varnish today is shellac made by dissolving the shellac resin from India in alcohol.

The use of solvents with the oil-resin varnish also seems to have been known at this time. When resin is dissolved in oil, the mass becomes heavy and sticky, depending on the amount of resin added. In order to facilitate application, solvent is added to make the mass less viscous. Within recent years solvents have been replaced with water, forming emulsions. On application, the solvent or the water evaporates, leaving the resin-oil mass on the surface. Thus varnish may be defined as a liquid preparation which, when spread on a surface, dries by evaporation, oxidation or both, forming a hard, lustrous coating.

Japanese lacquer belongs in this classification, since it dries by oxidation. It is obtained as a sap from the *Rhus vernicifera* (varnish tree) and was a highly developed art during early Chinese life (400 A.D.). It may be considered the first phenolic varnish, since the main constituent of this sap is a poisonous liquid phenolic substance known as urushiol, to which the formula $C_{21}H_{32}O_2$ has been assigned. The term "lacquer," as commonly used today, refers to a solution of nitrocellulose in a suitable solvent to which plasticizers and resins may or may not have been added. Pigment can also be dispersed in this medium.

We have used the term "resins." Resins may be defined as any of various solid or semi-solid organic substances, chiefly of vegetable origin, amorphous and yellowish to brown, transparent or translucent, and soluble in ether-alcohol but not in water. Natural resins are those obtained from the sap of trees, either living or decayed. Synthetic resins are chemically made by man.

In tracing early history, it becomes apparent that the desire to color or to paint was inherent in all men. Color is of increasing importance today, as studies show the beneficial effect of harmony and beauty on man. As civilization advances and man spends more time indoors, not only color but light reflection is important. The lighting of many dark-colored rooms can be stepped up 30 to 40 per cent by the proper use of paint, resulting in less eye strain. Following are some light reflection readings on various colors:

White	90%
Light ivory	81
Cream	75
Buff	66
Light gray	66
Sky blue	52
Steel gray	43
Black	2

When Noah pitched his Ark he was applying a protective coat to the wood. The term "protective coatings" covers many different types of materials. For example, galvanized iron is a sheet of steel coated with a protective layer of zinc. The paint, varnish and lacquer industry is mainly concerned with organic coatings in which pigments may or may not be dispersed; in other words, it is concerned with the manufacture of paint, varnish and lacquer coatings which may be applied by brush, spray, dip or roller coat to all types of surfaces—wood, metal, brick, concrete, and stone—and air-dried or baked to form a protective film or coating.

The paint products sold to a manufacturer, for example, of automobiles, are generally applied by spraying or dipping, and are baked at various schedules. Such products are known as "industrial finishes" and are highly specialized. They are formulated to meet specific conditions of application and baking time, and have the required properties at a competitive price. For example, some automobiles require eight different products, each for a definite purpose; these are applied in three different ways and are baked on various schedules. They will be further discussed in Chapter 20.

The paint products for sale in hardware or paint stores are generally formulated to apply with a brush and air-dry to a solid film. These products are classed as "trade sales" products. They are developed to meet home requirements: sealers for porous surfaces, undercoats for enamel, flat wall, semi-gloss and enamels, and emulsion paints in many colors, as finish coats; stain and varnish to bring out and beautify the natural grain, and exterior paint for protection. They will be further discussed in Chapter 21.

Table 1. Organic Protective Coating Production in the United States.

Year	Population	*Paints	Varnishes	Enamels	Lacquers	Total
		Gallons per capita				
1899	74,700,000	0.58	0.21	0.03	—	0.82
1909	90,300,000	0.69	0.26	0.03	0.02	1.00
1919	104,300,000	0.94	0.36	0.01	0.05	1.36
1925	114,200,000	1.10	0.43	0.18	0.19	1.90
1929	121,000,000	1.18	0.47	0.20	0.38	2.23
1935	126,200,000	0.87	0.39	0.28	0.36	1.87
1939	129,700,000	0.99	0.47	0.33	0.40	2.19
1941**	131,400,000	1.26	0.58	0.51	0.61	2.96

* Water Paints Excluded
** Estimated

The art of making paint and varnish remained in the hands of the painter until the Civil War. In fact the first paint mill in this country was owned by a Boston painter named Thomas Child, around 1700. It consisted of a granite trough in which was placed an 18″ granite ball. The first paint mills used commercially were the buhrstone type. As the industry progressed, other types of mills came into use, such as the roller mill, pebble mill, steel ball mill, and dough mixers.

Possibly the greatest advance in the shortest period has been made by the paint, varnish and lacquer industry since World War I. The installation of mass-production schedules demanded quick-drying finishes. In the early 1900's it took from a week to ten days to finish a car, starting with primer, following with surfacer, glazing putty, ground coat and finishing coat, color coat and finishing varnishes. The installation of baking equipment reduced the time to two or three days. However, the introduction of lacquer revolutionized the industry. As soon as the solvents evaporated from the lacquer—a matter of not more than thirty minutes—the car could be recoated. No longer was it necessary to wait over night for the finishing varnish to dry. Not only did lacquer make mass production of automobiles possible, but it entered the furniture and other industrial fields also, until it seemed as if there would be no further use for varnish-type products.

Lacquer or nitrocellulose-type finish was made possible by the discovery of a way to reduce the viscosity of nitrocellulose solutions; consequently the lacquers could be sprayed at such concentrations that the resulting films were much thicker, and fewer coats were required. Even now the average furniture lacquer at spraying consistency is only 21 per cent solids (approximately), whereas varnish is 45 to 50 per cent solids. Thus it is easily seen that one coat of varnish gives practically the same film thickness as two coats of lacquer.

Table 2. Lacquer Production Since 1923.*

Year	Lacquer Production (millions of gallons)	Estimated Consumption of Nitrocellulose in Lacquer (millions of pounds)
1923	11.5†	5.8
1925	22.1†	11.0
1927	32.9†	15.8
1929	46.0†	21.6
1931	30.9†	13.5
1935	42.3	18.5
1937	56.8	26.8
1939	51.8	23.5
1941	79.3†	36.5

* Lacquer production includes thinners.
† Partly estimated.

With the introduction of phenolic and maleic resins about 1926 it was possible to make four-hour drying wood-oil varnishes, and varnish products regained some of the ground they had lost in some fields. However, lacquer enamels on cars still had greater durability and more chalk resistance than the quick-drying varnish-type enamel. It was not until the alkyd-type enamel—made by chemically combining phthalic anhydride, glycerin, and fatty acid—was marketed in about 1930, that the luster retention and durability of the nitrocellulose-type finish was surpassed. This alkyd-type finish had the additional advantage that the solids at spraying viscosity were higher than in lacquer, and two coats of alkyd enamel have the same "build" as four coats of lacquer. However, as the alkyd-type enamel required time to dry, baking ovens were installed. The Ford Motor Company was one of the first to finish their cars with alkyd-type synthetic enamel.

The use of alkyd vehicles in lacquers as plasticizers also improved their luster retention and helped increase the solids, so that the two finishes more nearly approached each other in durability and luster retention. The good appearance of the finish on the 1941 cars today after more than six years' use and exposure attest the excellent durability of the present synthetic type of motor-car finishes.

The story of the development of our present synthetic white finishes is similar. In 1925 the best white finish was produced with either pigmented white lacquer or pigmented white Damar varnish. Neither finish would stand much heat. With the introduction of alkyd vehicles it was possible to make white synthetic enamels which would bake to a hard, tough, flexible finish in one hour at 300°F. A few years later the introduction of urea-formaldehyde resin and the use of this resin with alkyd enamels made it possible to shorten the baking time to 30 minutes at 300°F. This type of finish replaced white lacquer on refrigerators.

The introduction of titanium dioxide in 1924 and subsequent improvements in 1940 also contributed to the production of high-hiding white finishes. This pigment has four to six times the hiding of the principal types of white pigment (lithopone, zinc oxide, white lead [carbonate and sulfate] and leaded zinc) in use at that time. More information on the various grades and types of titanium oxide is given in Chapter 5. Each pigment has a definite place in the industry.

Table 3. Comparison of Consumption of White Pigments.

Year	Production of Paints Enamels and Pigmented Lacquers	Consumption of Lead and Zinc Pigments	Estimated Consumption of Titanum Pigments	Total	Lbs. per gal.
	(Millions of gals.)	Millions of Pounds			
1921	92.5	513.2	—	513.2	5.55
1923	131.3	264.5	—	624.5	4.76
1925	153.5	735.4	—	735.4	4.79
1927	161.4	751.6	10.0	761.6	4.72
1929	184.0	794.3	37.8	832.1	4.52
1931	128.6	560.2	50.4	610.6	4.75
1935	158.8	575.8	105.0	680.8	4.29
1937	194.9	612.3	185.0	797.3	4.09
1939	185.2	584.2	252.0	836.5	4 52
1941	255.8	815.4	287.0	1102.4	4 31

Numerous other resins have appeared on the market such as chlorinated rubber, vinyl chloride-vinyl acetate copolymer, vinyl acetate, methyl acrylates, melamine, etc. Industry had progressed from the use of natural resins and rosin in oil varnishes to the use of highly complex synthetic polymers. To show the severe requirements paint and varnish industrial finishes must meet, following are some tests required of a baked refrigerator enamel:

Salt Spray: Scratch panel to bare metal and expose 200 hours to salt spray. No rust creepage.

Humidity: Expose panel to 100 per cent relative humidity. No blistering, pimpling, softening or rust formation in 1,000 hours.

Washability: Combined soap and abrasion test.

Cold Checking: Twenty cycles from 120°F to minus 5°F. No sign of checking.

Chemical Test: One per cent sodium hydroxide, 5 per cent acetic, 10 per cent citric, saturated cold solution of tea, coffee, milk, mustard, lard oil, butter.

Tests are then rated as follows:

Appearance	10%
Adhesion	5
Hardness	5
Thickness	3
Flexibility	5
Impact	5
Abrasion	5
Color	2
Color retention	3
Salt spray	10
Heat and humidity	10
Washability	5
Cold checking	3
Chemical stains	21
Heat resistance	3

To meet home and industrial demands requires a large number of different resins, oils, pigments and solvents. Some plants alone at the present time carry more than 600 active raw materials in order to make products which meet the trade's demands. The minimum number of varnishes carried by the average plant is probably not much less than 40, and possibly many more, if products are made to serve both trade sales and manufacturers' requirements. I hesitate to give the number of pigments required but estimate that 100 would be conservative. It is therefore quite important to know the different properties of the various raw materials in order to understand why they are used in formulations.

Thus it is seen that the paint and varnish industry covers a broad field, and that to meet this field it has made many different products and has grown to a far greater size than most people realize. Last year the paint, varnish and lacquer sales in this country amounted to approximately $800,000,000. The total net worth of the industry is between $350,000,000 and $400,000,000. Some idea of the growth of the industry may be gained from the following tables.

What does this mean? It means that this industry offers an excellent opportunity for progress. I well recall that one of the men, who had been connected with the dye industry for some time, transferred to the paint industry after World War I and on being questioned stated that the technical director of the dye company, an old established one, felt that

Table 4. Synthetic, Modified, and Natural Resins as Finally Used in Protective Coatings.

Year	Alkyd	Pure Phenolic	Urea	Coumarone	Ester Gum	Phenolic Modified Ester Gum	Maleic Modified Ester Gum	Rosin	Natural Resin	Total
					(millions of lbs.)					
1923	—	—	—	0.5	37.5	8.0	—	47.2	42.9	136.1
1924	—	—	—	.5	36.0	9.1	—	48.6	32.5	126.7
1925	—	—	—	.5	36.0	10.0	—	51.5	40.8	138.8
1926	—	—	—	.5	42.7	11.4	—	40.1	41.0	135.7
1927	1.0	—	—	.5	45.0	14.2	—	39.3	51.6	151.6
1928	4.0	—	—	.5	42.0	18.2	—	45.9	49.4	160.0
1929	5.0	—	—	.5	36.0	31.0	—	57.6	46.5	176.6
1930	12.0	—	—	.5	18.8	21.0	—	44.9	26.2	123.4
1931	7.3	—	—	.5	13.9	24.5	—	31.2	21.5	98.9
1932	11.4	—	0.2	1.0	11.3	17.1	—	25.5	14.6	81.1
1933	9.9	—	.4	1.0	12.0	36.0	—	29.1	22.7	111.1
1934	15.4	—	.5	1.0	13.7	55.0	0.8	14.1	18.4	118.9
1935	35.0	—	.5	1.5	16.4	77.2	4.6	33.6	27.5	196.3
1936	46.7	1.4	1.0	1.5	18.8	72.1	5.1	18.6	27.7	192.9
1937	59.9	4.2	1.5	2.0	19.2	67.8	12.6	18.2	33.8	219.2
1938	38.8	1.4	1.0	2.0	18.0	63.4	15.3	16.9	21.2	178.0
1939	72.5	7.3	2.5	2.0	21.2	68.0	27.4	18.8	31.2	250.9
1940	94.0	8.8	3.0	2.0	21.8	63.7	28.5	20.8	40.4	283.0
1941	131.7	33.7	6.0	3.0	22.5	97.7	42.8	42.5	43.0	422.9

Table 5. Consumption of Drying Oils by the Paint, Varnish, and Lacquer Industry.

Year	Total Linseed Oil	Tung	Perilla	Fish	Soybean	Castor	Oiticica	Total all Oils Other than Linseed	Drying Oil
					(millions of lbs.)				
1899	258.3	2.6	—	—	—	—	—	2.6	260.9
1904	357.1	9.2	—	—	—	—	—	9.2	366.3
1909	352.2	19.0	—	—	—	—	—	19.0	371.2
1914	410.8	27.0	—	—	—	—	—	27.0	437.8
1919	385.8	46.2	4.7	—	20.0	—	—	70.9	456.7
1921	429.9	33.8	0.6	—	—	—	—	34.4	464.3
1923	565.0	74.0	6.4	—	6.6	—	—	87.0	652.0
1925	604.1	78.0	6.0	9.2	3.4	—	—	96.6	700.7
1927	635.5	76.0	5.4	9.1	2.3	—	—	92.8	728.3
1929	672.5	91.0	5.6	10.8	2.3	—	—	109.7	782.2
1931	411.6	81.7	10.5	12.1	6.3	1.8	0.3	112.7	524.3
1933	332.0	88.9	18.9	8.8	8.6	2.0	1.3	128.5	460.5
1935	409.0	116.7	49.8	18.3	13.0	3.5	1.9	203.2	612.2
1937	482.3	133.5	29.0	27.3	16.1	7.2	3.6	216.7	699.0
1939	463.3	97.2	38.3	25.0	21.7	11.4	17.5	211.1	674.4
1941	650.5	64.9	7.0	40.7	41.6	44.2	35.8	234.2	884.7

Table 6. Value of Materials Consumed in the Manufacture of Protective Coatings.

	1935	1937	1939
		(millions of dollars)	
Pigments	54.8	70.3	70.3
Drying oils	46.8	56.8	53.9
Resins	24.6	31.4	36.7
Solvents and thinners	22.6	25.1	21.1
Nitrocellulose	4.3	6.0	5.0
Shellac	4.6	4.9	4.4
Driers	3.2	3.9	3.7
Lacquer plasticizers	2.2	2.4	2.7
Casein	0.4	0.6	0.6
Miscellaneous	4.9	26.1	14.2
Total value of all materials consumed in manufacture of protective coatings	168.4	227.5	212.6

Table 7. Organic Protective Coating Sales.

Year (First eleven months)	Total Sales Reported by 680 Establishments	Trade Sales of Paint, Varnish and Lacquer
1946	$723,860,518	$388,552,945
1945	601,043,828	285,927,093
1944	574,333,153	274,656,694
1943	527,548,557	248,660,084
1942	492,604,211	243,872,329
1941	513,690,393	257,507,747
1940	384,207,659	201,635,065
1939	367,698,426	201,062,115
1938	326,400,788	186,078,135
1937	399,755,254	206,779,802
1936	367,538,406	189,146,362

Table 8. Volume of Production.

In 1899, about 60,000,000 gallons of protective coatings were produced; in 1941, production had grown to about 400,000,000 gallons.

Production per capita increased from 0.82 gallon in 1899 to 2.96 gallons in 1941.

The following table shows the production of the principal types of products on a per capita basis:

Year	Population	*Paints	Varnishes	Enamels	Lacquers	Total
				(Gallons per capita)		
1899	74,700,000	0.58	0.21	0.03	—	0.82
1909	90,300,000	.69	.26	.03	0.02	1.00
1919	104,300,000	.94	.36	.01	.05	1.36
1925	114,200,000	1.10	.43	.18	.19	1.90
1929	121,000,000	1.18	.47	.20	.38	2.23
1935	126,200,000	0.87	.39	.28	.36	1.87
1939	129,700,000	.99	.47	.33	.40	2.19
1941**	131,400,000	1.26	.58	.51	.61	2.96

* Water Paints Excluded
** Estimated

The value of the products of all industries in the chemical and allied products group in 1939 was $3,733,657,000.

The value of the products of the Paint, Varnish, and Lacquer Industry in that year was $434,960,000, or 12 per cent of this total.

The value of the products of the Paint, Varnish, and Lacquer Industry was greater than that of any other industry in this group in 1939.

The following table shows a comparison of several of the chemical industries.

Table 9. Comparison with Chemical Industries (1939)

	No. of Establishments	Salaried Personnel and Wage Earners	Value of Products (thousands of dollars)
Total chemical group	9,203	350,245	$3,733,657
Paint, varnish, & lacquer	1,166	38,154	434,960
Color and pigments	89	8,018	83,885
Drugs and medicines	1,094	40,392	364,985
Explosives	80	8,315	71,053
Plastic materials	38	10,080	77,653
Printing ink	206	4,376	49,131
Gum naval stores (processing)	755	1,892	17,361
Soap and glycerin	264	20,191	302,634
Wood naval stores	25	2,924	14,114
Refrigerators—Air-Conditioning	—	—	278,600
Stoves	—	—	223,400
Radio	—	—	275,900
Rubber tires and tubes	—	—	580,000

the paint industry offered more opportunity for advancement. The same holds true today. In the early 1920's there were very few chemists in this industry when it was in the process of changing from an art to a science. Now for every 1,000 chemists employed, 41 are in the paint, varnish and lacquer industry.

The introduction of lacquer started the revolution and the introduction of the alkyd resins established the industry as a truly chemical industry. In only three other industries—industrial chemicals, petroleum refining, drugs and pharmaceuticals—are larger proportions of chemists employed. Rubber, plastics, food, etc., all lag in utilizing the services of chemists. According to records, 40 per cent of paint chemists are engaged in research. However, this is not the only opportunity for advancement. The highly specialized industrial activities of the country require trained people who have the "know-how" of application to act as technical service men and salesmen to these concerns. The manufacturers of specialized products require supervisors who have technical background; they can no longer depend on the old varnish-makers' trick of dropping water into the kettle to determine the temperature. No longer does the industry depend solely on vegetable oils and resins obtained from the ground or sap of trees. These can be made synthetically. No longer do we solely look at a film and think in terms of oil length or pounds of resin per gallon of oil. We are interested in film properties, such as elasticity, flexibility, adhesion, and durability. From these properties we determine the correct chemical combination to use.

Many of the new resins in coating materials have been on the market less than twenty years. Every war accentuates industrial progress. We have seen the results of World War I, the change from varnishes to lacquer and synthetics. The next ten years, who knows? Therein lies the challenge to each of us.

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Chapter 2

Drying Oils: Their Origin, Manufacture and Properties

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The Archer-Daniels-Midland Company, Minneapolis, Minnesota

General History

In the commercial world a number of vegetable oils are known at the present time. In the raw state and without the aid of chemicals, these are capable of absorbing the oxygen of the air to a greater or less degree and becoming solid. They are commonly called "drying oils." By far the most valuable to commerce, both as to usage and results obtained, is linseed oil. Although many of the oils known to the industry today have been developed only in comparatively recent years, linseed oil and many others bear the hallmark of great antiquity, some having been discovered before the Christian era.

The history of these oils begins with that primitive impulse of man to make use of color. Archeologists have found cave drawings done with natural pigments on rocks before the last ice age. As early as the 18th century B.C., techniques far from crude had been developed in both Europe and Africa. The ancient Japanese, Chinese and East Indians had also developed interesting techniques using colored pencils for decorative purposes as early as 4000 B.C. From these early desires on the part of man to decorate his surroundings and to convey some sort of intelligence from one person to another, or from one generation to another, has developed the modern protective coatings industry. As knowledge of protective coatings increased, so did the needs or fields of use, until today organic protective coatings are used for one or more of four purposes: for decoration, for protection of structural materials, for sanitation, and for better light distribution.

During the early Egyptian period the dry climate of that part of the world did not serve as a stimulus for the development of durable protective coatings. Although drying oils were known and flax was cultivated for its fiber, there is little if any evidence that these oils were used in paints.

The fact that early Egyptian art treasures were sealed in caves did not create a critical need for lasting paints such as we now have.

During the classical period the materials used by the Greeks and Romans were similar to those employed by the Egyptians. Weak glues, egg albumin and honey were used as binders. Pitch was used during this period for tarring ships, and pitch and wax for protecting ships' bottoms. Resins and oils were used only for therapeutic purposes, and no mention was made of varnishes in any of the writings of this age.

Oriental mediums included such things as shellac, sealing wax, gum arabic, and natural tree saps. As early as the 7th century a tax was placed on the sap from the *rhus vernicifera* (varnish tree) by the Japanese. This sap was used in waterproofing drinking vessels and for coating armor and leather.

Early American Indians used salmon eggs, both fresh and dried, for vehicles. The vehicle was prepared by chewing the eggs with bark of the red cedar. Mountain goat fat was used for vehicles in preparing face paints, and in all the finest paintings the whites of pheasant eggs were added to the paint. Many of these paintings had excellent durability.

During medieval times in Europe, manuscripts giving information on paints and varnish materials were plentiful. These are available in many libraries. Aetuis, a medical writer of the 6th century, was one of the first to suggest the use of oil for varnish, while Theophilus, a monk of the 11th century, gave the first description for preparing an oil-varnish by incorporating molten resin in the hot oil. As late as the 14th century, however, egg albumin was still the traditional medium of the leading artists of the day.

After the Renaissance greater interest was shown in oils. The use of linseed oil in preparing rosin, amber and sandarac (gum of juniper) varnishes increased rapidly. The great artists of the day (Rembrandt, Leonardo da Vinci, Jan Van Eyck, etc.) used either oleoresinous vehicles, or as some believe, painted with egg-yolk emulsions and then employed an oil varnish glaze as a finish. Varnishes were applied with a sponge to crossbows, armor and other weapons, indicating increased usage in the protective coatings field. The use of driers in paints and of thinners in paints and varnishes was first mentioned as having a practical value. Driers were thought to be dehydrating agents. The bleaching of oil and its purification by boiling with water were practiced.

Watin, in 1773, was the first to describe the paint and varnish industry as we know it today. Copals and amber were the principal resins employed at the time of the American Revolution. The resins and oils were sweated before mixing, for purification. Linseed oil, walnut oil, hempseed oil, and poppyseed oil were used at this time and turpentine acted as the thinner. However, the industry still remained more or less in its infancy until the turn of this century.

Watin's book on varnish formulas was considered the varnish maker's standard until about 1900; yet it was reprinted, with but a few minor changes, only fourteen times between 1736 and 1900. The varnish and paint industry remained strictly an art, and few manufacturers could see why science should meddle in the field. Hence, progress at the beginning of the 20th century was naturally slow, and each new idea bordered on producing a major revolution in the industry. Gradually, new materials and scientific methods were introduced and shortly after 1900, progress became exceedingly rapid. Huge factories to manufacture the products and well equipped laboratories and pilot plants have been built, and continue to be built. New and better products are being conceived and synthesized at an increased rate. Skillful merchandising and capable servicing of products is the rule. Whereas in the past, the paint and varnish industry had necessarily been classed as an art, the innovation of new kinds of devices, the careful selection and control of raw materials, the application of a great number of fundamental and scientific principles, and the close control of finished products make the paint and varnish industries now much less an art and more a practiced science of far-reaching importance.

Types of Drying Oils

Although literally hundreds of oil-bearing seeds, nuts, plants in general, fish and animals have been tried and sometimes used as sources of drying oils, only a few of the more important sources will be mentioned here.

Until about 1850, the cultivation of flax in the United States was practiced with a view to the utilization of the fiber. The seed was a waste product, or at best, a by-product. Since that time, this condition has been wholly changed. The fiber is now the by-product, whereas the seed has become practically the sole object of cultivation. From it are produced linseed oil and linseed oil meal. The latter is consumed almost in its entirety in feeds for livestock, although smaller amounts find application in a few minor industrial uses.

Linseed oil has been the most important raw material for paint and varnish since the early ages, and it continues to be one of the most important in the industry; for example, in 1945, 322,052,000 pounds, or 67.9 per cent of all oils used in the paint and varnish industry, was linseed oil. The linoleum industry is the second largest user of linseed oil, while the printing-ink industry is third in consumptioñ of this important drying oil.

Linseed oil is obtained from the seeds of the common flax plant, *linum usitatissimum,* which is grown extensively in Argentina, Canada, India, Russia and the United States. It is also grown in many other countries and small amounts are imported annually from Mexico, Uruguay, and Paraguay. The oil content of flaxseed varies from 32 to 43 per cent; the iodine number from 170 to 190. The quantity and quality of the oil depends on the variety of seed grown and upon the climatic conditions that exist.

Linseed oil is probably the most versatile of the drying oils which are available in large quantities. It is the "standard" for house paints and also makes excellent varnishes either alone, or in conjunction with other drying oils, especially tung and oiticica oils. Its chief disadvantage in varnishes lies in its yellowing tendencies and its somewhat slow drying properties. Linseed oil is the only oil that has successfully satisfied all the requirements of oil painting.

Up to 1942, over half of the linseed oil was imported as flaxseed, principally from Argentina. Although domestic production of linseed oil has increased markedly in the years following 1942, the amount of flaxseed imported has dropped to a figure considerably less than half of that shown for that year. As the imports of the oil itself have increased only slightly, it is seen that the attempt to make the United States less dependent on foreign sources in times of emergency is being rapidly achieved in this field.

Next in importance from a tonnage standpoint is dehydrated castor oil. During 1945, 44,245,000 pounds, or 9.3 per cent, of all oil used in the paint and varnish industry was dehydrated castor oil. Another 7,703,000 pounds of *crude* castor oil, or 1.6 per cent of the total, was used in this industry, mainly as a plasticizer.

Castor oil obtained from the seeds of the plant *ricinus communis* is not a drying oil in its natural state, having an iodine value of from 81 to 91. It can be converted into an oil possessing a doubly conjugated system of unsaturated linkages by dehydration. The oil is heated in the presence of catalysts and preferably under vacuum to remove water, thus producing an oil with good drying properties having an iodine value of approximately 141 to 145. This fact has been known for some time, but it was only during World War II that dehydrated castor oil became of great importance due to the scarcity of tung oil.

Dehydrated castor oil is an excellent drying oil. It is very flexible and has extremely good color and color retention characteristics. It is much faster than linseed oil in kettling speed, but has a tendency to retain or develop tack on drying. This can be overcome, however, in varnish processing.

Of third importance in the paint and varnish industries is fish oil. Obtained chiefly from sardines, menhaden, pilchard and herring, this oil was consumed to the extent of 42,949,000 pounds, or 9.0 per cent of the total, during 1945.

These oils have been used extensively for cheap paints where soft films and after-tack are not undesirable. Due to their very high percentage of certain acids, fish oils usually have an undesirable odor. To be suitable for a drying oil, the oil must be refined in some manner in order to remove the saturated acids. This is often accomplished by refrigeration, and the so-called "winterized" oils remain clear at low temperature and have high iodine numbers (about 190 to 200). The full potentialities of fish oil have not yet been realized, and a research program which it is hoped will continue to improve the qualities of fish oil is now well under way.

Fish oils, nevertheless, have a tendency to develop after-tack. Hence, outside of the low-cost paint field, these oils find their greatest usefulness in conjunction with better surface drying oils, such as tung or perilla. Fish oils are generally believed to have greater elasticity than linseed, but this has not always been borne out in work with various types of varnishes and paints.

During the war the bulk of the soybean crop and the oil derived therefrom was diverted to the edible oil industry. In spite of this, soybean oil was of fourth importance from a tonnage standpoint in the paint and varnish industry, and 25,624,000 pounds of it were used in 1945. This represented about 5.4 per cent of the total oil used in this industry. Developments during the war and increased efforts at this time are responsible for a large number of new and useful soybean oil vehicles for the paint and varnish industries, and consumption of soybean oil in this field is definitely and rapidly on the rise.

Soybean oil is obtained from the seeds of the legume, *soja max,* which is native to China and Manchuria, but is cultivated widely in Africa, Australia, Europe, India and the United States. In the United States alone, the crop has increased 1000 times since a modest 4500 acres of soybeans were planted in 1922.

As indicated by its lower iodine number (around 135) the oil is slower-drying than linseed oil and generally is used with tung, perilla or linseed oil to overcome this fault.

Soya oil has excellent flexibility and non-yellowing properties. It is a good modifying oil for the manufacture of alkyds. Refining developments, showing great promise, have been under way for some time, and refined soybean oils of higher iodine number and drying times comparable to those of linseed oil should be on the market in the near future. The soybean contains about 16 to 20 per cent of oil; the remainder is being widely used as a feed as well as for a very large number of important industrial products.

Of next importance is the oil from the tung nut, often referred to as chinawood oil. The principal source of tung nuts has been China, although in recent years there have been wide-spread attempts to cultivate the tung tree in other parts of the globe, with some success. The United States produces, domestically, about 10,000,000 pounds of tung oil annually, but the world is still largely dependent on China for its supply. Imports of tung oil during the war were reduced drastically, however, and attempts had to be made to find substitutes for it in the paint and varnish industry. Whereas tung oil must still be considered the best all-purpose varnish oil, the necessary development of specialty oils from such oils as linseed, dehydrated castor, oiticica and others has convinced a skeptical industry of the frequent superiority of these products for specific use in the protective coatings industry.

Tung oil is obtained from the nuts of the tree *aleurites fordii,* and differs from all other vegetable oils with the exception of oiticica oil, in that it contains conjugated double bonds which account for the characteristic water-proofness, fast-drying and durability which it imparts to varnishes. It was for this reason that tung oil sold for a considerable premium over other drying oils for some years prior to the war. The kernel of the tung nut contains about 50 per cent of oil.

Tung oil is known for its extremely rapid bodying characteristics, durability and chemical resistances in varnishes. It is one of the few oils that will make quality varnishes with rosin. Tung oil is usually used in conjunction with some other, less reactive oil such as linseed or soya in order to control viscosities when kettling. It cannot be used in the raw state because it will dry with a "matte" or shriveled appearance. This is utilized in specialty finishes such as wrinkle and crystallizing finishes.

Of next importance in recent years is oiticica oil, imported principally from Brazil. During 1945, 13,128,000 pounds or 2.8 per cent of the total drying oil used in the paint and varnish industry was oiticica oil. This was an increase of 10,460,000 pounds over the amount used two years earlier; prior to that time, this oil was considered of only minor importance. The rapid increase in its use in the last few years has overcome in no small way the war-produced shortage of tung oil.

Oiticica oil is obtained from the nut of the oiticica tree, *licania rigida.* The tree grows over a wide area in the northern part of Brazil, and most of their annual crop is exported to this country. Oiticica oil resembles tung oil in that it contains a triply conjugated, unsaturated fatty acid. This acid differs, however, from the eleostearic acid of tung oil in that it also contains a keto group. Known as licanic acid, it is present to the extent of 78.2 per cent in oiticica oil. The fruit of the oiticica tree contains about 60 to 62 per cent kernels, of which 60 to 65 per cent is oil.

Oiticica oil is very similar to tung oil, but not quite as good. It tends to give brittle films when processed at temperatures above 560°F.

Reports for the first three quarters of 1946 show a steady and significant increase in the use of oiticica oil in varnishes and enamels.

Perilla oil, imported in large quantities a few years ago, has also suffered a set-back due to the curtailment of shipping during the war. In 1945, only 161,000 pounds, or a fraction of 1 per cent, was used in the paint and varnish industry. A continued decrease in the use of perilla oil reported in the first three quarters of 1946 make it appear that perilla, like tung oil, has lost at least some of its popularity due to the large number of specialized oils developed during the war from domestically produced drying oils.

Perilla oil is obtained from the seeds of the plant *perilla ocymoides,* cultivated in India, Korea, Japan and China. The oil content of the perilla seeds obtained from different sources will vary from 35 to 45 per cent, with an average of about 38 per cent. Attempts have been made to cultivate perilla seed in other parts of the world, including the United States, but without much success. The chief difficulty is in harvesting the seed before it is lost by falling to the ground, which it does after maturity is reached. The trouble lies in the fact that all the seeds do not mature at the same time.

Perilla oil has an iodine number of about 185 to 205, highest of all the drying oils, and is faster-bodying and faster-drying than linseed oil. Its higher linolenic acid content causes more yellowing and more brittle films than with linseed oil.

Although perilla oil sets slightly more slowly than does linseed oil, it dries to a harder film. It can be blended with soya oil to produce an oil very similar to linseed. Perilla should be given some kind of heat treatment before it is used in any manner, as the raw oil tends to crawl. Although the raw oil has a tendency to yellow more than linseed oil, heat-treated perilla oil has no more tendency to yellow than does linseed oil.

Several minor drying oils are consumed in varying quantities. A partial listing of the more important of these would include the following oils.

Chia oil is obtained from the seed of the plant *salvia hispanica.* It is cultivated in Mexico, where it is used chiefly for making a beverage rather than for oil. The seeds contain about 34 per cent of an oil having an iodine number of around 200, which is similar in properties to perilla oil.

Hempseed oil is obtained from the seed of the plant *cannabis sativa,* which is chiefly cultivated for its fiber, but which is also cultivated for its seed in China, India, Russia and Europe. The seeds contain 32 to 35 per cent of an oil having an iodine number of about 160. Although the iodine value is lower than that of linseed oil it dries fairly well and makes an excellent substitute in outside house paints from a durability standpoint. Slower-bodying than linseed oil, its bodied oil properties are somewhat similar.

Poppyseed oil is obtained from the seed of the plant *papaver somniferum,* cultivated in Europe, China, India, and many other places. The oil has an iodine number of about 140, and because of its non-yellowing properties, would probably be used in much larger quantities if it were available. Poppyseed oil is similar to, but has better drying characteristics than, soya oil. Artists use it because it is non-yellowing and will not crack on canvas.

Safflower oil is obtained from the seed of *corthamus tinctorious,* a plant cultivated in India, Egypt, Turkestan and parts of Europe. In India the oil is used principally for edible purposes and as a soap oil. Some attempts have been made to grow it on the northern great plains of the United States, and results have looked very promising. The safflower is a hardy plant which readily withstands wind, hail, frost, and drought. The seeds contain 24 to 36 per cent of an oil having an iodine number of about 150. Like poppyseed oil, much more of it could probably be used because of its non-yellowing properties if it were available. Safflower oil is similar to, but has better drying properties than, soya oil.

Sunflower-seed oil is obtained from seeds of the plant *helianthus annus,* believed to be indigenous to Mexico but cultivated in Russia, China, India, Argentina and the United States. Russia is by far the largest producer of the oil. In the United States the seeds are used largely for feed. These seeds contain 22 to 32 per cent of an oil having an iodine number of about 130, and the drying properties are very similar to those of soybean oil.

Walnut oil is obtained from the nut of the tree *juglans regia,* grown extensively in Europe, China, the United States, and elsewhere. The kernels contain 60 to 70 per cent of an oil having an iodine number of about 150. More of it undoubtedly would be used if the supply were more certain. Walnut oil is a good drying oil but is slower than linseed oil. The oil is non-yellowing and gives softer films than linseed oil. It is used chiefly as an enamel oil.

Manufacturing and Refining Methods

Probably the first commercial attempts to extract oil from oil-bearing seeds and plants consisted of crushing the seeds between heavy stones, first operated by hand and then powered by oxen or other work animals. The crushed meal was then boiled up with water and the oil skimmed from the surface of the water. One of the very early means used by the Chinese in extracting oil from the tung nut consisted of filling a hollow log with crushed tung nuts separated by wooden spacers. Wooden wedges were then driven between adjacent spacers providing the necessary pressure for squeezing a small amount of oil from the nuts. These crude methods, altered but slightly, are still practised in some parts of China and India.

The earliest method recorded for the production of *linseed oil* is a recipe by Theophilus, previously mentioned; it is particularly interesting to find that the treatment of the seed or method was almost the same as it is today: "Take linseed and dry it in a pan, without water, on the fire; put it in a mortar and pound it to a fine powder; then replace it in the pan, and pouring a little water on it, make it quite hot. Afterward, wrap it in a piece of new linen, place it in a press used for extracting the oil of olives, of walnuts, or of the poppy, and express it in the same manner." It can be seen from this early report that the seed was subjected to four operations: drying, crushing, cooking and pressing. With the exception of drying, which is not necessary, the operations involved today are the same.

In early European times the amount of linseed oil required was produced by the artist in small quantities, often in his own studio. As the oil found enlarged fields of usefulness, the crudest of mechanical apparatus was devised for its manufacture. Little is known of the extraction of oils in the time interval between the universal use of such equipment and the advent of more modern devices, *e.g.*, the hydraulic pressure units, which appeared over a century ago. Indeed, up to a comparatively few years ago, the invention and improvement of linseed oil machinery had been slow. Manufacturers in the United States are given credit for the greater part of the advancement made in the last 100 years.

In making linseed oil there are two very essential steps which must be watched; the first is the crushing or grinding of the seed; the second is the cooking or "tempering" of the ground seed. In the proper manipulation of these two processes rests the crusher's ability to make a good yield of oil. We find, in fact, in the early days that many times the ground seed was pressed entirely without cooking. Oil made in this manner was called "cold-pressed" oil and was beautifully light in color. Owing to the small yield of oil in the cold process, however, the cost is excessive and very little is now made.

The first attempt to manufacture linseed oil in quantities was by the ancient screw and lever press, a modification of the old cider press. After pressing, considerable oil remained in the dry residue, known as the oil cake. These cakes weighed about 25 pounds each and were about 18 inches in diameter and 8 inches thick, resembling a cheese in shape. Hence the press was known as a "cheese box" press.

The "cheese box" presses were retained in use as late as 1848. Some years before this, however, the improved Dutch mill or wedge press, imported from Holland, came into vogue. This was a great improvement over the old screw press and consisted of a heavy rectangular framework of oak or iron, placed horizontally on its base. The ground seed was shoveled by hand into woolen bags and these were hung vertically between hinged partitions, consisting of wooden plates. The pressure needed for the expression of the oil was obtained by driving wooden wedges between the plates by means of sledges driven by wind or water power. These presses were still in use in 1853.

The next logical and undoubtedly the most important step in the advancement of the industry was the introduction of horizontal hydraulic presses shortly after the War of 1812. In these, the plates were movable and were made of iron instead of wood. The ground seed was shoveled into woolen bags as before, molded by patting with the hands and placed in mats of horsehair. These were then placed vertically between the plates of the press and hydraulic pressure applied. The yield was increased tremendously by this process.

Horizontal presses had their disadvantages, however, and in 1851 the first patents on vertical hydraulic presses were granted to Edwin Halls. Although the capacity was not increased at first, the clumsy and unwieldy manner of packing the meal in the bags and filling the horizontal presses was eliminated. The ground seed was molded into soft cakes by hand, then packed in woolen bags, and placed in the press, one above the other, the plates of the press acting as shelves. A large saving was made in time and labor, resulting in a considerable increase in the daily capacity and a consequent reduction in cost.

With improvements in pressing came improvements in grinding and tempering. The earliest method of reducing the seed to meal was by use of a tamper mill. This was a mortar and pestle on a large scale. Although several tampers were run simultaneously, their small capacity slowed the mill operation and rolls run by machinery were soon introduced. These first rolls were arranged in pairs and were designated by the trade as "cracker" rolls, because they cracked or opened the seeds. After being bruised in these rolls, the seed was placed in an "edgerunner," also known as a "muller." This consisted of a circular trench of iron, several feet in diameter, placed horizontally on a firm foundation. Running around this, like wagon wheels in a rut, were two ponderous iron-shod wheels, 5 to 6 feet in diameter with steel rims 10 to 16 inches wide. Water was added and the meal acquired the consistency of putty or what was termed "dobby." It was then mixed or "mulled" for 10 or 15 minutes and then tempered with heat. The muller stones were very satisfactory as to results, but were clumsy and heavy and required a great deal of power.

The tempering or cooking of the crushed seed has a very important effect on the yield of the oil and has undergone many changes. There was a considerable variation in the temperature used, from cold to hot, according to the whims of the manufacturer. Often the spontaneous heat of the crushing was considered sufficient. Later, however, regular cookers began to be used; these were heavy iron drums or tanks slowly revolving over a charcoal fire. With the advent of the hydraulic presses improvements were made in cooking devices, and stationary heaters began to be used in which the meal was cooked by steam.

In 1856 a device called a "molder" was patented to form the cooked meal into soft cakes preparatory to placing them in camel's hair wrappers which, because of their resistance to heating, had replaced the woolen or horsehair bags formerly used. Although somewhat clumsy at first, the "molder" or "former" was improved until today it is a miniature press where a hydraulic tamper presses the required amount of meal into a square cake, which is then wrapped and placed with great ease onto a plate of the press. The plate press had been given preference over the old box press, which was rather clumsy.

For many years crushers had endeavored to find a substitute for the hydraulic press, necessarily intermittent in its action. The first practical mechanical press for the continuous extraction of linseed oil was built in 1904 by the V. D. Anderson Company of Cleveland. Many improvements have been made since by the various companies pioneering in this type of equipment. The operation of these mechanical presses or "expellers" is continuous and automatic. The pressing of the seed is performed in a perforated hardened steel cylinder, in which revolves a shaft carrying one or more hardened steel screws so arranged as to exert a gradually increasing pressure. The oil is expelled through the perforations and the pressed cake is discharged at the end of the cylinder.

Although improvements in oil expelling and refining have been made, they have in most cases resulted rather in a greater economy than in a greater yield. The mode of operation today in a large and completely modern mill using both the hydraulic and expeller type systems would probably be as follows:

After the flax has been harvested and threshed and the seed received in carload lots at the mill, it is run by bucket conveyor to any one of a large number of concrete storage tanks. Flax taken for immediate processing is first cleaned by passing the seeds over a series of shaking screens. (This operation may be done in some instances prior to the initial storage of the flax seed as received at the mill). Chaff and fine particles are blown off; husks, stalks, or large foreign particles are retained on the coarse screen; flax seeds are taken off the second screen, and broken pieces of flax seed pass through and are removed at the bottom of the cleaner. This thorough cleansing reduces the "dirt" (originally 10 to 20 per cent) to less than 1 per cent. The flax is then temporarily stored in a huge bin.

A bucket elevator removing the flax from the bin dumps it into a weighing device which automatically weighs and records each bushel of flax as it passes through. The flax seed is conveyed to the top of a 3 to 5 high roller grinder where it drops on a fluted feeder roll and is evenly distributed over the top of the series of grinding rolls. After being thoroughly ground the seed drops into a conveyor which delivers it to the top of the cookers.

The cookers consist of large cylindrical steam-jacketed tanks containing a series of horizontal, circular plates evenly spaced and fastened to the inside of the cooker. Scraper arms fastened to a centrally rotating shaft wipe the top surface of each plate clean, discharging the meal through suitably arranged openings to the next lower plate. In this way the meal is gradually dropped through the cooker until it is discharged from the bottom. Jacket and live steam are used to heat and moisten the meal in a process known as "tempering." The temperature of the meal is thus increased until it reaches the bottom of the cooker, at which time it is about 190 to 200°F. The moisture content and temperature of the meal at this point is extremely important, the whole operation being undertaken to facilitate the economical expression of quality oil.

If the tempered meal is to be processed in expeller equipment it is conveyed to a screw type feeder which moves the meal to the intake end of the expeller. The expeller proper is a long, cylindrical, hardened-steel block with a tapered bore. The bore is fitted with one or more screws in such a way as to provide maximum space at the intake end of the expeller. This spacing is so reduced that the flax seed is gradually squeezed as it is forced through the expeller, forcing out the oil, which drains out through fine grooves and perforations in the expeller core. The perforations will not pass any appreciable amount of meal particles, which are moved along and finally emitted at the discharge end of the expeller as flaxseed oil meal. This meal contains about 4 per cent of oil and is passed through a series of hammer mills where it is ground to specifications. It is then bagged and sold principally as animal feed.

The oil from the expellers is dropped through a coarse screen into preliminary settling tanks. Here any sludge settling out, called "foots," is recovered and returned to the system to be added to incoming ground and tempered flaxseed and rerun.

The oil from the settling tank is passed through a filter where the remaining suspended materials are removed. No filter aids are used in this filtering operation and the temperature of the oil has now dropped to approximately 180°F. The clear, raw linseed oil is then pumped to storage tanks and the oil is now ready for the refining operations.

If the ground, tempered flax is to be processed by hydraulic equipment it is conveyed from the cookers to the feed hopper of the "former." Here the correct amount of meal is automatically discharged into a mold where it is hydraulically compressed into a square cake. It is wrapped in a camel's hair mat and placed by hand between a pair of plates in a vertical, multiple plate, hydraulic press. When the press is filled, it is closed and sufficient pressure is applied to squeeze the oil out of the meal. The oil flows out of the press through the hair mat, which acts as a filter, and through grooves cut in the face of the press plates. Pressure is applied for about one hour and has been increased to about 4,000 psi at the end of this hour.

The oil meal cake is then unwrapped and sent through a set of cutters which trim off the oil-soaked edges of the cake. These trimmings are returned to the cookers to be mixed with incoming ground and tempered flaxseed, and rerun. The rest of the cake is conveyed to hammer mills where it is ground to specifications, bagged, and sold as feed.

The oil from the hydraulic press is then filtered and as in the case of the expeller oil is stored prior to the refining operation.

The linseed oil reaches the storage tanks from the expellers or hydraulic presses at about 170 to 180°F. On cooling, additional waxes and other substances, chiefly phosphatides, separate out and for the most part remain suspended in the oil. This oil is then fed to agitated tanks where a filter aid (diatomaceous earth) is added. The oil is then passed through the filter for the second time where the suspended material mentioned is removed. The "first" and "second" filtration constitute the so-called "double filtration process."

Oil from the second filtering operation is weighed into the refining kettle from a scale tank. The refining kettle is equipped with agitator, heating coils and a means of evacuating the kettle. Any number of operations can be performed; and while one, all or a combination of them may be undertaken, they will be described in the following logical sequence.

Ten per cent caustic soda solution is added, to give about 2 to 3 per cent caustic on an oil weight basis. The temperature is maintained at 60°F and the mixture is agitated. Soaps are formed and a large percentage of them are sludged out and removed at the bottom of the refining kettle.

The oil is then washed with clear water to remove the remaining soaps and excess caustic, and a vacuum is drawn to remove retained water.

Bleaching clay is then added to remove undesirable color and to produce the familiar pale yellow, bleached raw linseed oil. Filtration is then used to remove the bleaching clay.

An alternate refining and bleaching operation involves what is known as "acid refining." After the oil has been weighed into a lead-lined tank, sufficient sulfuric acid is added to char the "break" that is present in the oil. This charred precipitate is then filtered out of the oil, the excess acid removed by washing. This treatment produces an oil having a slightly higher acid number probably due to the formation of some sulfates of the oil.

The oil is next refrigerated in some cases, to cause certain waxes (sterols) which have a tendency to freeze or become semi-solid to be thrown out. The oil can then be filtered to remove these waxes.

Solvent Extraction

Solvent extraction of oil-bearing seeds and plants and particularly of soybeans has been carried out in batch equipment of several types, using a variety of solvents, but all American soybean mills which now use the solvent process, employ continuous systems. Although considerable effort has been expended toward developing solvent processes which can safely and economically be operated on a small scale, the solvent extraction systems, now used commercially, appear best suited for large-scale operation. One of the advantages of the solvent system is the high recovery of oil. Whereas pressing methods yield residual meals containing 4.0 to 5.5 per cent of oil, solvent-extracted meal contains 1.0 per cent or less. The continuous extraction systems employed in the U. S. include the Bollman (Hansa-Muhle), Hildebrandt, Allis-Chalmers, French and Ford extractors. The variety and sequence of operations are more or less the same in all these systems, their most characteristic features being chiefly in the designs of the individual extractors themselves, that is to say, the methods of contacting the cracked beans with the solvent in order to leach out the oil.

As finely ground beans would tend to cake and produce solvent channeling in the extractors, the beans are first cracked to a size which is determined by the thickness and shape of the flake desired and then rolled into a flake. The flakes are moistened, if they are very dry, by the addition of direct steam. Soybeans lend themselves readily to solvent extraction since they can be rolled into a thin, firm flake sufficiently rugged to withstand the solvent processing without disintegrating into a fine powder. One of the principal difficulties with the extraction of linseed and other oil-bearing seeds results from the solution of the intercellular binder during extraction. Consequently the flakes reduce to a powder and channeling of the extracting medium results. This accounts for the fact that continuous solvent extraction has been applied to soybean to a much greater extent than to other oil-bearing seeds. In producing the flake it is necessary to produce as thin a flake as possible consistent with maintaining considerable strength. Where mechanical agitation of the flakes is kept at a minimum, a thickness of 0.007 inch is found satisfactory. Where screw conveyors propel the charge through the solvent flake thicknesses of 0.009 to 0.015 inch are not uncommon.

As the results achieved in the various solvent extractors is the same, a few typical systems will be chosen as examples of the modes of operation.

The Hildebrandt extraction unit consists of a U-shaped tube. The flakes being added at the top of one leg of the U are carried down one side and up the other by a system of screws. The solvent, usually hexane, is pumped through the system countercurrently, starting at the point where the flakes are being discharged. The wet, extracted flakes are discharged into meal driers which are steam-jacketed cylinders. By use of vacuum, heat from the steam-jacketed cylinders, live steam or various combinations of the three, the last traces of solvent are driven off and returned to the extraction system. The discharged meal is treated further in some instances to produce any one of a number of desired products, and then packaged. This meal contains less than 1 per cent of oil. The oil-solvent mixture, or miscella, contains approximately 20 per cent of oil and is discharged through a strainer to intermediate storage tanks.

The complete removal of solvent is very important, and solvent distillation is carried out in several steps. The bulk of the solvent is removed by a considerable variety of evaporating apparatus, but rather specialized equipment is necessary for the removal of the last 5 to 10 per cent of solvent from the miscella. Bubble cap columns, vertical packed columns, and evaporators constructed to maintain continuously moving thin films of oil over the evaporating surfaces are effective for removing the last few per cent of solvent. Countercurrently flowing live steam removes the last traces of solvent. It is also essential to reduce the amount of fines contained in the miscella so that the final distillation can be carried out effectively. Settling, filtration, or centrifugal clarification methods can be applied to this end. The oil leaves the solvent-distillation equipment at a temperature of about 200°F and is in a form of a very fluid emulsion with water. This emulsion can be prevented by the judicious use of superheated steam in the last stages of solvent stripping, but most companies take advantage of this condition in removing phosphatides from the oil.

The water causes the phosphatides to become hydrated and to be precipitated out of solution. By centrifuging the emulsion, the oil is clarified and the phosphatides removed as an oily sludge which in many mills is used for the production of lecithin.

The Bollmann or Hansa-Muhle extractor differs in that it consists of a number of baskets having perforated bottoms attached to a pair of endless chains driven by sprocket wheels. A charging hopper introduces a predetermined amount of flakes into each basket as it passes by, and the freshly filled baskets start descending on their trip around the circuit. Fresh solvent, usually hexane, is sprayed on the *ascending* baskets near the top and percolates downward through successive baskets, washing the contents of each basket in countercurrent flow. This solvent-oil mixture, called the "half miscella," collects in a sump at the bottom of the housing and is pumped to a temporary storage tank, from which it is sprayed on the top of the *descending* baskets containing the fresh flakes. The fresh flakes are then washed concurrently and the "full-miscella" collects in a sump, whence it is pumped to strainers and then to miscella storage tanks. From this point on, the treatment is the same as related following the description of the Hildebrandt extractors.

The Allis-Chalmers extractor consists of a vertical column containing a series of horizontal, circular plates equally spaced and fixed to a central shaft which is slowly rotated. A series of wiper arms attached to this shaft wipe the top of each plate clean and discharge a portion of the flakes on the plate through suitably arranged openings in each plate. In this way fresh flakes charges at the top of the column are slowly moved downward and are finally discharged at the bottom. Fresh solvent is introduced at the bottom of the column and moves countercurrently to the flakes. This miscella is discharged at the top of the column after passing through a thick layer of fresh flakes which acts as a filter bed and removes any fines contained in the miscella. From this point on the treatment of the miscella is the same as that described in connection with the discussion of the Bollmann and Hildebrandt systems.

The Composition of Drying Oils

Since the chemistry of drying oils will be covered in Chapter 3, only a brief mention of their composition will be given in this chapter.

The drying oils are mixed glycerides of saturated and unsaturated fatty acids and the properties of the individual oil depend upon the type and proportion of the constituent acids making up the oil. Most of the acids are 18-carbon acids which contain one, two or three double bonds, although a small percentage of acids in fish oil contain four double bonds and some have a higher number of carbon atoms, up to 24. With the exception, then, of tung, oiticica and fish oils, all the oils described in the preceding section are made up of mixtures of palmitic, stearic, oleic, linoleic and linolenic acids with minute amounts of arachidic (20 C's), lignoceric (24 C's), and other acids sometimes present. The amounts of the latter are too small to influence the properties of the oils.

Tung oil contains a large quantity of elaeostearic acid, a triply conjugated 18-carbon acid which accounts for its unusual cooking, drying and durability characteristics.

Oiticica oil contains licanic acid, an 18-carbon acid containing one keto group, but in other respects it is identical with the elaeostearic acid present in tung oil.

Fish oils contain highly unsaturated straight chain acids of 20, 22, and 24 carbon chain lengths. One of the principal acids, present to the extent of about 17.2 per cent in the oil of the menhaden, is clupanodonic acid, a 22-carbon chain acid having five double bonds. Palmitoleic acid is also present to the extent of 16.3 per cent, as well as a large percentage of saturated acids. The saturated acids account for the softer films and sometimes undesirable odors associated with this type of oil. Various refining methods have been adopted which help to overcome these difficulties.

The drying of oils which do not contain a conjugated linkage depends largely upon the addition of oxygen at the unsaturated bonds. Consequently the oils of the highest iodine number, which is a measure of unsaturation, dry fastest. In the case of tung and oiticica the iodine number, as determined in the usual manner, is not a true measure of unsaturation, and these oils dry faster than some of the other oils of higher iodine number.

Drying oils are not only mixtures of fatty acids, but also of mixed triglycerides; that is to say, one, two or three types of fatty acids may be attached to the same glycerol molecule. This makes separation of one kind of fatty acid from another in an oil such as linseed impossible, unless the oil is first split into glycerin and fatty acids. Various means, such as fractional crystallization, precipitation, or separation of the solid materials formed by chemical reaction such as bromination, can then be used to separate the acids. These acids can then be recombined with glycerin to form an oil containing only one type of fatty acid. Oils differing substantially in carbon chain length, such as in fish oil, can be separated to a certain extent by fractional distillation.

The mechanism of the oxidation and drying is still the subject of much study and controversy, although rapid strides toward an understanding of the phenomenon have been made in recent years.

Future Developments

In the past few years striking developments have been made in drying oils. The next few years will see many more. The production of vehicles for the protective coating and allied industries is no longer a simple question of producing raw, boiled, alkali- or acid-refined, heat-bodied and blown oils. It becomes necessary to produce a greatly diversified line of special oils, each designed for a specific purpose.

The rapid development of synthetic resins, nitrocellulose lacquers, chlorinated rubber, water paints, and the possibility of cheap vehicles from the petroleum industry have forced oil processors to extend and intensify the improvement and development of new products.

Recent developments have practically eliminated the difficulties caused by skinning and poor color retention of linseed kettle oils. The bodying rate has been speeded up substantially. Oils are being combined more successfully with resin-forming materials such as the alkyds and phenolics. New methods of bodying oils in large quantities, with resulting reduced costs, are already in operation.

The successful dehydration of castor oil has added impetus to the search for tung oil substitutes, some of which involve new methods of processing oils and other new chemical treatments. The conversion of unsaturated oils of the linseed type into unsaturated oils with a conjugated structure is now beyond the laboratory stage.

Separation of the various fatty acids contained in the drying oils and blending to form more desirable combinations is receiving increased attention, particularly because of the increasingly large supplies of low-cost soybean oil which are available. Recent work with soybean oil has promised to bring forth appreciably faster-drying oils which will serve industry well. Such a process also promises to enable better advantage to be taken of the higher iodine number of some of the fish oils.

The possibility of obtaining satisfactory low-cost paint vehicles from the petroleum industry is continually being suggested by the large number of patents being issued in this field. There is no denying the threat to the vegetable oil processor from this source, but present indications are that such developments are far in the future and unlikely to displace natural drying oils except in specialized products which demand unique properties not likely to be obtained with present oils and resins.

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Chapter 3

The Chemistry of Improved Drying Oils

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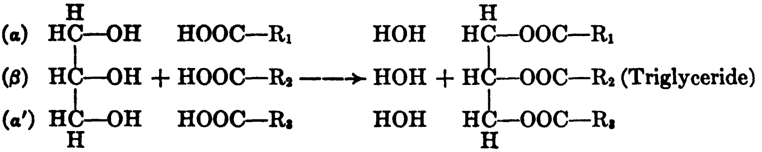
There is no need to review at length the various factors which caused treated drying oils to assume their present practical and commercial value. It is sufficient to recall that with the outbreak of World War II the flow of vital chinawood oil to this country was cut off, and that there was a world-wide famine of fats and oils of all types. This, coupled with the tremendous demand for protective coatings also occasioned by the war, gave rise to a situation in which the available supply of linseed oil was not sufficient to do the necessary job. In addition, to make matters worse, it was deficient in quality, in the sense that certain types of protective coatings demanded qualities that linseed oil alone could not impart. In this respect, of course, the various synthetic resins helped tremendously. However, chinawood oil substitutes and improved drying oils of *new and very special characteristics* were needed, and needed badly. Both from the purely technical and from the production point of view these needs were reasonably satisfied by the improved drying oils which became available. The present continuing shortage of linseed oil engenders a lively interest in treated drying oils, particularly those based on soybean oil. Many of these improved drying oils have characteristics which assure their being used for many purposes in the future.

In any discussion of treated drying oils, the question of terminology arises. Frequently they are termed "synthetic" oils, a term which the organic chemist is very likely to regard as a misnomer. They certainly are not synthetic in the sense that one starts with air, water, coal, and sand, so to speak, in the manner of some of the modern spectacular complete syntheses. There is some justification for the term in many cases in that the final material is chemically quite different from the original. There is also an analogy with some of the so-called synthetic resins, that is, they are synthetic as opposed to natural. Some objection has been raised to almost all the terms applied to these materials, but let us consider them as synthetic, treated, modified, or improved drying oils, or what you will, and proceed to a consideration of the chemical nature of the materials themselves.

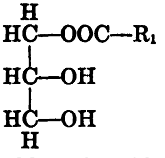
As background for the scope of this subject let us first review in a somewhat elementary fashion the composition and general characteristics of the glyceride fats and oils. The natural oils and fats are essentially the triglyceryl esters of the fatty acids, and structurally may be considered as derived from the condensation of a molecule of glycerin and three molecules of fatty acids:



$$\begin{array}{llclcl} (\alpha) & \overset{H}{HC}-OH & & HOOC-R_1 & & HOH \quad \overset{H}{HC}-OOC-R_1 \\ (\beta) & HC-OH & + & HOOC-R_2 & \longrightarrow & HOH + HC-OOC-R_2 \text{ (Triglyceride)} \\ (\alpha') & \underset{H}{HC}-OH & & HOOC-R_3 & & HOH \quad \underset{H}{HC}-OOC-R_3 \end{array}$$

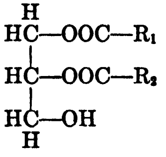
If R_1, R_2, and R_3 are the same, one has a *simple* triglyceride. If one or all three are different, the triglyceride is spoken of as *mixed.* A fact of paramount importance in the preparation of improved drying oils is that the triglycerides occurring in nature are generally highly mixed.

Mono- and di-glycerides do not occur naturally except where the oils have become partially hydrolyzed, as for instance in prolonged storage under humid conditions, etc. They are also of importance to any consideration of treated oils, however, and may be pictured as follows:



$$\begin{array}{l} \overset{H}{HC}-OOC-R_1 \\ HC-OH \\ \underset{H}{HC}-OH \end{array}$$

α-Monoglyceride



$$\begin{array}{l} \overset{H}{HC}-OOC-R_1 \\ HC-OOC-R_2 \\ \underset{H}{HC}-OH \end{array}$$

α, β-Diglyceride

The variations of these forms are obvious.

The fatty acid portion of the molecule comprises roughly 95 per cent of the total molecular weight, so it is not surprising that the characteristics of triglycerides differ widely according to the nature of the fatty acid chain. The fatty acids occurring in natural fats and oils are generally monobasic straight-chain compounds having an even number of carbon atoms. They differ from each other principally in chain length and in their degree of unsaturation. In the consideration of the subject at hand we are principally interested in the C_{18} fatty acids.

The oils which consist chiefly of saturated and mono-unsaturated fatty acids are non-drying; we may roughly classify the semi-drying and drying oils as those which contain predominantly fatty acids which are *at least* doubly unsaturated and relatively small amounts of saturated acids. As a further narrowing of the classification, it can be said that the natural *drying* oils contain appreciable proportions of triply unsaturated acids.

For a further understanding of the problems involved in "up-grading" of non- and semi-drying and otherwise treating glyceride oils to produce improved or synthetic drying oils we may study Table 10.

Table 10. Approximate Fatty Acid Composition.

	Number of Double Bonds	Cottonseed	Soybean	Linseed	Chinawood	Castor
Saturated acids (%)	0	25	12	9	4	2
Oleic acid (%)	1	27	30	15	5	7
Linoleic acid (%)	2	48	53	26	1	3
Linolenic acid (%)	3	—	5	50	—	—
Elaeostearic acid (%)	3 (Triply Conjugated)	—	—	—	90	—
Ricinoleic acid (%)		—	—	—	—	88

This table is of particular interest in the subsequent consideration of fractionated oils. The mixed nature of the natural fats and oils has already been mentioned. It is generally believed that distribution of the fatty acid radicals in vegetable oils follows Hilditch's "rule of even distribution," according to which each fatty acid should tend to be distributed as evenly as possible among the glyceride molecules. The table can also be used to point out some of the salient features which differentiate what are generally considered the drying and non-drying oils, as well as the unique fatty acid composition of chinawood and castor oils.

It is chemically possible, and indeed is the subject of considerable patent and other literature, to up-grade oils generally classed as non-drying (olive, corn, cottonseed, etc.) to drying oils. Generally, however, the commercial development of improved drying oils has been from the semi-drying oils, in particular soybean oil, and of course from the non-drying castor oil. Therefore, most of the chemical treatments later referred to have been applied principally to soybean and castor oils, and to the improvement of linseed oil itself. In view of the tremendous quantity of soybean oil now being produced in this country, and with every prospect for the continued expansion of the facilities and raw material necessary for this production, it is presently of the greatest interest.

It should be mentioned in passing that, as is generally true in organic chemistry, the resemblance of the actual triglyceride molecule to the structural formulas of the type generally used is limited. The actual structure of triglycerides is, of course, highly complex; there is no common agreement on their exact structure. It is sufficient here merely to call attention to their complex structure, and to remember that the fatty acid portions consist of long chains, with presumably free rotation about each carbon-to-carbon single bond and hindered rotation at the ethenoid linkages.

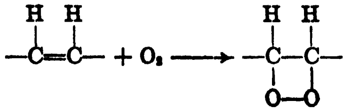
As a basis for an understanding of the chemistry of improved drying oils, let us first consider some of the chemistry involved in the drying and polymerization of the natural drying oils. We shall approach the subject from the standpoint of the chemical linkages involved and the mechanism of their formation, and particularly from the standpoint of polymer formation from the various types.*

When drying oils are spread out in thin films and allowed to "dry," or are otherwise processed to form gels, the products are largely insoluble and infusible, and relatively resistant chemically. The resultant poly films or gels contain varying amounts of smaller molecular species interspersed therein. This characteristic has led many investigators to approach the problem from the colloidal standpoint, but the view now generally taken is that the colloidal phenomena are secondary and result from the formation of a polymeric phase.[1] The importance of the resultant micellar structure to the characteristics of films such as that obtained from linseed oil must not be minimized, however.

Mechanism of Polymerization

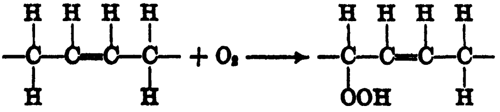
The ability of an oil to polymerize or to "dry" in films is related to its unsaturation, since it is the double bonds which are the reactive centers about which polymerization takes place. Many mechanisms have been advanced, and due to the complex nature of the natural triglycerides many different reactions are indeed involved.

Polymerization in the Presence of Oxygen. The "drying" of films and the preparation of "blown" or "oxidized" vegetable oils are representative of such polymerization. In either case the initial step is classically held to be the formation of peroxides:



$$-\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}- + \text{O}_2 \longrightarrow -\overset{\text{H}}{\underset{\text{O}}{\text{C}}}-\overset{\text{H}}{\underset{\text{O}}{\text{C}}}-$$

Recently, however, E. H. Farmer and co-workers[2] have shown that the initial product at ordinary temperatures is more likely a hydroperoxide in which oxygen has been added at the methylenic carbon atom in the alpha position to a double bond:



$$-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}- + \text{O}_2 \longrightarrow -\overset{\text{H}}{\underset{\text{OOH}}{\text{C}}}-\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-$$

Speaking of the formation of peroxides at the double bond, Farmer wrote: "This view cannot be maintained; the disappearance of olefinic

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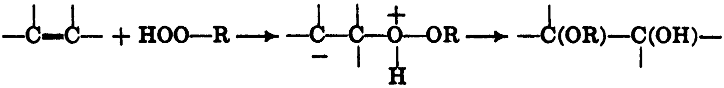
* Portions of the subsequent discussion are taken from *Oil and Soap* XXIII, 339–344 (1946).

unsaturation rarely keeps pace with the incorporation of oxygen, although under usual conditions of reaction severe diminution of unsaturation due to secondary reactions often occurs."

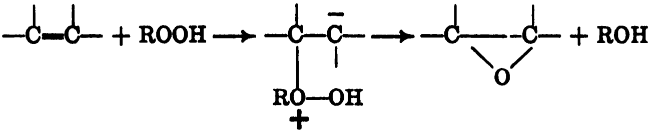
Although hydroperoxides decompose readily, some (including methyl oleate product) are sufficiently stable to be isolated; in the case of polyolefins, however, decomposition apparently takes place side by side with their formation, rendering the mechanism difficult to prove directly. Farmer's view is that autoxidation occurs through the hydroperoxide mechanism regardless of temperature, type of catalysis, etc. Several basic secondary reactions are presented to explain the presence of observed products of the oxidation of olefins; among them are:

(a) Polymerization to give ether-type dimerides:



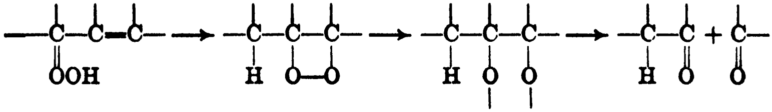
$$-\overset{|}{C}=\overset{|}{C}- + HOO-R \longrightarrow -\underset{-}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{+}{O}}-OR \longrightarrow -\overset{|}{C}(OR)-\underset{|}{C}(OH)-$$

(b) Reaction of hydroperoxide with double bond:



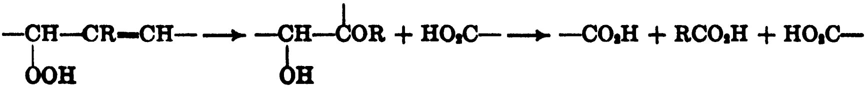
$$-\overset{|}{C}=\overset{|}{C}- + ROOH \longrightarrow -\underset{\underset{\underset{+}{RO-OH}}{|}}{\overset{|}{C}}-\underset{|}{\overset{-}{C}}- \longrightarrow -\overset{|}{C}\underset{\diagdown O \diagup}{\text{———}}\overset{|}{C}- + ROH$$

(c) Scission of carbon chain at the double bond:



$$-\underset{\underset{OOH}{|}}{\overset{|}{C}}-\overset{|}{C}=\overset{|}{C}- \longrightarrow -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}- \atop \quad\;\; O-O \longrightarrow -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{\underset{|}{O}}{|}}{\overset{|}{C}}-\underset{\underset{\underset{|}{O}}{|}}{\overset{|}{C}}- \longrightarrow -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{O}{\|}}{\overset{|}{C}} + \underset{\underset{O}{\|}}{\overset{|}{C}}-$$

(d) Subsidiary scission between ethylenic bond and a C atom:



$$-\underset{\underset{OOH}{|}}{CH}-CR=CH- \longrightarrow -\underset{\underset{OH}{|}}{CH}-\overset{|}{C}OR + HO_2C- \longrightarrow -CO_2H + RCO_2H + HO_2C-$$

Morrell and his co-workers[8] attacked the validity of Farmer's work, particularly as applied to drying oils, declaring that according to Farmer's mechanism one-half of the total oxygen absorbed by methyl linoleate would be present as —OH, whereas their analyses indicated only one-quarter present as such. They considered, however, only one of the pos-

$$(>C(OOH).\ CH{:}CH. \rightarrow >C(OH).\underset{\diagdown O \diagup}{CH.CH.})$$

sible secondary reactions described by Farmer. Further, there was disagreement as to the reliability of the analytical methods used to identify the products obtained, but this disagreement was not rigidly resolved.

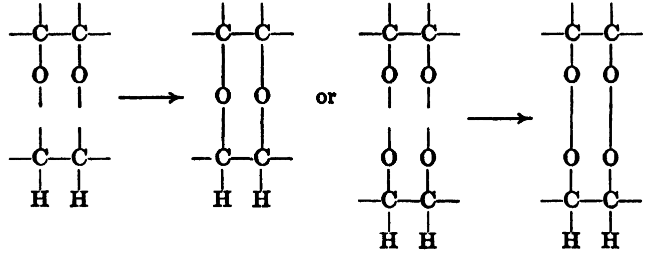
Atherton and Hilditch[4] studied the union of oxygen with methyl oleate at 20° and 120°C. The products were separated by absorption on silica gel; portions of the separated products were oxidized with $KMnO_4$ and the quantity and nature of the mono- and di-carboxylic scission products determined. At 20°C a substantial portion of suberic and octoic acids were found in the scission products, indicating peroxidation had to a large extent occurred at the $—CH_2—$ group adjacent to the double bond. From the oxidation of the products from the 120°C reaction, only traces of suberic and octoic acids were found; nonoic and azelaic acids were present in quantity, and also products indicating changes of a more complex nature. This indicates that direct peroxidation of the double bond predominates at higher temperatures, but does not obviate the possibility that the initial step consists of hydroperoxidation.

In a still more recent investigation of this same oxidation problem Gunstone and Hilditch[5] have concluded that, at least so far as oleates and linoleates are concerned, the initial association of oxygen is with the double bond (or with one of its carbon atoms) rather than with the adjacent methylene group. They consider, however, that hydroperoxide formation then takes place with the formation of a *new* ethenoid bond:

$$\text{—CH:CH·CH}_2\text{—} \longrightarrow \text{—}\underset{\text{O——O}}{\text{CH·CH}}\text{·CH}_2\text{—} \longrightarrow \text{—CH(OOH)·CH:CH—}$$

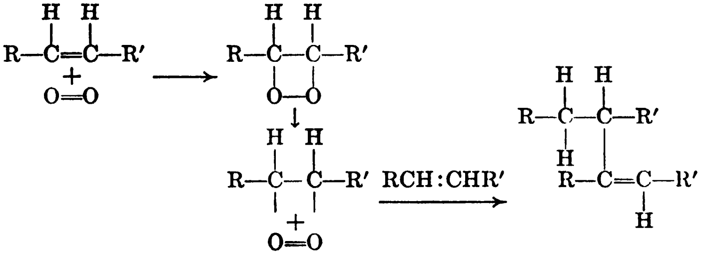
The ensuing secondary reactions could then take place in the manner previously described. This point of view is more or less in accordance with somewhat revised views presented by Farmer and by Bolland and Gee during the Faraday Society General Discussion on Oxidation (1946).

Whatever the nature of the initial step, polymerization could subsequently take place in such a manner as to result in either oxygen-linked or addition polymers. It has been suggested[6] that peroxides or similar oxidation products could form oxygen-linked polymers:



It is not generally believed that such structures are important in triglyceride polymers. The products of a hydroperoxide reaction with a double bond would be in better agreement with the observed formation of epoxy and hydroxy groups as well as polymers when vegetable oils are oxidized with air.

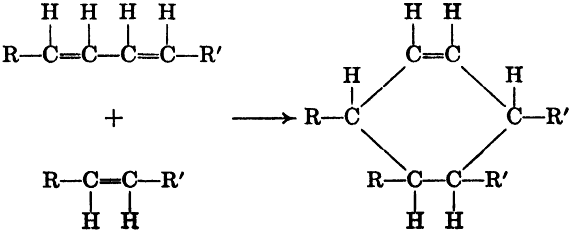
It is Powers' view[7] that the role of oxygen is primarily one of activation so far as polymerization is concerned, and that after activation polymer formation proceeds through the conventional vinyl mechanism, or at least that such a mechanism plays a more important role than heretofore recognized.



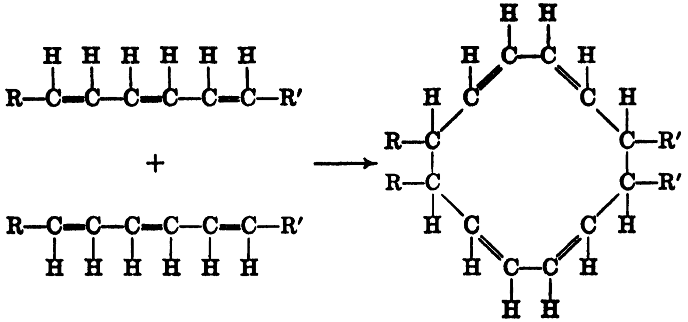
Heat Polymerization of Drying Oils. The "bodying" of drying oils for the preparation of varnishes and similar materials is representative of such polymerization. The polymerization takes place readily *in vacuo* or inert gas at temperatures in the vicinity of 300°C; somewhat lower temperatures are employed in the case of tung oil. Due to the relatively high temperatures necessary for the heat-bodying of drying oils, considerable quantities of decomposition products are obtained.

It is still general practice in the varnish industry to carry out the polymerization in open kettles; here oxygen probably plays a role of activator, since it is a matter of common observation that drying oils will polymerize at a given temperature more rapidly in the open than under vacuum or inert gas. However, the nature of the polymers obtained from open or vacuum-inert gas systems is essentially similar; the exclusion of oxygen prevents the formation of oxidation products, and the use of vacuum or inert gas flow removes other volatile decomposition products. In either case the possible oxygen-linked structures discussed in the preceding section are of no importance.

Considering the step of activation to have been accomplished, most schemes postulate the formation of cyclic dimers.[8] Dimerization might take place between fatty acid chains through a Diels-Alder reaction:



In the the case of tung oil (elaeostearic acid glyceride) there would be the possibility of the formation of a cyclic structure:



The formation of trimers and tetramers is similarly postulated.

Note that such schemes are valid only for conjugated systems, whereas most drying oils (except tung oil) contain relatively small quantities of the conjugated isomers. Fortunately, at the temperatures necessary for polymerization, a shift of the double bonds in the fatty acid chains of the triglyceride occurs in such a manner as to result in the conjugated form. The percentage of conjugated isomers builds up to a certain point before appreciable polymerization takes place. As an indication of this shift let us for a moment examine Table 11 and Figure 1, which show the iodine value-viscosity relationship for the polymerization of: A—Alkali-refined Linseed Oil; B—Commercial Fast-bodying Linseed Oil "B"; C—Commercial Fast-bodying Linseed Oil "C."

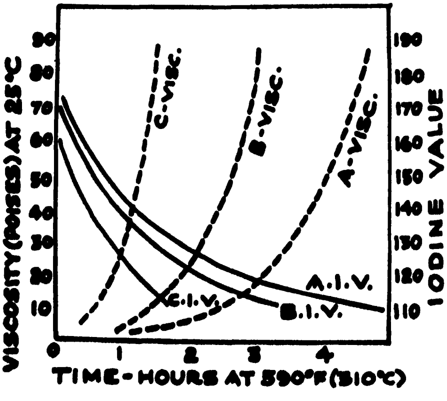


FIGURE 1

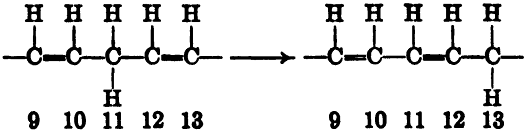
Referring for the time being to the first column (data for the polymerization of uncatalyzed linseed oil), it will be noted that the iodine value drops nearly 50 units at the end of two hours, while the viscosity increases to only 6 poises, and that the major portion of the viscosity increase (indicating polymerization) takes place subsequently with comparatively little decrease in iodine value. Since it can be demonstrated that in a conjugated fatty acid one of the double bonds is relatively insensitive to the addition of iodine, the initial large decrease in iodine value without corresponding polymerization can be attributed to conjugation. This preliminary shift to a conjugated structure has been investigated by absorption spectroscopy and other methods.[9]

Table 11.

	A		B		C	
Time (hrs. 590°F)	Viscosity (poises)	I.V.	Viscosity (poises)	I.V.	Viscosity (poises)	I.V.
0	0.5	174.6	0.6	173.4	0.8	167.2
½	1.0	157.5	1.65	152.2	5.2	133.8
1	2.0	142.0	4.35	135.2	28.0	118.9
1½	4.0	130.8	9.0	126.5	98.5	113.8
2	6.0	126.6	22.0	121.1		
3	18.0	120.3	98.5	112.3		
4	50.0	113.8				
4¾	98.5	108.7				

Powers has suggested the following sequence of events for the heat polymerization of drying oils:[10]

(a) Rearrangement to the conjugated diene structure—



$$-CH{=}CH-CH_2-CH{=}CH- \longrightarrow -CH{=}CH-CH{=}CH-CH_2-$$

(b) Formation of cyclic structures between chains, primarily between chains of the same glyceride ("intrapolymers")

(c) Ester interchange between an intrapolymer and another glyceride molecule.

The Chemical Nature of Drying Oils

Some mention of the functionality concept[11] is in order before proceeding to discuss specific types of improved drying oils. Natural oils which are chiefly composed of singly unsaturated (oleic) acids do not polymerize or dry, whereas those containing doubly and triply unsaturated acids in appreciable quantities polymerize or dry readily. Generally speaking, the higher the degree of unsaturation, the better the drying and polymerization characteristics. Considering the fatty acids themselves, no fatty acid as such has been demonstrated to form more than a dimer, regardless of its unsaturation. They are monofunctional, and are incapable of further reaction after the association to form a dimer. In the case of bifunctional compounds, the dimer will retain the same functionality as the monomer.

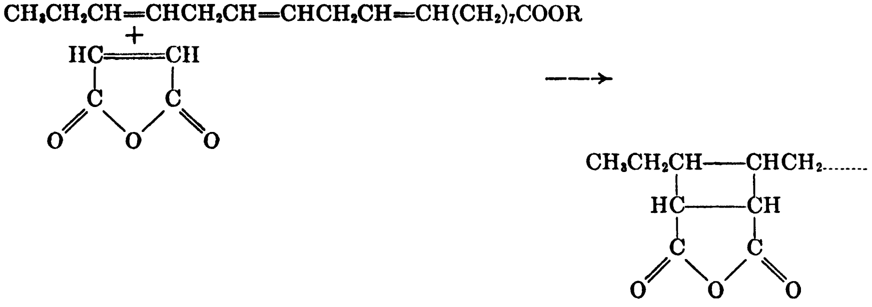
In the case of tri- or more functional compounds, the functionality actually increases with increasing degree of polymerization. Thus, fatty acids or their methyl esters would only be expected to form dimers, and then only if the fatty acid is of sufficient degree and proper type of unsaturation. Di-esters of the fatty acids will polymerize to a limited degree, subject to the same limitations. The triglyceryl esters of sufficiently unsaturated acids polymerize easily. In addition, the functionality increases when unsaturated fatty acids are esterified with higher alcohols, such as pentaerythritol, sorbitol, polyallyl alcohol, etc. This is not to indicate, however, that the functionality increases linearly with each OH of a polyhydric alcohol or for each additional double bond of the fatty acid chain. It can nevertheless be empirically employed in a very useful manner in considering synthetic resins and improved drying oils, which fall broadly under the polyester classification.

Against the background of the preceding general discussion, let us proceed to a more specific consideration of the chemical nature of the various types of treated drying oils. There are many aspects of their preparation and application which it would not be possible to discuss in detail here, but they may be broadly placed under the following classifications for the purpose of our consideration:

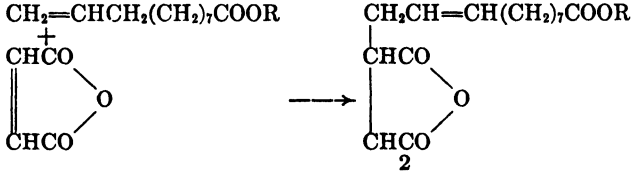
(1) Dibasic acid condensation products
(2) Alkyd type condensation products
(3) Fatty acid esters of higher polyhydric alcohols
(4) Catalytically isomerized oils
(5) Catalytic fast-bodying oils
(6) Dehydrated castor oil
(7) Hydroxylated-dehydroxylated oils
(8) Triglyceride-unsaturated compound copolymers
(9) Fractionated oils

This listing is, of course, without any significance as to their relative importance. It goes without saying that the characteristics of each are, in general, quite different so far as their applications are concerned. Depending upon their nature, the products will be improved in one or a combination of the following properties: drying time, film hardness, polymerization time, and chemical resistance. In addition, some will exhibit other and very unique properties which are desirable for very specific applications.

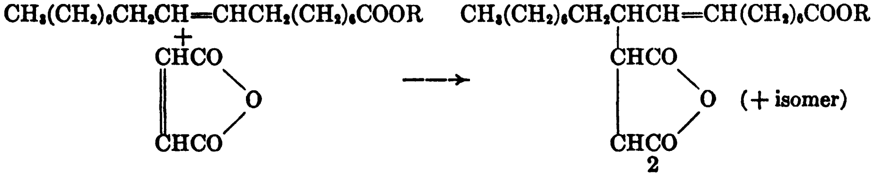
(1) ***Dibasic Acid Condensation Products.*** These are the unsaturated dibasic acid or anhydride adducts of unsaturated drying or non-drying oils. One type is stated to be the reaction product of unsaturated dibasic acids with isolated double bonds, in the following manner;[12]



Now while maleic anhydride undoubtedly condenses with isolated double bonds, such a structure involving the cyclobutane ring may be considered unlikely. More light has recently been thrown on this type of addition.[13] While maleic anhydride will not polymerize with itself, it will readily copolymerize with the vinyl type compounds. It has further been shown to condense in general with mono-olefinic acids or esters having a terminal methylene group:

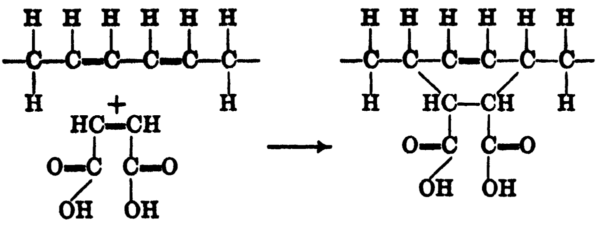


With compounds such as propene, maleic anhydride appears to substitute on the $—CH_3$ end rather than adding to the terminal $—CH_2$, but this appears to be only a special case of the above type of addition. Further, with compounds of the type of methyl oleate maleic anhydride has been demonstrated to add similarly:



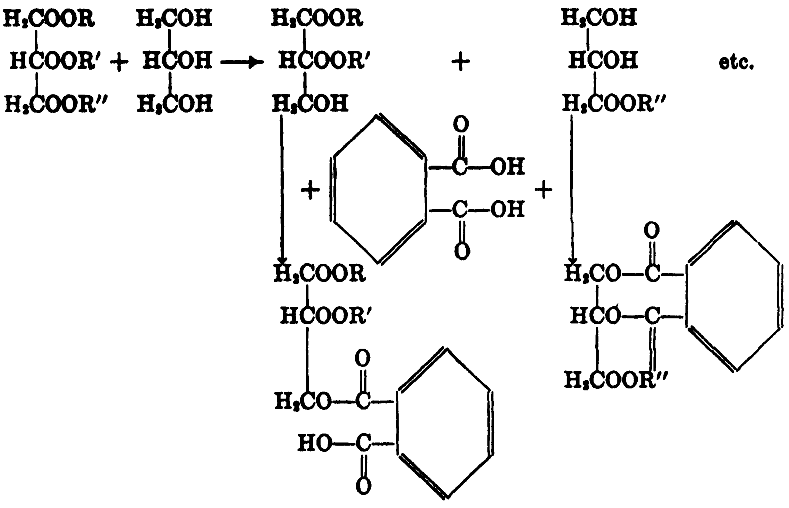
Note that such a monoethenoid compound will retain its degree of unsaturation in this case. The properties of maleic anhydride addition compounds with mono-olefinic triglycerides are in better agreement with this view.

Another type claims the Diels-Alder adduct, which chemically must be considered as taking place upon a conjugated system:[14]



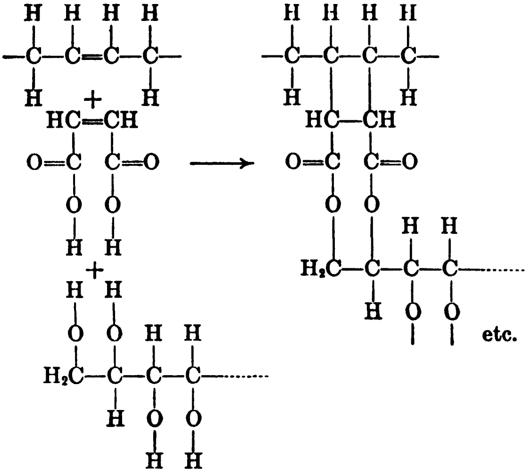
These adducts polymerize readily, particularly in the presence of oxygen. The polymers are water-dispersible in alkaline emulsions (polar groups) and find application in the modern water-thinned interior paints.

(2) ***Alkyd Type Condensation Products.*** Vegetable oils (drying or non-drying, but necessarily unsaturated) are reacted with a polyhydric alcohol to form mono- or di-glycerides, and the remaining glycerol OH's are then reacted with a dibasic acid or anhydride thereof to form mixed esters:[15]



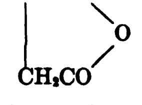
It can readily be seen how further reaction can take place with unreacted hydroxyl groups and also at the double bonds to result in three-dimensional polyesters of high molecular weight.

A modification of this type, which should result chemically in quite different products, is the esterification of the free acid groups of the adduct discussed under (1) with a polyhydric alcohol. It is difficult to avoid the formation of insoluble dibasic acid-polyhydric alcohol resins by this procedure; further, in many cases the final product of such a reaction is all but indistinguishable from the alkyd type described above, presumably through a mechanism of ester interchange. There is, however, a considerable quantity of patent literature.[16] Polyester formation in this case could be pictured:



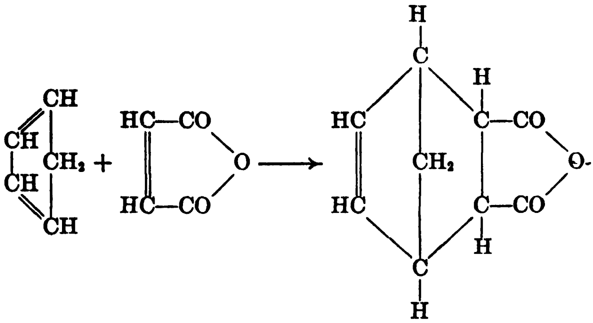
The very essential difference between the use of maleic anhydride and phthalic anhydride in this type should be pointed out. In the case of phthalic anhydride there is, of course, no possibility of the aromatic unsaturation adding to the double bonds of a glyceride. With maleic anhydride, such addition takes place even where the oil has first been reacted with a polyhydric alcohol (in this case polycondensation and addition take place simultaneously).

Many other dibasic acids and anhydrides may be used. Modification of the aromatic nucleus of phthalic anhydride to obtain such compounds as tetrachlorophthalic anhydride is an obvious means of introducing elements or groups known to have certain effects. For instance, the introduction of chlorine in a molecule generally increases heat resistance, and on occasion such properties can be in some measure carried through to the finished products. Fumaric acid apparently reacts much as does maleic; whether it isomerizes under the conditions of reaction is not known. Succinic acid derivatives of the general formula



(R unsaturated)

may be mentioned, as well as other dibasic acids which can be considered as arising from the addition of maleic anhydride to natural terpene or hydrocarbon materials. For example, endomethylene tetrahydrophthalic anhydride can be prepared from cyclopentadiene and maleic anhydride:[17]

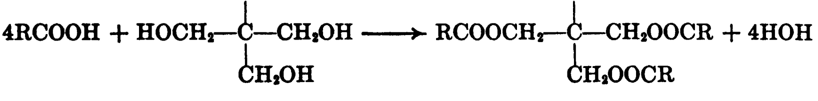


The double bond is still capable of the types of addition discussed previously.

Monobasic acids having conjugated diene unsaturation in the chain can be used for this alkyd type; here the functionality is largely in the olefin portion, but the carboxyl is present to take part in condensation with alcoholic —OH. As an example may be cited 2,4- hexadienoic acid (sorbic acid):

$$CH_3CH{=}CHCH{=}CHCOOH$$

(3) **Fatty Acid Esters of Higher Polyhydric Alcohols.** As pointed out in discussing functionality, the esters of polyhydric alcohols higher than glycerol dry better than the natural triglycerides. This is broadly true, the basic limitation being that the polyhydric alcohol must be of such nature that inner etherification does not take place in preference to esterification to any great extent. Such esters are generally prepared by the direct reaction of fatty acids (generally *at least* di-unsaturated in character) and polyhydric alcohols such as pentaerythritol (2-bishydroxymethyl-1,3 propanediol), polypentaerythritols (—C—CH_2—O—CH_2—C—, etc.), sorbitol (1,2,3,4,5,6- hexanehexol) and many others.[18] For example, with pentaerythritol:



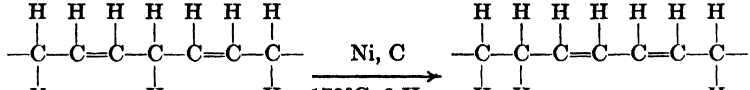
$$4RCOOH + HOCH_2{-}\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{\overset{|}{\underset{|}{C}}}}{-}CH_2OH \longrightarrow RCOOCH_2{-}\overset{\displaystyle CH_2OOCR}{\underset{\displaystyle CH_2OOCR}{\overset{|}{\underset{|}{C}}}}{-}CH_2OOCR + 4HOH$$

These reactions are carried out under a great variety of conditions of temperature and catalysis, depending upon the character of the polyhydric alcohol. Obviously, the choice of fatty acid can be varied to determine the nature of the product. Esters of carefully fractionated cuts from different acids have been commercially prepared.

(4) **Catalytically Isomerized Oils.** Biochemical investigations first indicated that the acids resulting from the alkaline saponification of natural glycerides were conjugated to a degree much higher than their state in the

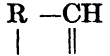
oil. This led to patents in which alkaline catalysts were used to isomerize fatty acids; the process was indirect and cumbersome but has been worked.

Other patents which claim the direct conjugation of oils by various catalysts, such as Al_2O_3, have appeared from time to time, but the catalysts claimed usually have little more effect than heat alone, except as to decomposition of the oil. More recently the Northern Regional Research Laboratory at Peoria has developed a Nickel-Carbon catalyst and process:[19]



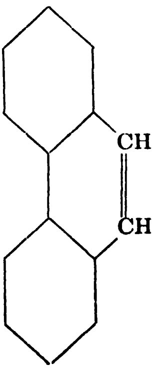
$$\begin{array}{ccccccc} H & H & H & H & H & H & H \\ | & | & | & | & | & | & | \\ -C- & C= & C- & C- & C= & C- & C- \\ | & & & | & & & | \\ H & & & H & & & H \end{array} \xrightarrow[170°C,\ 6\ Hrs.]{Ni,\ C} \begin{array}{ccccccc} H & H & H & H & H & H & H \\ | & | & | & | & | & | & | \\ -C- & C- & C= & C- & C= & C- & C- \\ | & | & & & & & | \\ H & H & & & & & H \end{array}$$

Conjugated soybean oil having about 35 per cent of the double bonds in the conjugated position will dry at roughly the same rate as linseed oil, and will have similar film characteristics. The limiting feature of such a process as applied to soybean oil is of course the residue of saturates and mono-unsaturates which are present in relatively high quantity. The polymerization rates of such oils are, of course, much faster than those of the unconjugated oils; but, once polymerized, there is little difference in the final polymers or in their film characteristics.

(5) ***Catalytic Fast-Bodying Oils.*** The simplest in treatment of the chemically processed triglycerides are those to which a minor amount of a polymerization catalyst has been added which causes them to body much more rapidly than the uncatalyzed oils. One process[20] claims as such a catalyst the "oxidation products of coal-tar hydrocarbons having the formula  $\begin{array}{ll} R & -CH \\ | & \| \\ R'- & CH \end{array}$, where R and R′ are aromatic nuclei, in amounts of 0.05 to 0.5%". Hydrocarbons having this general formula would be:

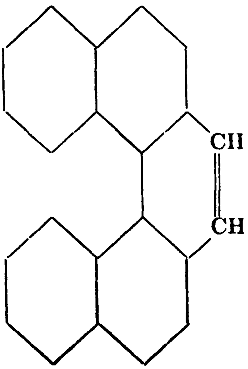
Phenanthrene

$\begin{array}{ll} C_6H_6- & CH \\ | & \| \\ C_6H_6- & CH \end{array}$



Chrysene

$\begin{array}{ll} C_{10}H_6- & CH \\ | & \| \\ C_{10}H_6- & CH \end{array}$



etc.

The oxidation products themselves are not named, but inferentially they would be the corresponding quinones.

One patent claims β-methyl anthraquinone and like compounds.[21] Another claims specifically diphenol carboxyl anthracene.[22]

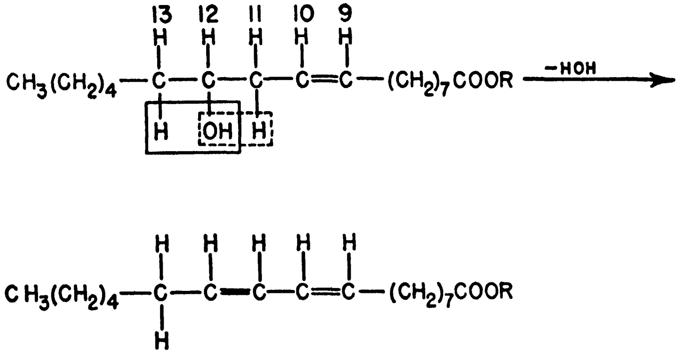
The type of substances discussed above belong to a class generally regarded as polymerization inhibitors. Both β-methyl anthraquinone and diphenol carboxyl anthracene will inhibit the polymerization of styrene as well as hydroquinone, a recognized stabilizing agent. This makes it doubtful whether ordinary drying oil polymerization is of the vinyl type, even under oxidative conditions.

No explanation of the catalytic activity of such substances has ever been presented. In view of the dehydrogenation of hydrocarbons by certain aromatic quinones, it seems reasonable to propose that they act to catalytically isomerize the double bonds of the fatty acid chains to the conjugated positions. As support for this view reference can again be made to the data in Table 11. It will be seen that polymerization proceeds for the two commercial catalytic oils (Columns B and C) in essentially the same manner as for the uncatalyzed linseed oil with respect to iodine value-viscosity relationship. However, some low iodine value stage (about 130) preceding appreciable polymerization is reached much more quickly. This would be in accord with the catalytic isomerization view, and there is other evidence.

(6) ***Dehydrated Castor Oil.*** Castor oil, a non-drying oil, has long been valued for its lubricating and hydraulic properties. It is not miscible with petroleum oils, a serious disadvantage since, where mixing occurs, the lubricating properties of the film break down. Many years ago it was discovered and recognized that the dehydration of castor oil rendered it soluble in mineral oils, and it was further recognized that such dehydration could lead to a drying oil.[23] The fact that the classical dehydrating catalysts could be used in the process was also disclosed in the literature of the same period.[24] During World War I considerable quantities of mineral-soluble castor oil were used in the lubrication of aircraft engines, etc. ("Castorlubrin"). The early commercial methods employed for the dehydration resulted in only partial dehydration, and the resulting oils were still non-drying in the usual sense. Thus, it was only comparatively recently, and under the pressure of an unstable chinawood oil market, that it became generally recognized that excellent drying oils of good polymerization characteristics could be obtained from castor oil. Improved processes were patented about 1930.[25] There are probably more patents regarding the dehydration of castor oil than there are in all other phases of drying-oil chemistry; comparatively few are of basic nature.

The processes and product have been vastly improved, however; several patents may be cited to typify the development of the technique.[26]

Chemically, dehydration comprises the removal of OH and an adjacent H from the ricinoleic (12-hydroxy-9,10-octadecenoic acid) portion of the triglyceride. Fortunately, castor oil is one of the relatively few naturally occurring triglycerides which is composed largely of one acid, the acid portion being largely ricinoleic. The dehydration may proceed in two ways, according to whether the 11 or 13 hydrogen is removed; it was formerly believed that the greater part of the resulting dienoic acid was conjugated, but according to Priest and von Mikusch,[27] the nonconjugated isomer predominates:

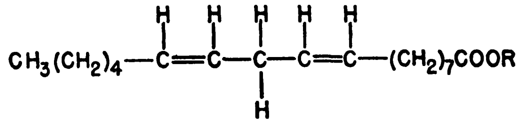


$$CH_3(CH_2)_4-\underset{H}{\overset{\overset{13}{H}}{C}}-\underset{OH}{\overset{\overset{12}{H}}{C}}-\underset{H}{\overset{\overset{11}{H}}{C}}-\overset{\overset{10}{H}}{C}=\overset{\overset{9}{H}}{C}-(CH_2)_7COOR \xrightarrow{-HOH}$$

$$CH_3(CH_2)_4-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{C}=\overset{H}{C}-(CH_2)_7COOR$$

(17-26% 9,11-octadecadienoic acid)

or



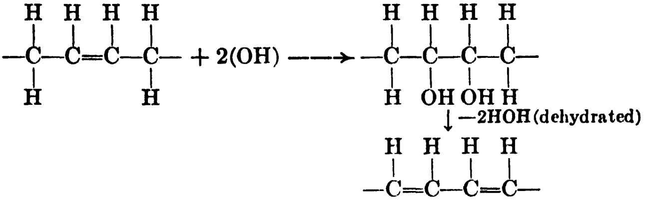
$$CH_3(CH_2)_4-\overset{H}{C}=\overset{H}{C}-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}-(CH_2)_7COOR$$

(59-64% 9,12-octadecadienoic acid)

One patent[28] claims the dehydration of castor oil by using as a catalyst an alkyl sulfate, specifically 0.2 to 0.5 per cent of diethyl sulfate, and heating under vacuum at temperatures above 500°F.

(7) ***Hydroxylated—Dehydroxylated Oils.*** Referring back to the discussion of the oxidation of drying oils, it will be seen how a new double bond might possibly be introduced into the conjugated position in a fatty acid chain by the means of hydroxylation followed by dehydroxylation. However, as previously pointed out, the possible types of oxidation are legion; the hydroxylation of a double bond is accomplished only under very carefully controlled conditions. Further, once such an oxidative stage

is attained, there are a number of directions in which the reaction may subsequently proceed. There is, however, considerable patent and technical literature[29] based upon some form of oxidation followed by dehydration. If oxidation took place to any extent at points removed from the double bonds in such a manner as to introduce hydroxyl groups, isolated double bonds would be set up on dehydration. Generally, the basic idea would involve oxidative attack at the double bond, and can be presented as follows:



$$-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\underset{H}{\overset{H}{C}}- + 2(OH) \longrightarrow -\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-$$

$$\downarrow -2HOH\text{(dehydrated)}$$

$$-\overset{H}{C}=\overset{H}{C}-\overset{H}{C}=\overset{H}{C}-$$

The preparation of drying oils by high-temperature oxidation (bis-oils) was similar in concept; here oxidation and dehydration were possibly simultaneous.

(8) ***Triglyceride—Unsaturated Compound Copolymers.*** Many early attempts were made to utilize such high polymers as polystyrene, polyvinylchloride, polymethylmethacrylate, etc., and the many hydrocarbon polymers as resinous materials in the preparation of oleo-resinous varnishes. These attempts were not generally very successful, the major reason being that such high polymers are soluble only in high-powered solvents, such as benzol, toluol, and xylol; thus they were incompatible with polymerized drying oils and other varnish ingredients. However, realizing that the unsaturated triglycerides were potential copolymerizing materials, the attempts were turned toward copolymerization with the highly active monomeric materials.

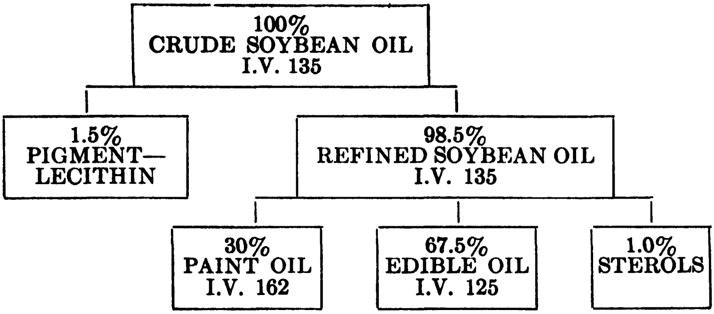
In the 1930's German Patents were issued[30] dealing with the joint polymerization of fatty oils with such compounds as vinylchloride, chlorobutadiene, vinyl alkyl ketones, etc. Since that time various investigators have copolymerized unsaturated glycerides with almost every conceivable type of polymerizing material. The products are variously claimed to be adhesives, synthetic resins, improved drying oils, etc. Naturally the products do vary widely in character, but the fundamental principles involved in their preparation are similar. The chemistry involves either (a) the addition of the vinyl type of double bond, or (b) the 1,4 addition characteristic of conjugated dienes to the double bonds of a fatty acid. Since these additions have been discussed at some length previously it is not necessary to depict them here. The conditions of the preparation of this type of synthetic resin or improved drying oil will depend on the monomer being used. Increased pressure is generally necessary, since most of the monomers are highly volatile, and various catalysts (principally of the Friedel-Crafts type) are used when the reactions are carried out at low temperatures.

As a specific example, dehydrated castor oil and linseed oil have been copolymerized with styrene[81] to yield clear liquid or resinous, soluble products which form films stated to be fast drying, non-frosting, of good initial color and excellent durability.

(9) ***Fractionated Oils.*** The fractionation of linear high polymers by means of the differing degree of solubility in organic solvents of their constituents having different molecular weights has long been one of the most useful methods employed in their examination. In this manner it is possible to fractionate, for example, a sample of polystyrene into several fractions of different molecular weight range; here one is dealing with molecular weights which are vastly different, on the order of 10,000 to 100,000. Solubility depends, of course, on many factors—chemical as well as physical—other than molecular weight, and the molecular weight differences do not by any means have to be as gross as those mentioned in order to affect solubility. At any rate, one of the earliest approaches to the fractionation of oils containing both saturates and unsaturates (capable of polymerization) was first to heat-treat the whole oil to partially polymerize the unsaturated portion, then to segregate the polymerized and unpolymerized portions by selective solvent action. Organic solvents such as ketones and higher alcohols, particularly acetone,[82] have been used to accomplish this. Usually sufficient solvent is added to result in a cloudy mixture, which then stratifies into two layers, the upper layer containing solvent and the more-saturated fats, while the lower contains less solvent and the polymerized portion of the oil. The following applies to sardine oil segregated by such a process:

	Original Oil	Heat-Treated Oil	Settled Polymerized Oil	Non-Drying Oil
Iodine number	201	112	118	100
Viscosity (Gard.)	A	X	Z5	G
Ability to gel	No	No	Yes	No
Dry	Fast, tacky	Slow, tacky	Fast, hard	Non-drying

Even more efficient solvents for the fractionation of oils are furfuraldehyde and liquid propane. With these it is not necessary to heat-treat the oils to cause partial polymerization. Whether the solvency depends entirely on the slight difference in molecular weights or upon other chemical and physical factors is problematical, although it is stated to depend on molecular weight. The use of liquid propane makes possible the separation of non-glyceride components of the oil. A continuous process using liquid propane can be used to fractionate soybean oil, for example, into four fractions: (1) pigment-lecithin, (2) edible oil, (3) paint oil, and (4) sterol concentrate.



Linseed oil of 185 Iodine Number is said to be separable into two fractions, (a) Medium Iodine Number 160, and (b) High Iodine Number 210; the former could be used to extend linseed oil, the latter to extend tung oil.

Also under fractionated oils belongs the group mentioned earlier, in which the fatty acids are separated from the glyceride by twitchellization, and are then vacuum-distilled to achieve cuts of various unsaturation. These fatty acids can then be used as raw materials for the preparation of improved drying oils by the methods discussed herein.

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Chapter 4

Pigments—General Classification and Description

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Definition of Paint

Broadly speaking, paint can be defined as a mixture of pigment and binding medium, which can be spread to a dry, thin film to decorate or protect a surface. Such a definition includes all types of paint and many other types of protective coatings, such as lacquers, Portland cement paints, paper coatings, emulsion paints and printing inks. But since these products are all fundamentally alike in that they contain a pigment and a binding medium and are used to decorate or protect a surface and can be applied to surfaces in a thin film, they may be included under the definition of "paint."

The components, therefore, of any paint system are first, the pigment and second, the binding material. A third component which acts to allow the combination of pigment and binding material to be spread to a thin film, is at times included. In the normal paint or lacquer, this is generally a solvent or dispersing medium for the binder. The mixture or solution of binding medium and solvent are known to the paint industry as the vehicle. Consequently, for sake of simplicity of discussion, we will consider that a paint consists of two components—namely, pigment and vehicle.

Purposes of Pigments in Paint

The obvious purpose of including a pigment in a paint is, of course, to obscure the underlying surface and to decorate that surface. There are, however, very definite reasons for the use of pigment other than merely to obscure or decorate the surface. For example, linseed oil, when exposed in a thin film on wood to weathering conditions, would last but for a few weeks. If this oil, however, is pigmented, the durability of the oil film is extended over a period of years. Similarly, the pigmentation by zinc chromate of a varnish will definitely enhance the value of a film varnish in protecting a steel panel by developing some passivity in the metal and thus reducing the amount of corrosion.

Thus, the decorative and protective value of pigments are readily understood. But there are many other reasons for including pigments in paint, which are not readily understood by the laymen, but which are familiar by the paint formulator. In some cases, the pigments added have little decorative or protective value. The inclusion of a pigment to a vehicle increases the consistency or viscosity of the vehicle, giving it a definitely better quality in applying it to a given surface. Consistency helps to build up a film thickness which permits better obscuring of the surface and better protection. Pigments are added to vehicles to produce definite durability characteristics, as has partially been pointed out before. On the other hand, they may be added solely for such durability characteristics and play no part in obscuring or decoration of the surface. For example, the inclusion of fibrous or micaceous magnesium silicate to outside house paints adds no hiding power to the paint but definitely improves its durability or crack-resistance. Pigments are added to control the penetration of the vehicle into the surface so that the paint can be more easily applied to porous surfaces. They are added to improve flow characteristics and for many other practical properties which are desired in a paint film.

The type of finish which is obtained from a paint is controlled to a degree by pigmentation. As may be readily seen, paint films have a variety of surface appearances. Paints are made which have a glossy finish, a sheen finish like satin or eggshell, and a complete flat or "matt" finish with many intermediate degrees. To a large degree, these finishes are obtained by the manipulation of pigment. Lastly, pigments may be added to paint largely to bring them to a satisfactory raw material cost to meet the marketing standards of buyers, and at the same time to impart a durable decorative and protective film. It is very well to think of paint in a completely theoretical way, but practical paint formulators must always be concerned with the raw material cost; therefore, this point of economy will always be considered.

Types of Pigments

Generally speaking, there are but two types of pigments: (1) colored, such as red, green, blue, yellow and black; and (2) white pigments. Colored pigments absorb a portion of the light which falls upon them and reflect to the eye a given group of color bands which determines their color. White pigments, while they may absorb some light and convert it to heat, do not select particular light bands and thus return to the eye an appearance of white. This ability to reflect light gives pigments their value as an ingredient in a decorative or protective coating.

Principles of Hiding Power

In paint technology, this ability to reflect light is the source of the hiding power of a pigment. With colors, such as red and blue, it is obvious that the hiding power accrues to the pigment, by virtue of its ability to absorb, as heat, certain light rays and to reflect others. Those reflected rays give our eye the sense value of red, green or what not. With a white pigment, light enters the pigment particle, is changed in direction according to the pigment's index of refraction, and by multiple changes is reflected back to the eyes as white. Some light is absorbed as heat and some bands are selectively adsorbed, giving these white pigments their distinctive undertone tints such as blue and yellow, since no pigment is a completely perfect white pigment.

The hiding power of a white pigment is determined by the difference in index of refraction between it and its surrounding medium; it is proportional to the square of the difference of the index of refraction of the pigment and the index of refraction of the surrounding medium. A pigment such as calcium carbonate, which has an index of refraction of 1.60 when exposed in air, has a definite obscuring or hiding power, because it is surrounded by air, the index of refraction of which is 1.0. If, however, it is surrounded by a medium such as a phenolformaldehyde resin with an index of refraction of 1.60, it will show no hiding power. On the other hand, Rutile Titanium Dioxide, with an index of refraction of 2.76, will show hiding power, both when surrounded completely both by air and by phenolformaldehyde resin.

White pigments are divided into two classes—the prime or hiding power pigments, which have indices of refraction substantially above the index of refraction of the common paint vehicles, or substantially above 1.5. Such pigments are basic carbonate white lead, basic sulfate white lead, zinc oxide, zinc sulfide, antimony oxide and titanium dioxide. The second class of white pigments are known as pigments of low refractive index. These pigments have indices of refraction very close to that of common paint vehicles, namely, 1.5. Pigments of this class are barium sulfate, calcium sulfate, magnesium silicate, aluminum silicate, silica and calcium carbonate.

Now, in the true sense of the word, these pigments of low refractive index can be seen to have hiding power providing the medium surrounding them is of lower refractive index. For example, if the pigments are used to make a flat paint, their particles may extend outside of the oleoresinous vehicle film into the air; they are surrounded with air having an index of refraction of 1, which would therefore give them some hiding power. However, in paint technology, this class of pigments is considered in the non-hiding power classification, simply because when completely surrounded by an oleoresinous film, they show little, if any, hiding power.

Hiding Power of Paint

The above description of hiding power, of course, is the most simple conception of pigment hiding power. It would be impossible, in a limited space, to give a full discussion of hiding power. It should be pointed out that hiding power of pigments should be applied and considered only in respect to the hiding power they produce in a given paint or protective coating film. There are many interesting and fascinating problems and conceptions of hiding power, but the fundamental and essential hiding power is that exhibited by the paint film. We know that the hiding power of a paint is dependent on the pigment particle size, pigment dispersion in the film, the concentration of pigment in the film, the thickness of the film, and many other considerations.

There are two distinctions, however, in the hiding power of a paint which should be made at this time, namely wet and dry hiding power. When the film of paint is first applied before the solvent portion of the vehicle has been evaporated or driven off, the paint has a hiding power known as "wet" hiding power. As the paint film dries, solvent evaporates, the binding medium may be oxidized or chemically changed, and pigment changes may take place; finally a dry, firm film of paint is obtained. The hiding power of such a film is known as its "dry" hiding power. "Wet" and "dry" hiding powers of paints may be exactly alike or widely different. "Wet" hiding power is essential so that the workman may observe the quality of his work. "Dry" hiding power is the final obscuring value of the paint. In flat or "matt" finish paints, the amount of binder may be inadequate to cover all pigment particles and some particles protrude into the air, with a lower index of refraction. This phenomenon develops further hiding power in the paint film. Such hiding power is known as "flat dry hiding power."

EXTENDER PIGMENTS

With this introduction as to general nature of pigments and their purpose in the paint system, we come to the specific group of pigments to be considered, namely those of low refractive index. In the past ten years, this group of pigments has come into far greater prominence than it has enjoyed in the entire history of paint manufacture. In the past they were known as fillers, extenders and inerts. The term "inert" is inapplicable because it implies chemical inertness, which is not true of many of the pigments of this class. The term "filler" implies adulteration, and though some conservative paint technicians may still consider these products as fillers, they are becoming more and more definite components of paint; they are not adulterants, but are expressing their value in paint quite widely. The term "extender" was applied to these pigments because they were used to extend the hiding power white pigments and colors so that these prime pigments could be more economically used or could be processed more economically. The term is not entirely satisfactory because it still implies that these products have no value other than the extension of the hiding power pigment. We prefer to use the term "extender pigment" largely because we want them to be classed as true pigments, which they are, yet to imply that generally speaking they are not pigments which will induce hiding power in a paint. Therefore, this group of low refractive index pigments will be called "extender pigments."

It was stated before that the incorporation of pigments into a paint is carried out not only to produce hiding power or color, but to develop in the paint and the paint film certain characteristics which are definitely of importance in the application, durability, appearance and cost of the paints. The place of the extender pigments in the paint system lies in this field of developing paint characteristics and developing economical paints, rather than in producing hiding power, though at times they may be called on to act as hiding power pigments.

A few points of interest will help to develop the recent history of extender pigments and to emphasize the position of extender pigments in the paint industry. For some years, paint formulators were anxious to obtain a pigment which could provide a large increase in the consistency, increase the yield value of paint, or develop "build" in the paint film without materially affecting its gloss and hardness. Such a material is desired in protective coatings which, by virtue of other specifications must, of necessity, have low pigment volume and a low pigment concentration. A producer of extender pigments has produced a colloidal calcium carbonate which meets this demand.

In 1930, the value of incorporating magnesium silicate in outside house paints was just coming to be realized. Prior to that time, it had been used largely to cheapen the paint, since it sold for approximately a cent a pound, whereas hiding power pigments sold for many times that. Continuous research has shown that this extender pigment has very definite values in the inhibition of cracking of outside house paints; so that even though magnesium silicate does keep down the cost of outside house paints, it adds definitely better durability characteristics to them.

General Properties of Extenders

In the light of present-day technology, extender pigments have the following general descriptive properties.

Color. Pigments of high dry brightness are, of course, desired and preferred. In practice, pigments with as low dry brightness as 70 per cent and as high as 98 per cent are used. An important factor in brightness or color of an extender is its tint. Some pigments have a yellow or brown tint, while others have a blue or gray undertone. The preferable pigment is one with a high brightness and a neutral tint. It is also essential that the pigment be fast to light and not accelerate the yellowing tendency of the paint vehicle.

In the testing of extenders for color, a common practice is to mix or rub them up in linseed oil for comparison of color with a standard or similar product. Because of the very slight hiding power of the extender pigment, this method does not give a true comparison. Testing for brightness or color of extenders is much more easily carried out by comparative test in the dry state. Such dry testing shows more clearly the actual color development accruing in a paint from the extender pigment than the information obtained from rub out in oil.

Specific Gravity. It is preferable that an extender pigment have as low specific gravity as possible. This allows for higher paint yields per pound of pigment, since the lower the specific gravity, the higher the bulking value per pound of pigment. Except for one class, most extender pigments have a specific gravity from about 2.5 to 3.0. For what it may be worth, the relation to settling, as Stokes Law may apply, pigments of low specific gravity also have a lesser tendency to settle.

Particle Size and Shape. In the field of extender pigments, we have quite a wide range of particle sizes and shapes. Some widely used pigments show quite a residue on a 325-mesh screen, indicating that particles of the pigment are, or may be, above 44 microns in size. There are also pigments used as extenders which have very small particles down to 0.04 micron.

A brief mention of particle size and its measurement should be made. There has been a great deal of discussion in the literature concerning the determination of particle size and shape and its importance on pigment properties. If one follows closely the data presented, it will be evident that there is a great deal of conjecture based at times on assumptions which can be said to apply very narrowly. From a practical standpoint it is important that these assumptions be kept in mind; but the facts must be scrutinized fully when pigments of different chemical composition are to be compared.

In the field of extender pigments there are spheroid shapes, needle-like, micaceous and fibrous pigments, at least.

Reactivity. To be a satisfactory extender pigment, the pigment should not react excessively with the other components of the paint system, particularly the vehicle components. Likewise, the pigment should contain as low a percentage of water-soluble salts as practical. Adsorbed or occluded salts may act as reactants in the paint system or may be washed out when the paint system is exposed to the weather, or to water by washing or immersion. Actually, the extender pigments used commercially vary widely in reactivity with some pigments actually on the acid side, namely many china clays and others distinctly on the alkaline side, such as the precipitated calcium carbonates. On the other hand, it should be remembered that it is possible to have a neutral pigment with relatively high water solubility, such as calcium sulfate.

Binder Demand. For years the paint industry has been determining the oil absorption of pigments by a number of testing methods. Essentially, these test methods determine the weight of oil or other binder required to make a paste of some flow characteristics, with a unit amount of pigment. The mixing, rubbing or grinding method used to mix the pigment and oil is the governing procedure of the testing method. In any event, the pounds of oil required to make a typical paste of 100 pounds of pigment is determined.

It can be conceived, for academic discussion, that we have determined the oil necessary to fill the void space between particles of pigments. It can be conceived that this is the oil necessary to cover the surface of pigment particles defined and separated by the force used in the testing procedure. If these two conceptions are used solely, oil absorption should increase as pigment fineness increases. For the pigments of the same chemical composition or same manufacturing history, it generally follows that as particle size decreases, surface area increases and oil absorption increases.

However, a further conception should be considered, namely the ability of the pigment surface to adsorb the vehicle molecules and molecular agglomerations to its surface. If the pigment surface is highly active to part of the molecular structure of the vehicle, it can be imagined that forces can be set which produce structures which improve flow and reduce the amount of binder necessary to make a paste. It can be conceived that two pigments of the same chemical composition, but subjected to differences in temperatures and pressures during manufacture, might readily have different surface characteristics and thus have different amounts and types of energy available for attracting or repelling the binder from its surface.

To summarize, the amount of binder required to make a paste of a given amount of pigment depends on its particle size and the pigment's ability to accept binder at its surface.

It can readily be seen that the greater the binder demand of the pigment, the thicker will be the consistency of the paint made with this pigment and a given amount of binder. Except in the cases where the pigment "leafs," as is the case with aluminum powder, the higher the binder demand of the pigment, the more binder is required to produce a continuous paint film. Paints which must have gloss and luster, nonpermeability to water and washability and exterior durability, must have a reasonably continuous film.

In the field of extender pigments, particularly, and in many white pigments and colors, binder demand becomes of fundamental economic importance. Extender pigments as a whole are cheaper per gallon than the paint binder. For example, 22.6 pounds of calcium carbonate extender pigment are needed to produce a gallon of pigment when completely wet by liquid, as in a paint. (Specific gravity x 8.33 wt. of gal. of water or 2.71 x 8.33) at 2.0 cents per pound, a gallon of pigment, $CaCO_3$ costs 45.2¢. A gallon of linseed oil costs approximately 7.5 pounds x 30¢ per pound.

It can readily be seen that a pigment of low cost with low specific gravity and low binder requirement is economically desirable. It should also not be forgotten that a pigment of high binder demand and producing a thick consistency per pound of pigment may be cheap because it allows the use of a larger amount of cheap vehicle solvent to be used before a satisfactory paint film can be laid down, or until adequately thin consistency is developed for application.

In the discussion of binder demand we have illustrated the subject by a comparison with oil absorption testing. It should not be implied that oil absorption tests can discover completely the binder demand of pigments. Such tests can be brought to good use as indices of binder demand, but characteristic consistency determinations, "enamel hold-out" or recoatability tests and washability tests more nearly establish a comparative basis.

PIGMENT MANUFACTURING

Pigments are manufactured by grinding and processing of naturally occurring raw materials or by chemical precipitation and processing. Natural materials are mined or quarried, classified and concentrated as ores, then subjected to grinding by dry or water-grinding systems and classified for particle size in some cases. The chemically precipitated materials are first precipitated, then filtered, washed and dried, disintegrated and packaged. In the processing of many pigments, the distinct step of calcination or firing at elevated temperatures is essential for the development of pigment properties. For example, lithopone, a mixture of barium sulfate and zinc sulfide, is made by reacting barium sulfide with zinc sulfate. The freshly precipitated material does not have commercially valuable properties, but when calcined at temperatures about 750°C it develops pigment properties. Some pigments are made both by grinding natural ores as well as by chemical precipitation—for example, calcium carbonate. Similarly, extender pigments are made by grinding and chemical precipitation and in some cases, processing by calcination is employed. In Table 12 is given a list of some common extender pigments together with their important properties.

Silicate Pigments

The largest group of extender pigments are those produced from silica or the silicates, particularly of aluminum and magnesium.

Silica itself is used in two forms commonly known as amphorous silica and diatomaceous silica. Amphorous silica is produced by grinding natural deposits of quartz. The use of silica in paints is limited largely to wood fillers, undercoat or priming paints, house paints and floor paints. Its abrasive nature and the health hazards involved limit its use. It is chemically inert and gives good "tooth" to priming coats.

Table 12. Extender Pigments

Pigment	Approximate Chemical Composition	Refractive Index	Specific Gravity	Bulking Value Gal. per pounds	Oil Absorption
Silicate Pigments					
Silica	SiO_2	1.55	2.6	0.0460	25.0
Diatomaceous Silica	SiO_2	1.40–1.50	1.95–2.35	0.0615–0.0510	25.0–150.0
Clay	$Al_2O_3.2SiO_2.2H_2O$	1.56	2.60	0.0460	36.0
Pyrophyllite	$Al_2O_3.4SiO_2.2H_2O$	1.588	2.85	0.0422	
Talc	$2MgO.4SiO_2.H_2O$	1.59	2.85	0.04212	27.0
Mica					
Muscovite	$K_2O.3Al_2O_3.6SiO_2.2H_2O$	1.59	2.5–3.0	0.04272	47.5
Phlogopite	$K_2O.6MgO.Al_2O_3.6SiO_2.2H_2O$	1.606	2.5–3.0	0.04365	24.0
Barium Sulfate Pigments					
Ground Barytes	$BaSO_4$	1.64	4.476	0.02650	6.0
Blanc Fixe	$BaSO_4$	1.64	4.35	0.02753	14.0
Calcium Sulfate Pigments					
Gypsum	$CaSO_4.2H_2O$	1.53	2.35	0 05107	21.0
Anhydrite	$CaSO_4$	1.59	2 95	0.04070	25.0
Precipitated Calcium Sulfate	$CaSO_4$	1.59	2.95	0.04070	50.0
Calcium Carbonate Pigments					
Precipitated Types					
Colloidal	$CaCO_3$	1.63	2.68	0.0448	55.0
High Oil Absorption	$CaCO_3$	1.63	2.68	0.0448	40.0
Low Oil Absorption	$CaCO_3$	1.63	2.68	0.0448	17.0
Surface Treated	$CaCO_3$	1.63	2.65	0.0453	15.0
Natural Types					
Calcite					
Water Ground	$CaCO_3$	1.60	2.71	0.0443	15.0–6.5
Dry Ground	$CaCO_3$	1.60	2.71	0.0443	9.0
Limestone	$CaCO_3$	1.60	2.71	0.0443	10.5
Imported Chalk	$CaCO_3$	1.60	2.71	0.0443	12.5

Diatomaceous silica made by grinding and processing deposits of diatoms, geological remains of unicellular plants, has in recent years been used widely in the paint industry. Its high binder demand, ability to produce low sheen paints, and chemical inertness are significant. It is used in emulsion paints, flat paints and traffic paints where complete flatness or low sheen is required. During the war, it was used widely in camouflage paints. It is used to impart a large increase in consistency to the paint system by use of small quantities of pigment.

Hydrated aluminum silicates make up the second group of extender pigments. This group of pigments consists of the *clays,* commonly called china clays in the paint industry, and *pyrophyllite.* This group of pigments is obtained by grinding and processing natural deposits of kaolin or pyrophyllite. There are quite a number of commercially available clays which vary in composition and physical properties. All types of these products are distinguished by their micaceous or plate-like particle shape, their very fine ultimate particle size, and their ability to produce thixotropy in paint systems employing water as a part of the vehicle. Pyrophyllite is distinguished from clay by a definitely larger particle size.

China clays are used largely in water or emulsion paints because of the thixotropy and dry hiding power they induce to such paints. Likewise, paper and textile coatings employ clay. Metal undercoaters and other priming paints are often made with clay. Similarly, pyrophyllite is used in such products, but its larger particle size induces greater cracking resistance. Pyrophyllite has good durability in outside house paints.

Talc, more generally called *magnesium silicate* is used widely in protective and decorative coatings. It is produced by grinding and processing natural deposits and occurs in two particle shapes, fibrous and micaceous. Commercial products generally contain particles of both types. Talc is the standard extender for outside house paints because of its ability to inhibit cracking. Because of its chemical inertness, low cost, good settling characteristics and good durability, talc is used in all types of paints except those of relatively high gloss. Recently, exceptionally fine-ground products have reached the market and the field for this pigment has widened.

Mica, until recently, was confined in its use to coatings for asphalt shingles, wallpaper and paper coatings, rubber coatings and similar products. Outside house paint studies have shown mica, particularly of the water-ground muscovite type, to be the best pigment for the inhibition of cracking. In emulsion and water-thinned paints, mica is used to improve crack resistance and brushing characteristics. The partially kaolinized phlogopite type of mica is relatively new in the field, but is characterized by the same plate-like structure, though smaller particle size, and finds use in many of the same items as does muscovite mica. Both products are made by grinding and processing natural deposits.

Barium Sulfate Pigments

Two pigments are made from barium sulfate—*ground barytes* and *blanc fixe*. Ground barytes is made by grinding and processing natural deposits of barytes. Two types are on the market—"crude" and "bleached" barytes. Bleaching is carried out by treating the crude material with acid, which dissolves impurities such as iron, and thus improves the brightness of the pigment. Barytes is used where its chemical inertness and high specific gravity are required. Formerly, when the weight of a gallon of paint was a selling point, barytes was widely used. Now it is confined largely to acid-resistant paints, metal and wood primer coatings.

Blanc fixe is not used widely *per se* in the paint industry, but is used in inks and leather coatings. As a component of lithopone and titanium pigment barium base and as a base for extended colors, it is widely used. It is made by chemical precipitation and has a very fine particle size. It is chemically inert, but commercial products must be highly controlled to maintain low adsorbed or occluded water-soluble compounds.

Calcium Sulfate Pigments

Calcium sulfate extender pigments have been used for centuries in paint making, but except in the composite forms of titanium pigment calcium base or Venetian Reds, they have never been used widely. Even today, the supplies of gypsum (the hydrated form) or anhydrite (the dehydrated form) are commercially small as separate extender pigments. Nevertheless, calcium sulfate has excellent pigment properties. It can be made from naturally occurring deposits of gypsum or by precipitation, and has high brightness and high bulking value. It shows fairly good durability characteristics and flocculates in orthodox paint systems when water is added to induce false body and good brushing characteristics. Coupled with a hiding power pigment such as titanium dioxide or iron oxide, it is used in practically all types of paints, both interior and exterior. Caution must be exercised when it is incorporated in paint systems which contain water or are subjected to water immersion or high humidity conditions.

Calcium Carbonate Pigments

The last group of extender pigments is made from *calcium carbonate*. Extender pigments are made (1) from the natural deposits of calcium carbonate, calcite, limestone and chalk, and (2) by grinding and precipitation by a number of chemical reactions and further processing. The high brightness, low specific gravity, wide availability and low cost make these products the most widely used extender pigments today. They are used in all kinds of decorative and protective coatings from inks through dry cement and casein paints and paper and textile coatings, to fine gloss enamels and house paints. They are used in putties, caulking and glazing compounds, wood fillers and similar allied products. The only limiting factor in the use of these products is that they cannot withstand highly acidic conditions either in manufacture of the coating or during the application or use.

As a consequence, there are on the market today a great variety of calcium carbonate extender pigments which are designed for specific uses. No attempt will be made to describe any of these products specifically. Several examples are listed in Table 12 which are representative of this group of products. It will suffice to state that in this group of pigments there is a wide range of particle size and distribution; there are pigments of exceptionally high binder demand and those of exceptionally low binder demand. In this group of pigments are products designed to give paints of low sheen and those of the highest gloss.

Specific Extenders

Any discussion of extenders for protective coatings would not be complete without mentioning certain pigments which are not used widely in paint manufacture, but are used in allied industries, particularly in printing inks. Generally speaking, these pigments are chemically reactive with paint vehicles and are consequently used in small amounts to effect specific paint or ink properties. Reference is made to such compounds as magnesium oxide, magnesium carbonate and basic carbonate, barium carbonate, aluminum hydrate and gloss white (a mixture of aluminum hydrate and blanc fixe).

The Future of Extender Pigment Technology

Mention has been made of the importance of the binder demand of pigments. The conception that such paint film properties as durability, washability, elasticity, impermeability and abrasion resistance are a function of the binder held by the pigment particle in relation to the so-called "free" binder is relatively new. Work is only just beginning in this field. The present world shortage of fats and oils will greatly accelerate the study of this field, particularly as it applies to extender pigments, since such studies will conserve drying oils and tend to reduce the cost of paints. It is significant in Table 12 that naturally occurring extender pigments generally have lower binder requirements than the same pigments made by chemical precipitation. Secondly, in the past two years, more attention has been drawn to the effect of reactivity of the water-soluble components of pigments, again particularly extender pigments, on paint properties. Work carried out on this phase shows great promise in developing new and better extender pigments.

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Chapter 5

White Hiding Pigments

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In this chapter there will be a general consideration of the various white hiding pigments in common use. This subject is a very large one; therefore it will not be covered completely but only the more important points will be considered. There isn't any good short definition of what we mean by a white hiding pigment. However, it may be defined as a material which "tends to color something white."

In order to clarify the topic under consideration it is best to list the white hiding pigments which will be taken up. The following are included:

White lead (basic carbonate)
White lead (basic sulfate)
Zinc oxide
Leaded zinc oxide
Lithopone
Zinc sulfide
Titanium-barium pigment
Titanium-calcium pigment
Titanium-magnesium pigment
Titanium dioxide (Anatase)
Titanium dioxide (Rutile)
Titanated lithopone
Zinc sulfide-barium
Zinc sulfide-calcium
Zinc sulfide-magnesium
Antimony oxide
Lead titanate
Basic lead silicate
Zirconium oxide
Lead tetra-phosphate

Of these 20 white pigments, white lead is the oldest, while titanium dioxide (pure and extended) is the most important today. The last three are relatively new in the pigment field. Probably more will be learned about these in future years.

Figures 2 and 3 summarize the production figures of three important white pigments. A study of these graphs reveals interesting information on the production of these materials. Attention is called to the effect of the depression years and how the introduction of a new pigment tends to affect one already in production.[*]

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[*] For a more complete review of white pigments reference should be made to Mattiello's "Protective and Decorative Coatings," Volume II, John Wiley & Sons, 1942.

As mentioned above *White lead* is the oldest white pigment in use today. It was known at least 400 B.C. The first plant in America was built in 1804 by Samuel Wetherill & Sons in Philadelphia. There have been recent advances in the improvement of manufacture which is enabling the industry to make better white lead pigment. It is manufactured by five different processes. These vary primarily in the type of raw material used.

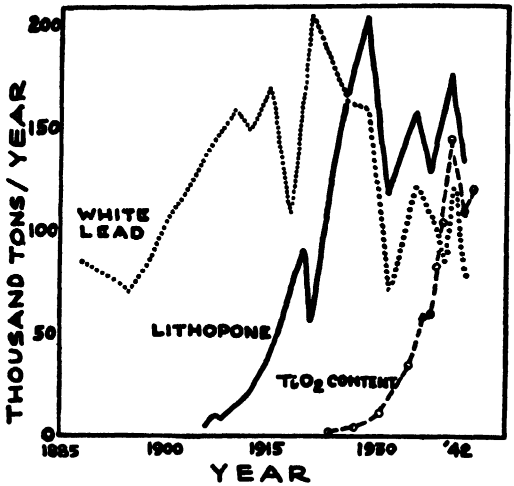

FIGURE 2. Some white pigment sales.

The oldest process is probably the Dutch process, which uses refined metallic lead in the form of perforated discs. It takes about three months to make the white lead. The Carter process dates from 1885. It uses powdered lead in revolving wooden cylinders and takes only 12 days. The Euston process puts the refined lead in solution and precipitates the white lead. Feathered lead is used as the raw material, which is made by running molten lead into water. The Sperry process is the electric process using a lead anode and iron cathode. The electrolytes, sodium acetate and sodium carbonate, are separated by a membrane. The Thompson-Stewart process is a recent development similar to the Carter process in that lead oxide is formed. However, all the lead oxide is first formed; then carbon dioxide is added and controlled to form a definite chemical compound: $4PbCO_3.2Pb(OH)_2.PbO$.

Basic carbonate white lead has the ability to impart adhesion, toughness, elasticity, and durability to a paint. It is used in various types of paint, principally in exterior paints. Basic carbonate white lead is the only white pigment which will produce a durable exterior paint if used alone without other pigments. A large proportion of the total white-lead production is used in white-lead pastes, which are thinned to paint form by the painter or other consumer. The two types of commercial white-lead paste are heavy paste and soft paste. The first is composed of about 91 per cent white lead and 9 per cent linseed oil, while the latter contains about 89 per cent white lead, 9 per cent linseed oil, and 2 per cent turpentine. The linseed oil used is refined oil with an acid number of 6 to 12.

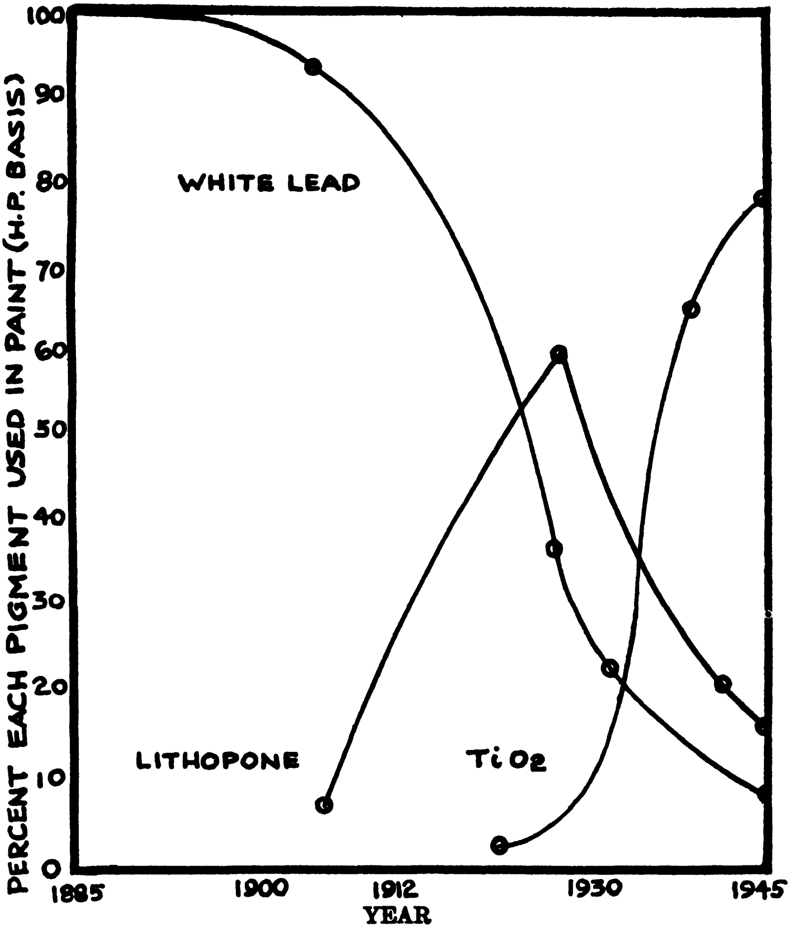

FIGURE 3

About 95 per cent of the total production of white lead is consumed by the paint industry, with a small amount used in putty and by the ceramic and other industries.

Basic lead sulfate is quite widely used as a paint pigment. It is called white basic lead sulfate, basic sulfate white lead or "sublimed white lead." White basic lead sulfate is a quite recent pigment in comparison to basic carbonate white lead. It was originated in 1855 by E. O. Bartlett. He was at that time making zinc oxide directly from zinc ores by the American process. Applying the same principles to the production of a lead pigment from lead ore, he found that it was possible to produce a white powder having pigment properties.

The first plant was built in 1876 in Joplin, Missouri, where lead ore deposits were sufficiently free from other metals for the production of white basic lead sulfate. It is manufactured by two processes, called the fume process and the chemical process; these are self-explanatory as far as manufacturing is concerned. Almost the entire production of white basic lead sulfate goes into mixed-pigment exterior paints, either directly or as the basic lead sulfate portion of blended leaded zinc oxides.

White basic lead sulfate, like basic carbonate white lead, has the ability to impart to paints adhesion, toughness, elasticity, and durability, but is not as effective in this respect as is the basic carbonate. In exterior mixed-pigment paints, it is used principally as a substitute for basic carbonate white lead.

White basic lead sulfate may be used for the "white lead" content of many specification paints, such as Federal Specification paints TT-P-40 and TT-P-81. White basic lead sulfate is a less expensive pigment than basic carbonate white lead, and this has been an influencing factor in its use. White basic lead sulfate is not generally used for single-pigment paints or pastes but is used in conjunction with other pigments in ready-mixed exterior paints. Ninety-seven per cent of the total production of this material is used in the paint industry, the remaining 3 per cent being used in the rubber and other industries.

Zinc oxide pigments are made primarily by either the American or French process. In both these processes the characteristics of the pigment are determined by:

(1) The temperature of the oxidation of the fume;
(2) The time the zinc oxide is held at a high temperature;
(3) The composition of the gases;
(4) The rate of cooling.

The French process uses purified metal which is melted and vaporized at 1650 to 1850°F under controlled conditions. The main difference in the American process is that this process uses ore instead of refined metal.

However, the effects for which it is used in paints can be summarized, together with the known or suggested explanations for the results:*

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* See Mattiello, "Protective and Decorative Coatings," Volume II, John Wiley & Sons, 1942, pages 373 and 374.

"Use of Zinc Oxide in Paints
(Nelson-Mattiello)

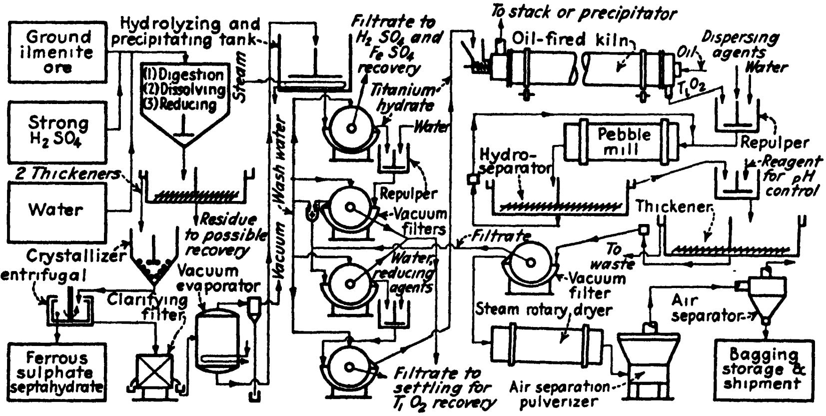
To aid mixing and grinding
Consistency control
Penetration control and sealing
Drying
Hardening or solidifying the film
Gloss and gloss retention
To minimize discoloration and yellowing
Reduced chalking
Color and tint retention
Dirt shedding (self-cleansing), washability, and ease of polishing
Mildew control
Resistance to moisture and to blistering under moist conditions
Neutralizing and inhibiting"

Leaded zinc oxide was first introduced into the paint industry about 1896 as a result of developments on smelting Colorado complex zinc and lead ores. With improvements in the manufacturing process the product was standardized. Several grades were developed containing 5, 20 and 35 per cent lead sulfate and basic lead sulfate, the remainder being zinc oxide. The more recent developments have been the introduction of a 50 per cent grade of leaded zinc and the manufacture of leaded zinc oxides by blending white basic lead sulfate and lead-free zinc oxide. A considerable portion of the leaded zinc oxide on the market today is entirely or in part a mechanical mixture. Practically the entire production of leaded zinc oxide is used by the paint industry. It is used in conjunction with other white pigments in exterior house paints. When leaded zinc oxide is used in a paint it usually furnishes the entire amount of zinc oxide required in the particular paint.

Co-fumed leaded zinc is made in the same general manner as American process lead-free zinc oxide. Dry-mixing zinc oxide and basic lead sulfate in the proper proportions yields blended leaded zinc oxide.

Lithopone was not very important for some time after its introduction. This is often characteristic, and some attribute this condition to the fact that people do not like to make changes. However, the fact that lithopone was not light-stable prior to about 1920 no doubt had a definite effect on its acceptance. The improvement in lithopone at this time was very marked and made it possible for the material to be used much more widely than previously. Lithopone is primarily used in paints, rubber, textiles, paper and printing inks. It is receiving very stiff competition from titanium dioxide and extended titanium dioxide.

High strength lithopones are made by blending lithopone with zinc sulfide or titanium dioxide. The former are made in several "strengths," the 50 to 55 per cent zinc sulfide grade being the most popular. This is also known as zinc sulfide-barium pigment. Blends with titanium dioxide are called "titanated lithopones," and usually contain about 15 per cent of titanium dioxide. Also in this same class are the zinc sulfide-calcium and zinc sulfide-magnesium pigments; these are blends of zinc sulfide with calcium sulfate or magnesium silicate.



(From *Chem. & Met.*, Vol. 42, Nov. 1935)

FIGURE 4. Titanium dioxide pigment.

Zinc sulfide is a relatively high-strength pigment, but it has not been used as widely as the blends with lithopone or extenders.

Extended titanium pigments were introduced shortly after World War I. First to be produced was titanium-barium pigment, consisting of 25 per cent titanium dioxide and 75 per cent barium sulfate. Later came titanium-calcium pigment, with 30 per cent titanium dioxide, and a 30 per cent titanium-barium pigment. Relatively recently, titanium-magnesium pigment (30 per cent titanium dioxide and 70 per cent magnesium silicate) was made for use in house paints.

These pigments, particularly straight titanium dioxide, met great resistance because of their relatively high price per pound, and a long educational program was required to convince the pigment users that these prices were really low when considered on the basis of cost per unit of hiding power developed in the finished product.

Titanium dioxide has the highest hiding power of any of the white pigments, but its manufacture is more complicated and more expensive than any of the other pigments which have been considered. Figure 4 shows the manufacture of titanium dioxide pigment.* Examination of this flow sheet shows how complicated the manufacture of this pigment really is. In order to manufacture pigment of a high quality today, extreme care must be taken in all steps, and impurities controlled very accurately.

Previously the subject of hiding power was mentioned. It is this quality of titanium dioxide that makes it very important in the paint field. The comparison of the hiding power of various pigments is given in Figure 5. There may be some disagreement in the actual values of hiding power. This disagreement is due primarily to the fact that different conditions are used in measuring it. However, in general, the order given in Figure 5 will be found under usual conditions.

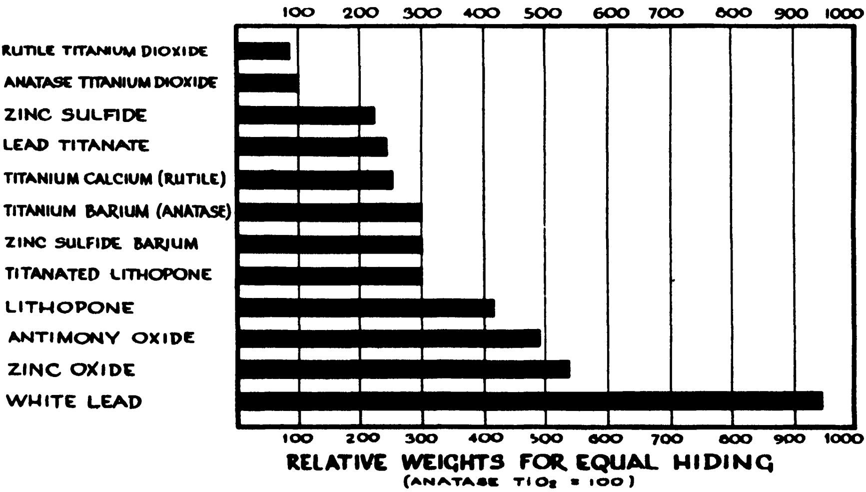


FIGURE 5. Comparison of the hiding power of various pigments.

Hiding power and economical use of pigments are very important today to all in the paint field. No one can get all the white pigment he wants. A paper was presented at the meeting of the American Chemical Society in September of 1946, on the subject: "The Economical Use of Titanium Dioxide"; Figures 6, 7 and 8 have been taken from this paper. They show the importance of understanding hiding power and of using pigments properly under these trying conditions. It is not thought advisable to go into this study in more detail in this chapter.

In 1941 rutile type titanium dioxide was offered to the trade. This

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* *Chemical & Metallurgical Engineering* (November, 1935).

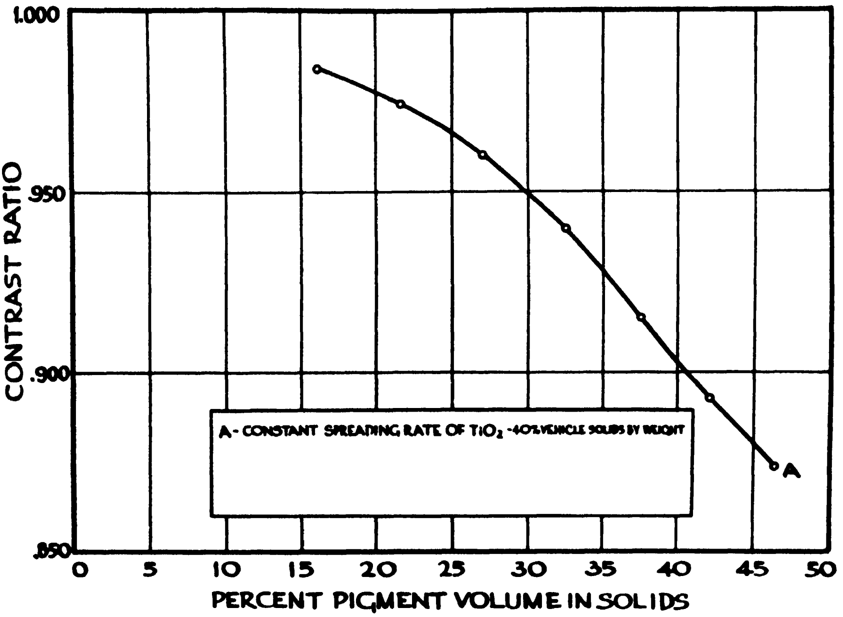

FIGURE 6. Hiding of rutile titanium dioxide in a urea-alkyd enamel.

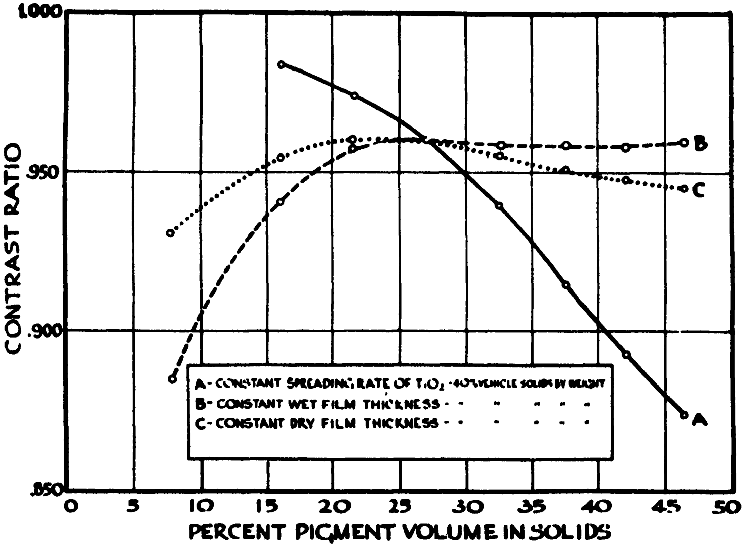

FIGURE 7. Hiding of rutile titanium dioxide in a urea-alkyd enamel.

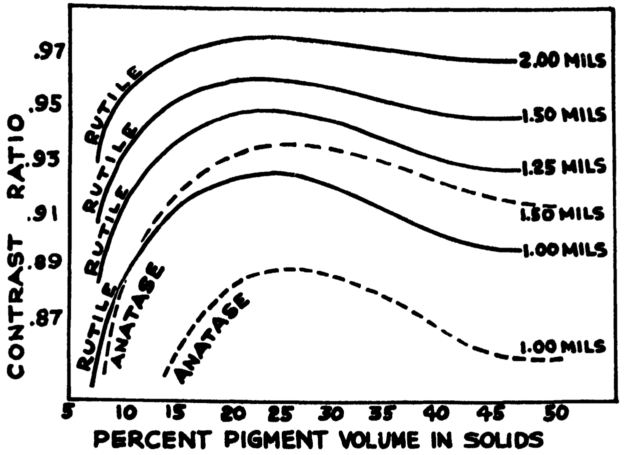

FIGURE 8. Hiding of titanium dioxide in urea-alkyd binder at several dry film thicknesses.

material has a definitely higher hiding power than the anatase form. Figure 9 shows the molecular structure of the two materials. The small balls represent titanium atoms; the larger balls, oxygen atoms.

So far we have considered titanium dioxide primarily from the manufacturing standpoint. Some may have the impression that titanium dioxide is used only in the manufacture of surface coatings. However, this material is very widely used as shown in the Table 13 below.

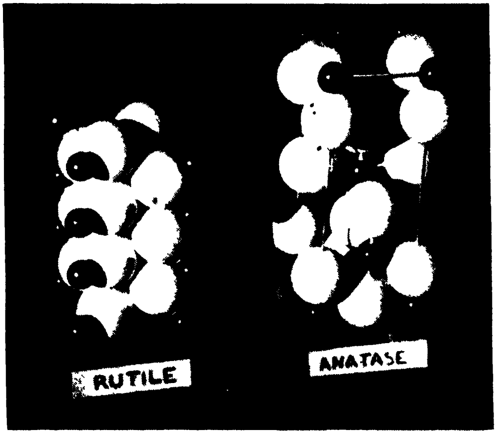

FIGURE 9

Returning to the comparison of anatase and rutile, it was stated that rutile has much higher hiding power than anatase. Tables 14, 15 and 16 and Figure 10 show the comparisons of anatase and rutile. There is a third form of titanium dioxide, Brookite. However, as far as we know this form has never been made commercially.

Table 13. Use of Titanium Dioxide Pigments.

- Paints (interior, exterior, industrial)
- Paper (beater, coatings)
- Floor Coverings
  - a. linoleum
  - b. printed
  - c. tiles
- Printing Inks
- Coated Fabrics
- Leather and Leather Finishes
- Rubber
- Plastics
- Delustering (Rayon and Nylon)
- Textile printing
- Ceramics (vitreous enamels and glass)
- Asbestos shingle coatings
- Roofing granules
- Wallboard coatings
- Shoe dressings
- Welding rod coatings
- Cosmetics
- Soap

Table 14. Properties of Anatase-Rutile Titanium Dioxide.

	Anatase	Rutile
Specific gravity	3.88	4.20
Bulking (pounds/gal.)	32.32	34.99
Refractive index*	2.53	2.71
Relative hiding power	100%	133%

* Average values, using monochromatic yellow light.

Table 15. Ratio of Spreading Rates of Rutile to Anatase Titanium Dioxide.

Equal Weight of TiO_2 at Equal Pigment Volume

Contrast Ratio	Vehicle B	Vehicle C	Vehicle E
0.96	123	128	125
0.90	127	121	122

Contrast Ratio	Vehicle F	Vehicle G	Vehicle H
0.96	117	115	121
0.90	121	117	122

Table 16. Hiding Power of Rutile and Anatase in Same Films Laid Down from Emulsion and from Conventional Paint.

Paint	Reduction	TiO_2	Dry H. P.	Wet H. P.	Brightness
Emulsion	2:13-Water	R	82.5	79.1	87.2
Emulsion	2:13-Water	Anatase	79.3	75.9	86.8
			3.2	3.2	0.4
Conventional	2:06-Min. spirits	R	87.5	82.3	88.2
Conventional	2:06-Min. spirits	Anatase	83.0	79.1	87.4
			4.5	3.2	0.8

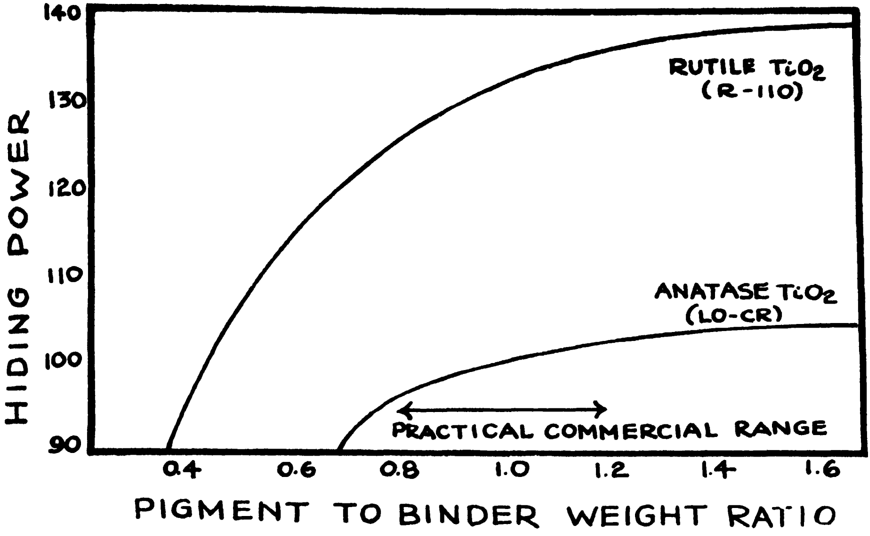

FIGURE 10. Relative hiding powers of urea-alkyd baking enamels (40 per cent urea; 60 per cent alkyd).

In this consideration of titanium dioxide so far mention has not been made of the fact that there are various grades of titanium dioxide pigments. Each of the manufacturing companies makes a number of different grades having specific properties with respect to use in paint or other materials. Whenever a pigment is used it is necessary to employ the right grade and the one best suited for the particular process.

Figure 11 shows the comparative chalking rates of some of the grades of titanium dioxide manufactured by the DuPont Company. The primary difference shown in this figure is the time when the material starts to chalk. In white house paints a material is desired that will clean

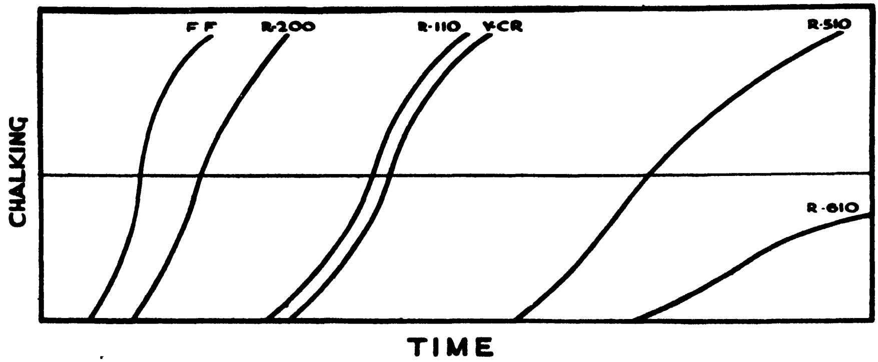

FIGURE 11

up, and therefore it must chalk freely. Such a material is anatase titanium dioxide. For automotive finishes a material is wanted that resists chalking; therefore the best selection would be "TI-PURE" R-610, based on Figure 11. Much more information of this type is available from the manufacturers of titanium dioxide to those interested. Table 17 compares the relative chalking characteristics of various grades of titanium dioxide as determined by exposure in an automotive finish. These results show how important it is to have the proper grade of material in the manufacture of a specific product.

Table 17. Fading of Automotive Enamels.

26 Months—Delaware 45°S—Air-Dry, Spray Alkyd
Milori Blue P/B (Anatase) = 1/1.11 P/B (Rutile) = 1/1.38

	Months									
	3	4	6	8	11	12	15	18	23	26
R-610	10	10	10	10	10	10	5	2	2	2
R-510	10	10	10	10	10	10	4	0	1	1
R-110	10	7	4	3	3	1	1	0	0	0
Y-CR	1	0	0	0	0	0	0	0	0	0

In the manufacture of automotive enamels it is very desirable to have high gloss. Figure 12 shows a comparison of gloss as the pigment concentration is increased. This shows that in many products the pigment concentration should be kept as low as possible in order to get high gloss. Low pigment concentration further tends to give better chalk resistance; but care must be taken not to exceed a critical point, as low pigment-binder ratio finishes tend to check and crack more rapidly than high.

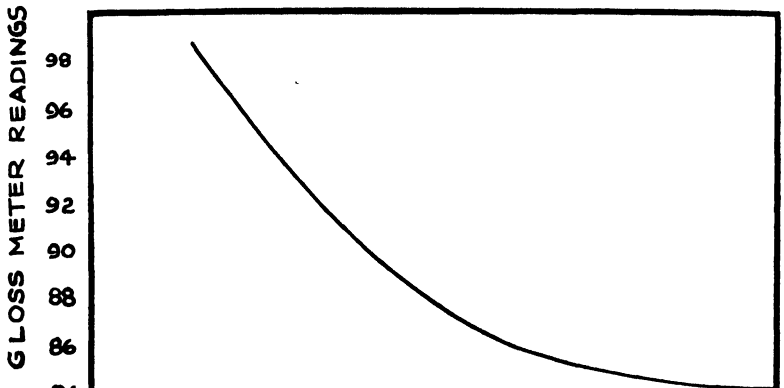

FIGURE 12. Effect of pigment/binder ratio on gloss. Rutile (R-110) and anatase (LO-CR) in urea-alkyd baking enamels (40 per cent urea; 60 per cent alkyd).

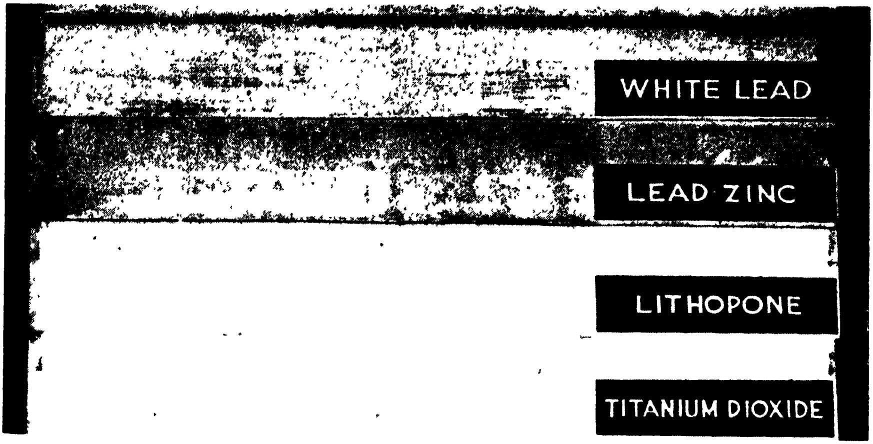

FIGURE 13. Delaware north vertical—1½ years, white.

It is impossible to discuss titanium dioxide without considering house paints. Figure 13 shows "150 years' history of house paints." The first sample is white lead, which was widely used at least 150 years ago and which has a certain amount of popularity today. The next improvement was lead-zinc, and this was followed by a lithopone paint. Finally we have a titanium dioxide paint which we believe is the best pigment to use in outside house paints today. It is understood that this material is formulated properly and contains leaded zinc oxide and inert substances.

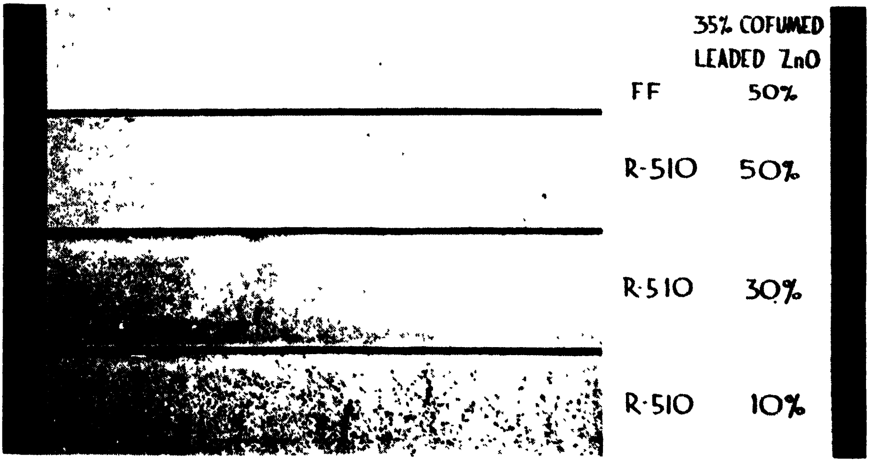

FIGURE 14. Delaware south vertical—2 years. TiO_2/35 per cent leaded, ZnO/Mg silicate, 35 per cent P.V., Z Linseed oil.

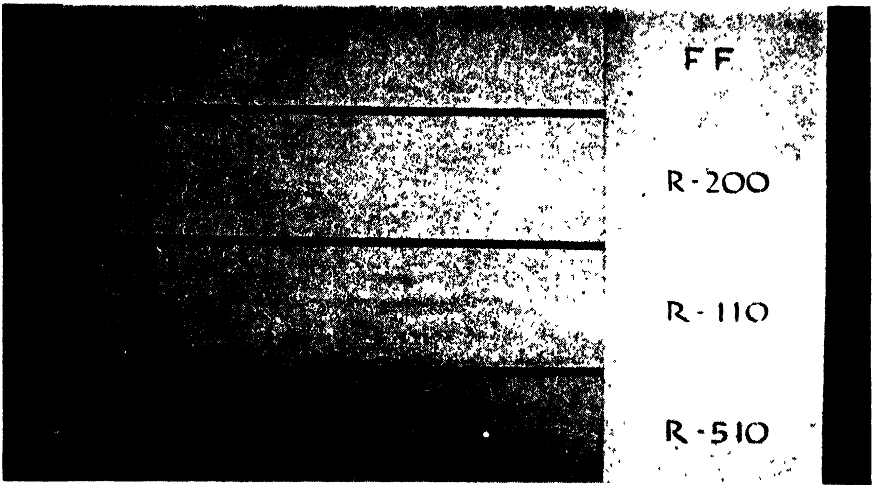

Figure 15. Delaware south vertical—2 years. TiO_2/35 per cent leaded, ZnO/Mg silicate (15/50/35) 35 per cent P.V.; Z-4 linseed oil.

In formulating house paints remember Figure 11. For a white paint, it is necessary to use a free-chalking pigment and for a tinted paint a chalk-resistant titanium dioxide.

In testing pigments and formulations it is very important that the testing include both North and South exposures. This is shown in Figure

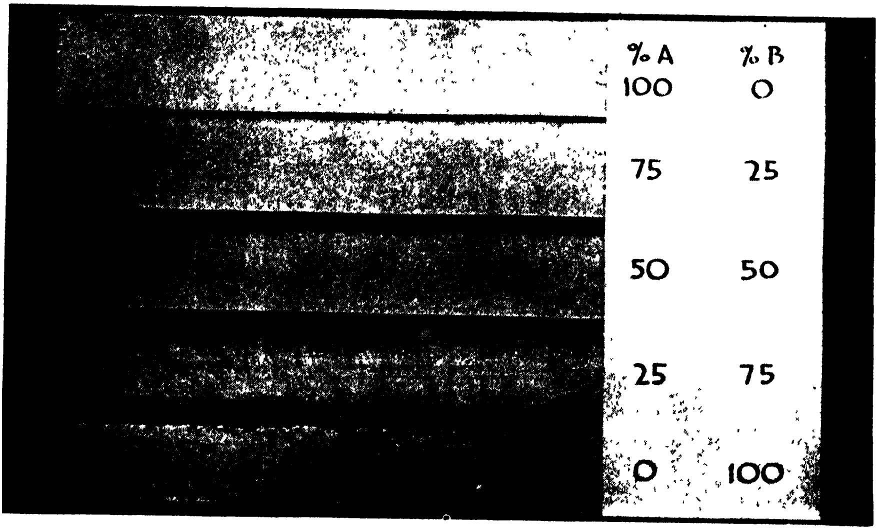

Figure 16. Delaware south vertical—2 years. A—TiO_2/35 per cent leaded, ZnO/Mg silicate (15/50/35). B—BCWL

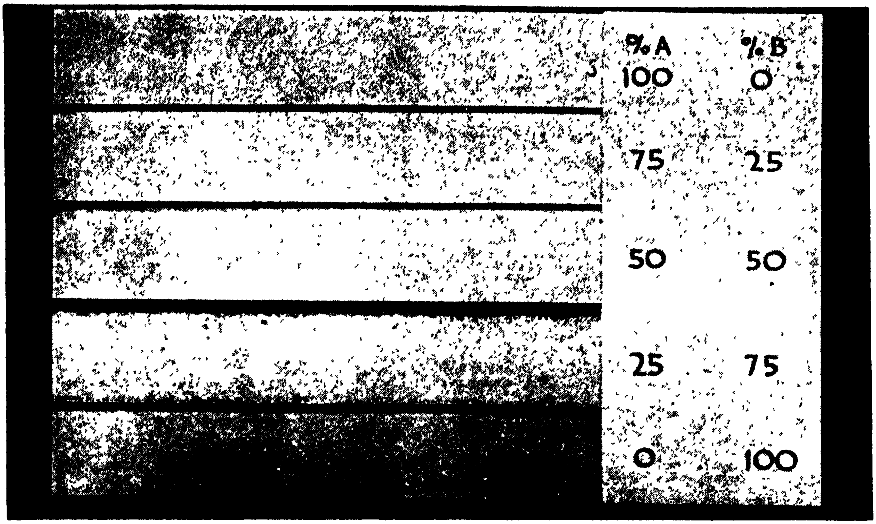

FIGURE 17. Delaware north vertical—2 years. A—TiO_2/35 per cent leaded, ZnO/Mg silicate (15/50/35). B—BCWL

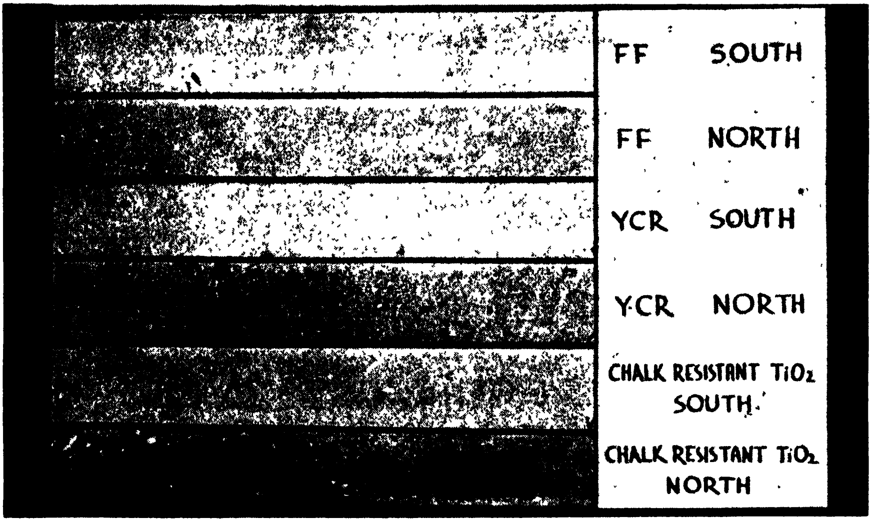

FIGURE 18. Delaware south and north vertical—2 years. TiO_2/Mg silicate/35 per cent leaded, ZnO/BCWL (15/22/18).

14. If only one exposure is made a definitely different story is obtained. Further, we do not believe that South 45° exposures are desirable for house paint. They give an accelerated picture but not a true picture, since the paints are normally applied to vertical walls. The importance of

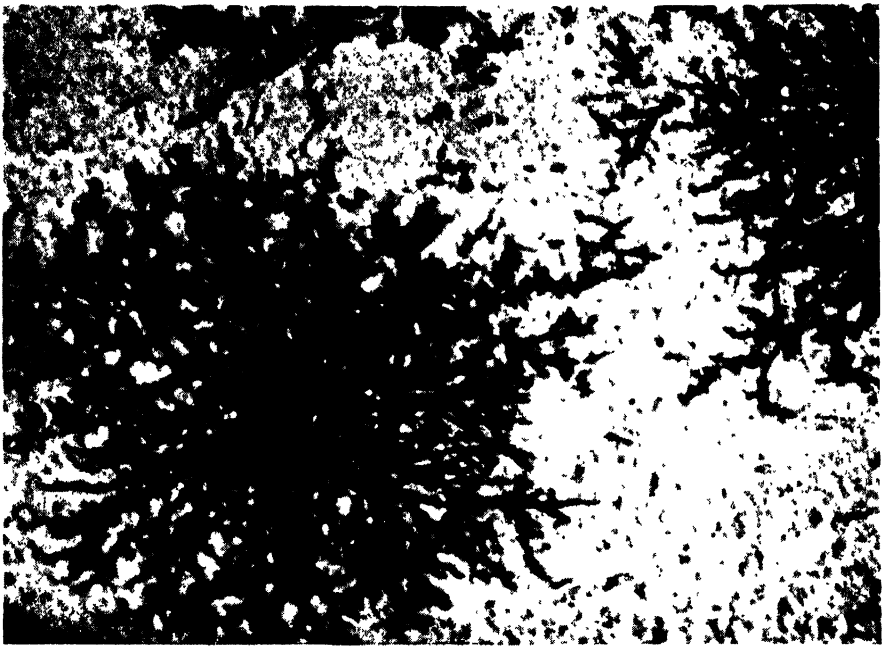

FIGURE 19

FIGURE 20. Delaware west vertical—4½ years—white repaint.

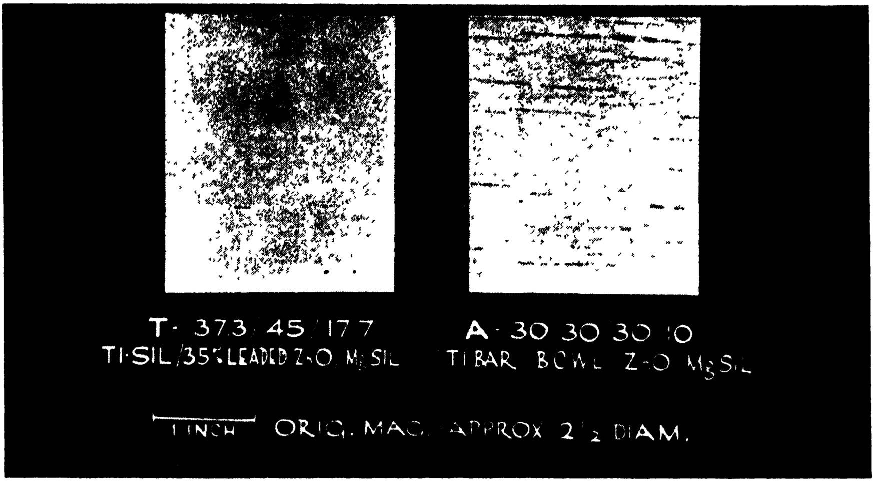

FIGURE 21. Delaware west vertical—4½ years—white repaint.

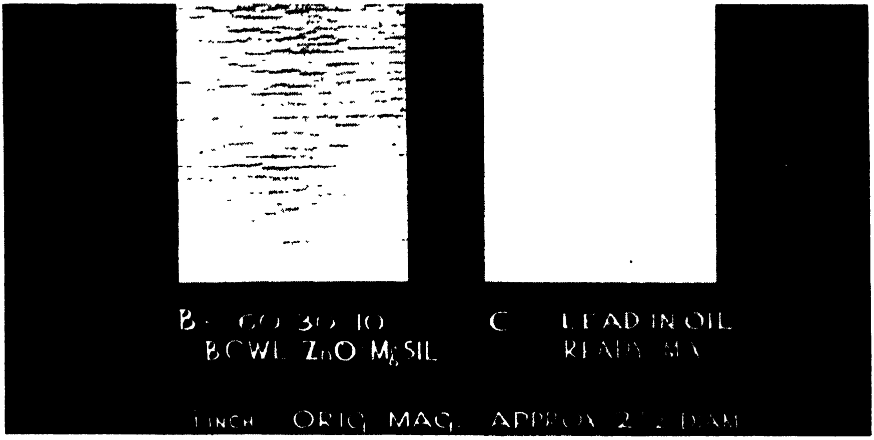

FIGURE 22. Delaware west vertical—4½ years—white repaint.

picking the right grade of pigment is shown in Figure 15. This figure shows that "TI-PURE" FF cleans up and stays much whiter than "TI-PURE" R-510, for example. Figures 16 and 17 are self-explanatory in that they show the improvement obtained by the elimination of basic carbonate white lead from outside house paints.

Figure 18 shows the necessity of having a paint which is resistant to mildew. Mildew may be controlled in the present day formulation by the use of zinc oxide or leaded zinc oxide. Figure 19 is an enlarged sample of mildew on a white house paint panel. Other means of controlling mil-

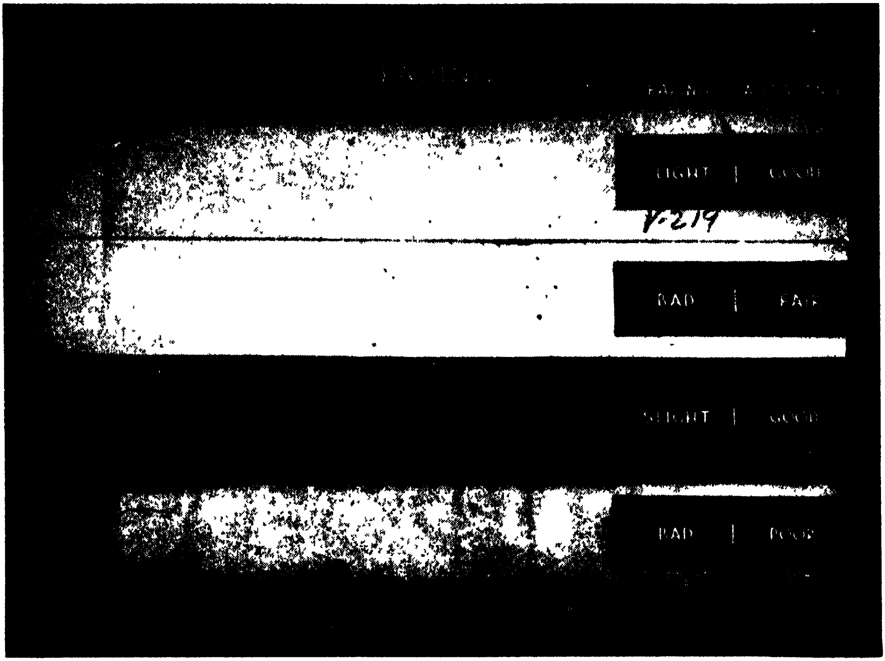

Figure 23

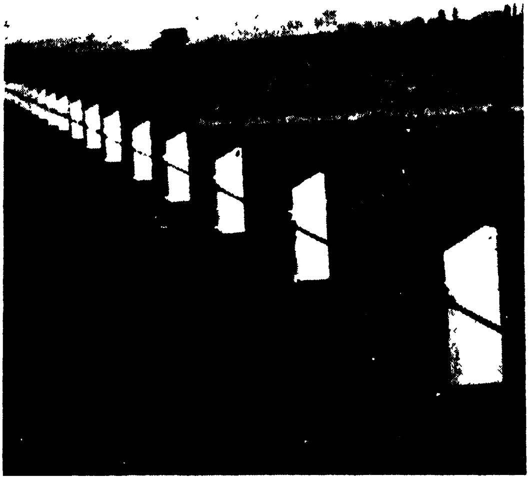

Figure 24

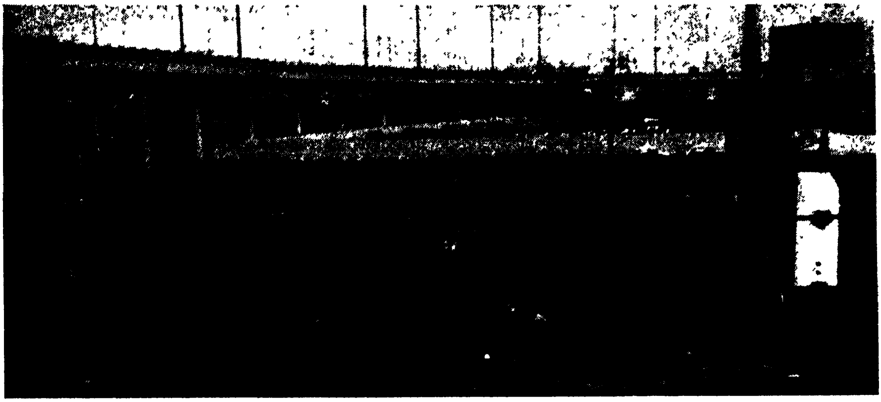

FIGURE 25

FIGURE 26

dew are very desirable and laboratories are working on this problem today.

Figures 20, 21 and 22 should be considered together. These show 4½ years' history on what we believe is one of the best outside house paints to date compared with three other currently marketed outside house paints.

The results indicate the importance of a properly formulated outside house paint to get optimum results.

Figure 23 illustrates what happens too often in the house paint field. A person buys a white paint and tints this gray or some other color. White paint is formulated to stay white. When this is tinted gray the material fades too fast and produces the bad fading illustrated in the figure. If one wishes a tinted paint, such a material should be purchased or one should be sure that the base used is meant for tinting purposes.

Figures 24 and 25 illustrate what happens when rail fences are painted with a properly formulated paint and with one which is not meant for an area containing hydrogen sulfide or a dirty area. The posts which remain white are formulated with a titanium dioxide pigment under proper conditions. The dark post contains material that turned black on exposure to the fumes in the area. Figure 24 shows the posts as originally painted and Figure 25 shows the same posts 2 years later.

This discussion shows the importance of properly testing all formulations. That is why emphasis is placed on the testing of pigments in all formulations. It further illustrates why it is necessary to maintain an elaborate testing farm like the one shown in Figure 26.

In summary, the important points of the white pigments have been reviewed. The necessity of checking and of being certain that the proper material is used under the proper conditions cannot be emphasized too strongly.

Chapter 6

Organic Toners and Mineral Pigments

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A few metals and a wide variety of chemical compounds are available to the modern paint maker as coloring agents. In a few cases these colorants are used as chemicals, but in the main they are used for one or more of their physical characteristics. The best example we can give of the use of a pigment for its physical characteristics is: if a yellow paint is wanted, a yellow pigment must be used. Moreover, the pigment must obliterate, obscure, or, as the paint man puts it, *hide* the original color and present the yellow, blue, green or red desired.

Therefore, let us review briefly the thoretical knowledge that the paint formulator should have in order to select the correct pigment. The obliterating value, or *hiding* power of a pigment, is due to the difference in refractive index between the clear, un-pigmented paint vehicle and the dry pigment coupled with its chromatic absorption. Generally speaking, clear paint vehicles have a low index of refraction, so the best hiding pigments, in theory at least, have a high refractive index. The better a pigment hides, the greater value it has in paint making, other factors being equal. Deeply colored pigments hide primarily as a result of color absorption.

According to Gardner,[8] white refined linseed oil has a refractive index of 1.4796, soybean oil 1.4760, titanium dioxide 2.76 and silica 1.55. Silica has no practical hiding power in paint vehicles, whereas titanium dioxide is the best-hiding white; and there is little difference between the refractive index of silica and linseed or soybean oil, whereas the refractive index of titanium dioxide is much higher than that of the oil. As in the case of white pigments, high refractive index contributes to the hiding of color pigments; but the selective absorption of light radiation also increases hiding, and deep or strong colors generally hide very well.

"Paint" is a very broad term which covers dispersions of pigment in the vehicles commonly encountered in the protective-coating industry, such as linseed oil, varnishes, synthetic resins, nitrocellulose lacquer, water-thinnable resin emulsions, etc. Obviously, problems vary as the vehicle changes, but we want particularly to give a broad picture of color pigments as used in the protective-coating industry, rather than a detailed study of any particular problem. Similar applications and problems are found when working in related industries, such as the manufacture of printing inks, carbon paper, wax and chalk crayons, show-card paints, etc.

Before studying physical characteristics, it should be pointed out that in a number of cases pigments are used almost solely for their chemical properties and may actually be considered as chemicals rather than pigments. A classic example of this is red lead (Pb_3O_4), which has been used in very large quantities for years in making excellent metal protective coatings with outstanding rust-inhibiting properties. This is attributed to the fact that red lead is basic in reaction. Red lead paints are seldom, if ever, used as finishing coats because when exposed to the atmosphere, a carbonation of the red lead takes place which changes the color from red to pink and finally to the white basic carbonate of lead. Therefore, red lead priming paints should be protected by finishing coats carrying pigments which are stable to atmospheric conditions.

Another and more recent example of the use of a pigment for its chemical composition is zinc chromate, commonly referred to as zinc yellow. During World War II zinc chromate assumed a dominating position in the field of rust-inhibiting pigments. In 1908 the American Society for Testing Materials started to conduct comprehensive tests at Atlantic City using several hundred steel panels to evaluate the rust-inhibiting properties of 35 pigments. When evaluated in 1913 (5 years exposure), zinc chromate was rated 8 (on the basis of 10 being perfect), red lead 6.3 and American Vermillion (Basic Lead Chromate—XX Deep Chrome Orange) 9.8. When the tests were completed in 1914, the XX Deep Orange (American Vermillion) was rated 7.5 (the highest of all pigments), red lead 4 and zinc chromate 4.*

In one of C. F. Kettering's talks several years ago, he said that, in effect, it took about 25 years for an idea to become established commercially, after which time it made progress. It was not until about 1940, 25 years after the Atlantic City tests, that zinc chromate assumed outstanding commercial importance. During the war years tremendous quantities were used for making metal protection paints for all kinds of war equipment. Several other interesting applications of pigments developed during the war.

High-flying reconnaissance planes equipped with infrared cameras

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* *Proceeding A.S.T.M.*, 15, 1, 220 (1915).

made aerial photographs to spot military installations, munition dumps, oil tanks, etc., etc.[2] The foliage of the open spaces in the country photographed white or light grey (pine trees showed black), but the smoke stacks, munition dumps, oil tanks, etc., appeared black. The problem was to camouflage these munition dumps, military installations, etc., so they would appear as harmless countryside. This was done, in a measure, by formulating paints with pigments which photographed the same as the foliage of the countryside. Ultra-marine blue was one of the pigments which was widely used because it photographed white with the infrared camera. All the commonly used blacks photographed black, so it was necessary to utilize black antimony sulfide for the black component. Unfortunately, black antimony sulfide has extremely poor pigment properties and is not used as a black pigment today. However, our knowledge of its characteristics served us well during the war effort. Antimony oxide found special use in making flame-retardent paints used for coating canvas, and probably many a costly fire was avoided because army tents and tarpaulins were coated with them. Camouflage, flame-retardent and rust-inhibiting paints were important contributions to the war effort. They were possible because the paint technologist had information regarding the physical and chemical characteristics of pigment materials.

Color pigment manufacturing falls into four general groups:

(1) **Fire Process**
    Examples: Ultramarine Blue, Cadmium Reds, Chromium Oxide
(2) **Fume Process**
    Examples: Carbon Black, Lamp Black
(3) **Chemical Precipitation**
    This accounts for by far the largest number of colors
    Examples: Chrome Yellows and Greens, Iron Blues, Organic Toners, etc.
(4) Earth colors or mined products.

Most chemical pigments are selected because of one or more desirable physical characteristics. On the strength of this, these pigments are evaluated commercially and purchased largely on the basis of physical characteristics. Before detailing characteristics, certain terms should be briefly described. These terms may well have different applications in other discussions, but for the sake of this material they can be briefly defined as follows:

Masstone and/or full strength and/or pure tone means a dispersion of the pigment in a paint vehicle with no extender or other pigment being present.

Tint tone and/or tint shade (*not undertone*) means a dispersion of a relatively small amount of color pigment with a relatively large amount of opaque white pigment, such as zinc oxide or titanium dioxide in paint vehicle.

Tinting Strength. Typical of the method for determining the tinting strength of dry colors is that used for toluidine toner.[4] Accurately weigh 0.5 g of dry toluidine toner; carefully transfer to a lithographer's stone or ground plateglass slab; add 0.5 g of white refined linseed oil; make a paste of the oil and color with a 3 inch flexible spatula; mull 5 x 30 rubs with a ground glass muller. Disperse 0.1 g of color paste in 5 g of previously prepared white zinc oxide paste. Apply paste to glass slide or bright tin panel and compare against known standard. Ratios and number of mulls will vary with different pigments.

Permanency or lightfastness (*full strength*) *masstone* means dispersing a pigment (no inert or other pigments present) in a suitable vehicle, exposing to required light source and evaluating the color change. The light source can be artificial, such as a carbon or mercury arc, or exposure in the atmosphere to sunlight.

Permanency or lightfastness (*tint-tone or tint shade*) means dispersing a relatively small amount of color in a relatively large amount of opaque white in a suitable paint vehicle, exposing to suitable light source and evaluating the color change.

Hiding. The hiding power of pigments varies widely, and what constitutes satisfactory hiding varies with method of application and other factors. In order to give some idea of the hiding power of a family of pigments, where practical, figures will be given which may be considered as a starting point. Adjustments will be necessary to meet particular conditions. The figure given will be the approximate number of pounds of pigment per gallon to give satisfactory hiding in enamel formulations.

Bleeding in linseed oil is an extremely important characteristic and has great practical significance. Let us assume that your porch furniture is red and you want to make it white. Now, if the red pigment used in making the original enamel is a bleeding pigment, when you apply your coat of new white enamel, the red will bleed right through the white and you will have a terrible looking pink or white mottled job.

Bleeding in solvents is more prevalent and pronounced than oil bleeding. When overstriping is necessary, accurate knowledge of the bleeding characteristic of the pigments used should be available. By solvents those generally employed in the protective coating industry, such as petroleum thinners, coal-tar thinners, alcohols, esters, etc., are meant.

Money Value. The per pound price of color pigments varies widely, from about 7¢ for the cheapest to about $5.00 for the most expensive. Actually, the price per pound is not the full story and from a commercial standpoint, the paint formulator must consider hiding power, amount used, and cost per pound and then arrive at money value.

Dispersion (ease of grinding). The amount of work necessary to disperse a pigment is extremely important. Various pigments belonging to the same family may show marked differences in ease of dispersion due to special manufacturing technique employed by the pigment manufacturer or other factors.

Resistance to alkali is important to know, particularly where the paint is to be used in a chemical plant, in making washing machine finishes, in felt base floor covering and in other products subjected to alkali or soap. The method of testing varies widely.

Resistance to mineral acids and fruit acids is important in many commercial applications.

Baking is highly important when making industrial finishes.

Only broad general statements can apply when giving such characteristics as described above. Where specific interest demands, careful tests should be made by the individual formulator on the particular pigment and vehicle combination in question, taking into consideration the conditions under which the paint is to be used.

Color Blending

Many times it is necessary to use several pigments in order to secure the required shade. Generally several combinations of pigments are possible to produce the final shade, and the combination used will to a large degree depend on the properties of the finished product. Several suggestions may be in order to avoid pitfalls and costly errors. The blending of several pigments generally detracts from the brilliancy and clarity of the individual pigment. However, when making blends, this down grading of brilliancy can be minimized by using two pigments which are relatively close in hue. The greater the difference in original shade of pigments being blended, the greater will be the loss of brilliancy. Thus, if you want a lighter or darker shade, tint with the next lightest or darkest pigment of the same family of pigments. In this way you will maintain maximum brilliancy and have essentially the same characteristics in your finished product. Generally speaking, it is a good rule not to blend inorganic with organic pigments without first making a careful study of possible reactions, and also to know the effect on package stability, settling and lightfastness.

Let us assume that the permanency of a lighter shade of red than can be secured with toluidine toner is required and that a 50/50 combination of c. p. deep chrome orange and toluidine red toner is used. Both of these pigments alone have excellent permanency of masstone, but a blend of this kind would be greatly inferior in permanency because the effect of blending is to make a semi-tint of the toluidine with chrome orange. Toluidine tints fade prematurely and are not sufficiently permanent for outside exposure. One should use a Chlorinated Para Red Toner or Light Cadmium Red to give the closest approximation for shade.

Or, let us assume that a combination of Dark Para Red Toner and c. p. Chrome Orange would give the required shade for a farm implement paint. Here again one would run into serious trouble from the standpoint of permanency and possible reactivity; a Light Para Red Toner should be used. There are exceptions to the above but a general observation will in many cases avoid trouble.

Metallic Pigments

Some few metals have application as pigments.

Aluminum. Two methods of manufacture apply. Thin sheets of metallic aluminum and 3 or 4 per cent of fatty lubricant are charged into a heavy stamping mill and pounded out into aluminum powder which is polished and used as a paint pigment. Aluminum pastes are made by charging finely divided aluminum and a suitable lubricant into a ball mill with mineral spirits. The end product is a paste which is used as a paint pigment. Various grades are available. Approximately 1½ to 2 pounds of metal per gallon gives good hiding. Aluminum paints are non-bleeding, have good lightfastness, are heat-resistant and are used principally for metal protection paints. They are also used in combination with suitable color pigments for making the metallics which are so popular for automotive and industrial finishes. Aluminum is also used for wood surfaces. The characteristic "aluminum shade" and "metallic sheen" governs to a large degree the use of aluminum finishes.

Copper Bronze Powders. The so-called copper bronze powders are made in essentially the same way as aluminum and are usually alloys of copper with small amounts of zinc and iron. Approximately a pound to two pounds of metal per gallon will give good hiding. Copper bronze in combination with small amounts of toxic substance, such as a mercury or arsenic compound, is used for making anti-fouling ship bottom paint. Various shades, ranging from a light brass to a dark antique copper, are used in nitrocellulose lacquer to make the popular brass and bronze finishes.

Gold. Gold Leaf has limited application in sign writing, picture framing, book-binding, mouldings, etc.

Zinc Dust. Distillation of zinc under proper conditions yields a grey metallic zinc powder carrying about 3 per cent of zinc oxide on the surface.

This grey powder, known as zinc dust, has recently achieved some importance as a pigment for making metal protective coatings. The evolution of hydrogen gas is possible when zinc dust is dispersed in an organic paint vehicle, and this presents a hazard which must be guarded against.

Blacks

Carbon Black. This is the most important and widely used black in the paint industry. It is made by burning natural gas. Carbon content varies from 80 to 95 per cent, the balance being Hydrogen, less than 1 per cent, oxygen, and volatile components. Carbon blacks vary in color or blackness, but the best grades are the blackest of the black pigments. They are high in oil absorption, difficult to disperse and tend to absorb paint dryer; they have excellent lightfastness and are fast to acids, alkalies and heat. They represent excellent money value pigments as approximately two ounces per gallon will give excellent hiding. The pigments are non-bleeding in oils and solvents and in many ways can be used as the measuring rod for excellent durability, low cost and excellence of hiding power. Red shade iron blues are extensively used for toning carbon blacks. The high grade automotive finishes use carbon blacks, which also find wide application in all types of paint products, both as a straight color and as a tinting color.

Lamp Blacks. Lamp Blacks represent an important family of blacks. They are made by burning oil high in hydrocarbon with incomplete combustion in special firebrick furnaces, equipped with baffles and velocity control. Carbon content varies from 80 to 95 per cent with a trace of sulfur, small amounts of occluded hydrogen and nitrogen, and the balance hydrocarbon oils. Lamp blacks are soft pigments which disperse more easily than most other blacks. The color varies from the low-color grey black similar to graphite to the more jet shades. Lamp blacks are blue in undertone, non-bleeding, low in oil absorption, have excellent lightfastness, are fast to acids and alkalies and have excellent heat resistance. They offer excellent money value and approximately 2 to 4 ounces per gallon will give complete hiding. They are used in all types of paint products both as a straight color and for tinting.

There are a great many other blacks which have limited application in the paint industry; among them are the following:

Graphite. Graphite is found in natural deposits and can also be manufactured by heating coke with about 3 per cent of iron in an electric furnace. The material has the characteristic grey graphite color and varies in carbon content from approximately 40 to 90 per cent, the remainder being mineral ash. It has poor strength, is low in oil absorption, is fast to light, heat, alkalies and acids, and finds limited application for use in making metal protective paints.

Blue Basic Lead Sulfate. This pigment is slate grey in color and is seldom used as a black pigment. It is a combination of carbon, lead sulfide, lead sulfite and basic lead sulfate. The material is a fume process pigment made from a mixture of galena and coal and has greater basicity than white basic lead sulfate. It has considerable application for making metal protection paints, particularly rust-inhibiting paint. It was given a rating of 6.0 in the Atlantic City tests of 1914.[8]

Gilsonite. This is a natural mined black resinous product which is not a true pigment but which has application as a colorant for the manufacture of black baking Japans.

Vegetable Blacks. In this family we have the so-called vine black, blue black, wood black, etc. They are made by carbonizing vegetable matter, washing the calcined product to remove salts, and then grinding. Carbon content is 50 to 90 per cent and the balance mineral matter. They have greater tinting strength than animal black but less than lamp blacks. They have fair light resistance, are unaffected by acids and alkalies, and are low in oil absorption. They have limited use in paints and find application in cement colors. They are non-bleeding in oils and solvents.

Animal Blacks. In this family we have bone, drop and ivory blacks, made by charring animal bones after the fatty material has been removed. Carbon content is low (10 to 20 per cent), the balance being calcium phosphates. Animal blacks are low in oil absorption, tinting, and hiding, but the high-grade products have a blackness which compares favorably with the best high-grade carbon black. They are easily dispersed and are of moderate importance in the paint industry. They are used for making enamels, artist's colors, paints, etc. They are non-bleeding in oils and solvents.

Other Synthetic Organic Blacks. Nigrosene and induline blacks are typical of the bleeding type of organic blacks which are used for making certain specialty finishes and for toning carbon blacks, lamp blacks, etc. This group of colorants is limited in use because the blacks bleed in solvents and oils and tend to fade rapidly in sunlight. Their principal use is for cable coatings, stains, etc.

Earth Colors

These pigments occur in deposits throughout the earth and were probably the first pigments known. They are found in various shades and, generally speaking, are iron compounds. They are mined, and in some cases the commercial value is enhanced by leaching, calcining, burning, or otherwise purifying or modifying the natural product. Generally speaking, they lack brilliancy but are widely used because of their low cost, good permanency in masstone and tint shades; they are non-bleeding and are available throughout the world. Composition and strength vary widely.

Yellow Ochre. French and domestic ochres vary in shade and composition. The ferric oxide content will vary from approximately 11 to 22 per cent, with the balance silicious material. French ochres as a class are preferred in many cases to domestic material.

Siennas (dark yellows). Siennas have greater transparency than ochres. Burnt and raw siennas give pleasing shades of yellow to brown; they vary in shade and composition from about 30 to 70 per cent ferric oxide, with the balance mainly silicious material. One of the important applications is in stain making because of their desirable translucency.

Umbers (browns). Raw and burnt turkey umbers are a combination of manganese and iron oxide with silicious material. The composition varies from approximately 8 to 17 per cent manganese oxide, approximately 40 to 53 per cent ferric oxide, the balance being mainly silicious material.

Red and Maroon. There is a rather wide range of shades carrying various commercial designations, such as, metallic reds, metallic browns, Spanish oxide, Persian gulf oxide, etc. The composition will vary from as low as approximately 8 per cent ferric oxide to approximately 80 per cent ferric oxide, the balance being chiefly silicious and carbonaceous material. These natural products find application as single color pigment for making such finishes as freight-car paints, roofing paints, etc., and also as tinting pigments.

Because of their source, earth colors are not always uniform, and this is a limiting factor in their use. In many cases, synthetic products of uniform compositions have replaced the natural earth pigments. This is particularly true in the yellows and reds, where synthetic red, yellow, brown and maroon oxides of iron are available; these offer the advantage of better strength, greater uniformity and better money value.

Inorganic Blues

Ultramarine Blue. This is a fire-processed pigment made by heating in a crucible such materials as soda ash, china clay and sulfur, with a reducing agent like charcoal, pitch or resin. Although none of these materials is blue, the process yields a blue whose brilliancy and clarity of tone are equalled by no other. The shades vary from a reddish blue to a greenish cobalt shade. The pigment is very sensitive to acids but is fast to alkali. It is non-bleeding in oils and solvents, is low in hiding power and tinting strength, but does not have good outside durability. It is fair money value and is widely used in the paint industry, particularly for tinting work.

As a side light it might be mentioned that ultramarine is the pigment used almost exclusively in the manufacture of blue roofing granuals, which are used in making colored asphaltic shingles.

Iron Blues (Prussian, Chinese, Milori). These are all members of the family of complex insoluble sodium-ferric-ferro cyanide blues, or ammonium ferric-ferro-cyanide blues. The terms "Prussian," "Chinese" and "Milori" are loosely used but do have some significance with individual suppliers. Probably it would not be out of order to attempt a rather broad definition of what they mean today, remembering that individuals and companies will use these terms differently. For purposes of this consideration, the following definitions apply.

Prussian Blue may indicate a blue suitable for paint making which has a deep jet masstone shade (not red) and a reddish-blue tint shade. It may be harder grinding than other blues, give greater tinting strength, and be deficient in permanency of tint shade.

Chinese Blue may indicate a blue suitable for paint making which has a clean, greenish-blue tint shade. It may be slightly easier grinding and have superior lightfastness in tint shade than Prussian Blue.

Milori Blue may indicate a blue suitable for paint making which is somewhat weaker than Prussian or Chinese, less jet in masstone shade (mainly unsuitable for making deep jet non-bronzing type automotive finishes), considerably easier grinding, either red- or green-toned in tint shade, and with better lightfastness of tint shade than Chinese or Prussian; it is also less reactive and lower in consistency and oil absorption than Chinese or Prussian.

Iron Blues do not bleed in oils and solvents, bake at 350°F, they are fast to acids and generally speaking are destroyed by alkalies, though within the past decade iron blues have become available which have alkali resistance of marked practical significance.

At this point it may be well to consider the surface treatment of pigments. All pure pigments have various characteristics peculiar to their composition. Some of these characteristics are highly desirable, whereas others present definite disadvantages. In iron blues, one of the major disadvantages has been its poor resistance to alkalies. By the addition of a suitable coating agent, the pigment technologist has produced iron blues which have definite alkali resistance (not alkali fastness) of commercial significance.

In other families of pigments, the pigment maker will employ surface coating agents to give better baking characteristics, better chalk resistance or better lightfastness. All the surface-coating agents are used in small amounts, usually ranging from less than 1 per cent to 2 or 3 per cent.

Linseed oil tends to deoxidize iron blue. Tints of iron blue fade out in the paint can on long standing, but usually recover their original shade when brushed out, due to the reoxidation of the pigment from the white to the blue. Iron blues as a class have excellent lightfastness, but various blues show marked differences in the weathering of the masstone shade and the lightfastness of tint and semi-tint shades. Various iron blues also show marked differences in ease of grinding, reactivity and bronzing.*

Iron blue is probably the most important blue pigment used by the paint industry. About 8 oz. per gallon gives good hiding. In addition to wide application for making blue paints, enamels and lacquers, iron blues are also used for toning blacks. They represent excellent money value.

Organic Blues

***Indanthrene Blue* (Vat Type).** This is an expensive, reasonably clean, red tone non-bleeding blue, which has exceptional lightfastness in light tint and medium tint shade. It is fast to acids and alkalies and non-bleeding in oils and solvents. When used in high concentration it tends to bronze on prolonged outside exposure. Tint shades are permanent in the can and the blue finds application as a tinting pigment for making specialty finishes, as well as limited use in the automotive finishing field. Poor money value limits its application.

***Phthalocyanine Blue*.** This is the most recent development in blue pigment which first came on the United States market about 1937. It is a clean green tone blue which is non-bleeding in oil and solvents and is characterized by the exceptional lightfastness of weak tints. It is unaffected by acids and alkalies and is one of the real contributions to pigment technology in recent years. The toners are very hard grinding, and the blue generally cannot be used in high concentration because of bronzing on exposure. When used in tints in the presence of coal-tar thinners, the pigment tends to crystallize and thus the shade of the paint or enamel is changed.

There are two shades, both of which are clean green blues, but the more expensive shade is the greenest and cleanest and least used. The pigment finds application in specialty finishes, automotive finishes, and particularly for tinting work. Reduced types and surface-treated water-dispersible types find application for tinting casein and water-thinnable paints carrying alkali.

Blue Toners and Lakes (Phosphotungstic Acid Colors). These pigments are used primarily in the printing-ink industry. However, because of their great strength and brilliancy, they do find some application for special

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* For a discussion of bronzing see "Phenomena of Bronze in Surface Coatings" by Buc, Kienle, Melsheimer and Stearns—*Industrial & Engineering Chemistry*, 38 (Feb. 1947).

work in the paint field. Because of unsatisfactory masstone shades, they are never used alone. When used in combination with sufficient white or tinting pigments to produce a semi-tint or tint shade, they do not have sufficient permanency to be generally acceptable for wide paint application.

A very clean, strong, reddish shade blue pigment is produced by precipitating victoria blue dyestuff with either phosphotungstic or phosphomolybdic acid. The resulting color is approximately 30 times as strong as ultramarine blue and is the closest approach to the brilliancy of Ultramarine. The color is non-bleeding in oil, bleeds badly in solvent, has good alkali and acid resistance, bakes at 250°F. It is used in toy finishes, bicycle enamels, screen stencil paints and other specialty items.

A greener shade pigment with essentially the same characteristics is made by precipitating the dyestuff "Setoglaucine" with phosphotungstic or phosphomolybdic acid.

Browns

Brown pigments are limited in number. VanDyke Brown consists of approximately 64 per cent organic material with some carbon and ferric oxide and the balance principally water and impurities. It is a specialty pigment used mainly for artist's colors and stains.

Synthetic iron browns are prepared by precipitation of an iron compound with alkalies. Because of incomplete oxidation there is a combination of red Fe_2O_3 and black Fe_3O_4, which makes brown. These pigments are non-bleeding, have excellent light resistance, and offer excellent money value, although they are lacking in brilliancy. Most brown shades are made by blending several pigments, such as red and black, and then tinting to secure various tones. Several organic browns have been offered from time to time but none have achieved wide commercial acceptance.

Greens

Inorganic (Chromium Oxide). This is a fire-process pigment which is limited in use because of its lack of brilliancy, poor strength and abrasive characteristics. The best grades are approximately 98 per cent Cr_2O_3. This pigment represents one of the most permanent types of green pigments. It is non-reactive, non-bleeding in oils and solvents, will stand ceramic heats, is fast to acids and alkalies and finds application where maximum permanency of masstone or tint shade is required. The pigment is poor money value.

Hydrated Chromium Oxide. This pigment should not be confused with chromium oxide. It has practically all the good characteristics of chromium oxide: it has exceptionally good lightfastness in tint and semi-tint shade, it is unaffected by acids and alkalies, and will stand high baking temperatures. The pigment contains water of crystallization and will not stand ceramic temperatures.

The masstone shade of this pigment makes it unsuitable for use in high concentration, but the tint shades approach the brilliancy and cleanness of the organic toners. Of course, hydrated chromium oxide has the advantage of being very much more lightfast than the organic pigment of the PTA type. The color is hard grinding and has thixotropic characteristics, which make it difficult to disperse and reactive in paste form. The pigment is high priced and represents very poor money value.

Within the past decade there has been developed a new pigment, namely, phthalocyanine green, which has many of the good characteristics of hydrated chromium oxide and which has largely replaced the hydrated chromium oxide because of easier grinding and better money value. Phthalocyanine Green will be described later. The pigment is used for making weak tints which are permanent in the can and have excellent lightfastness.

Chrome Greens. This family of greens represents the most important green pigments used by the paint industry. They are combinations of iron blue with chrome yellow. They come in a wide range of shades from a very light yellow tone green to a very deep blue tone green. The lighter the shade of green, the higher the chrome yellow content and obviously, the darker the shade of green, the higher the iron blue content. Iron blue content will vary from approximately 2 per cent for the very lightest shades to approximately 70 per cent for the darkest shades. The balance is chrome yellow. Few dark greens carry more than 45 to 50 per cent of iron blue.

These greens are made by chemical precipitation, and the method of manufacture is carefully controlled so as to achieve maximum strength, lightfastness, ease of grinding, and brilliancy of tone, as well as other desirable characteristics. Generally speaking, it is not possible to reproduce the brilliancy and cleanness of shades by dry blends of iron blue and chrome yellow. Marked differences in shade can be achieved by using different types and shades of chrome yellow and iron blue for making chrome greens. Two large families of greens are widely used; namely, the nitrate green and the acetate green. The nitrate green derives its name from the fact that a nitrate yellow is used as the yellow component, and acetate green means that an acetate yellow was used. As a family, nitrate greens are bluish in tint shade and have maximum lightfastness, whereas the acetate greens have maximum brilliancy of masstone shade, a yellowish tint shade and tend to darken more on exposure than nitrate greens. None of these differences is of great magnitude. The redder shades of chrome yellow are used for making the olive-toned greens. These pigments are non-bleeding in oils and solvents, are destroyed by alkalies and have fair acid resistance; they bake at 300°F and have good money value.

Because of the difference in composition, there are pronounced differences in grinding characteristics as well as in hiding. The lighter shades require approximately 2 pounds of pigment per gallon to achieve satisfactory hiding, the medium shades 1½ to 2 pounds and the dark shades approximately a pound per gallon. The darker shades will grind considerably harder than the light shades, whereas the medium will be in between. All the pigments tend to darken in masstone shade on outside exposure and the permanency of the tint is not suitable for the most severe outside exposure conditions. Chrome greens are used throughout the paint industry for manufacturing a wide line of industrial and architectural finishes.

Organic Greens

Phthalocyanine Green. The development of phthalocyanine green followed the announcement of phthalocyanine blue. This pigment is a chlorinated phthalocyanine. It is really remarkable in many respects. In common with most organic blues and greens, it cannot be used for straight masstone work or in high concentration because of the very strong bronze reflection. The pigment is fairly easy grinding, gives little or no trouble from the standpoint of reactivity, is fast to acids and alkalies, is non-bleeding in oils and solvents, and has remarkable lightfastness in weak tint and semi-tint form. The tint shade is exceptionally clean and brilliant. It is about 15 times stronger than hydrated chromium oxide, which it has in a large measure replaced because of its much better money value, easier grinding and lower reactivity. The price per pound is still high and it represents relatively poor money value when compared with chrome greens; but despite this, it has found acceptance in the paint industry for making specialty finishes, particularly for tinting work where maximum permanency is a factor. The bronzing masstone shade and poor money value limit its usage.

PTA Green Toners (Phosphotungstic Acid). The principal use for these pigments is in the printing-ink industry, but because of their exceptional brilliancy and strength, they are sometimes used in the paint industry. They are manufactured by precipitating such dyestuffs as malachite or brilliant green with phosphotungstic or phosphomolybdic acid. The resulting pigments are exceptionally brilliant and clean in tone and are several times stronger than chrome green. However, they cannot be used for straight masstone work because of the bronzy appearance of the pigment. When used in combination with opaque white or other tinting pigments, they do not have sufficient permanency to be generally acceptable in the paint industry. The pigment resulting from the precipitation of brilliant green dyestuff has a yellowish tint shade, whereas Malachite Green gives a pigment with a bluish tint shade. These pigments are non-bleeding in linseed oil, water and mineral spirit and show some bleeding in solvents. They are relatively easy grinding and bake satisfactorily at 300° F. They find limited application for tinting work where the finish is to be used inside and also for making screen stencil paints and other similar products.

Maroon Pigments

Maroon shades are in demand, but their use is limited because the low-cost, good money value pigments are generally very fugitive to light or lack brilliancy, while the pigments with good lightfastness are high priced and find only limited application because of poor money value.

Inorganic Maroon. *Synthetic Maroon Shade Iron Oxide* (*Pure Indian Reds*). This is a low-cost, excellent money value pigment limited in use because of the lack of brilliancy. The color has excellent permanency, is non-bleeding, acid- and alkali-fast, easy grinding, and has excellent baking characteristics. For hiding, use approximately 1 to 2 pounds per gallon. Typical uses are for floor paints, undercoatings, stain, and coloring cement.

Cadmium Maroon. *Permanent Non-Bleeding Maroon.* This is one of the interesting family of cadmium reds and yellows. Some pure cadmium colors are produced but the big tonnage is of the lithopone type. The maroon shade, in common with all members of the cadmium red family, is easy grinding, non-bleeding in water, oils and solvents, fast to acids and alkalies and has excellent permanency in masstone and tint shades. Use approximately 2½ to 3 pounds of pigment per gallon for hiding. Money value is poor. The pigment has good brilliancy of masstone shade but is surpassed in this respect by the most brilliant of the organic toners. It withstands high baking temperatures and is non-reactive. This is one of the few maroons which is sufficiently permanent and non-bleeding to be used in automotive finishes. It is used in manufacturing specialty enamels and paints; for manufacturing automotive finishes, it can be used either alone or in combination with the expensive organic maroons to give added opacity or durability. Cadmium pigments find application because of their alkali resistance, and are used as tinting pigments in casein paints and other water-thinnable paints where alkali is present.

Organic Maroons. *Amaranth Type.* This is a low-cost, fugitive type dark maroon possessing good brilliancy. It is easy grinding, has good money value, is non-bleeding in oils and solvents, bakes at 300°F, but is not fast to acids or alkalies. It is the most widely used of the fugitive type organic maroons.

Lithol Maroons. These are popular because of low cost, good baking characteristics, limited bleeding and good hiding. They have better permanency than amaranth but are not considered satisfactory for severe outside exposure, although they are used for bicycle enamels. They have fair resistance to alkalies, somewhat better resistance to acids, are practically non-bleeding in oil and mineral spirits, with some bleeding in other solvents. Use approximately 1 to 2 pounds per gallon for hiding. Bake at approximately 250°F. Tint shades fade rapidly on outside exposure. Used for architectural and industrial finishes, particularly toy enamels.

Madder Lake. This is a deep brilliant transparent maroon which has excellent permanency in masstone and tint shades. Contrary to most organic toners, this pigment has excellent permanency in weak tint and is used for making "flesh pinks" which have excellent permanency. Usually Madder Lakes carry approximately 35 to 45 per cent alizarin on a reactive base composed largely of alumina hydrate. The alumina hydrate reacts with many vehicles, which is one of the limiting factors in the use of the pigment. The color has poor money value. It is non-bleeding in oils and slovents and has enjoyed long usage for making specialty finishes. In the past the pigment found some application for making automotive finishes but has been largely replaced by the newer, stronger, better-hiding organic maroons which will be described later.

Alizarin Maroon. The characteristics of this family are essentially the same as those of Madder Lakes, although they are somewhat less permanent in tint than Madder. Despite this slightly deficient permanency, the tint shades are the standard for making clean permanent type orchid tints. Use is limited by reactivity and poor money value.

Toluidine Maroon. This family of pigments is one reason why the automotive industry has been able to offer improved maroon finishes during the past 15 years. It has many desirable properties but leaves some things to be achieved. It is a deep brilliant Maroon possessing acceptable permanency for automotive-type nitrocellulose finishes, but not having generally acceptable permanency when used for pigmenting automotive-type alkyd enamels. It bleeds somewhat, but not enough to bar its use in certain finishes. Popular automotive finishes are made by using approximately 12 ounces per gallon, with the addition of cadmium red or maroon, to enhance permanency and/or opacity. It is also used in combination with aluminum to make metallic finishes. Poor money value further limits its use to specialty applications.

Indanthrene Maroon. This belongs to the so-called vat dye family and is probably the most permanent and most expensive of the organic maroons available today. They are deep brilliant pigments with excellent permanency in masstone and tint shade, are non-bleeding in oils and solvents, but because of the high cost are limited mainly to use in high-grade automotive finishes. Approximately 12 ounces of this pigment is used alone or in combination with cadmium maroons or reds for automotive work. This family of maroons, along with toluidine maroon, is one of the principal reasons why maroon automobiles have become so popular during the last decade.

Lithol Rubine. This is a light maroon or deep red which has some application where maximum permanency is not essential. Bicycle finishes are a typical example. Lithol Rubines are not fast to alkali, have only fair resistance to acids, are non-bleeding in oil, and show some bleeding in solvents. They have good baking characteristics at 300°F which is one of the main reasons for their use. Permanency of tint shade is better than the usual organic pigment and money value is fair.

B.O.N. Maroon (Beta-Hydroxy-Naphthoic Acid). This family of maroons has achieved considerable commercial importance during the past decade. The pigments are not fast to acids or alkalies, are non-bleeding in oil and show little bleed in solvents. They have sufficient permanency for making automotive enamels used for refinishing work and also wheel enamels. However, they have not yet achieved wide commercial acceptance for production line automotive work, where major emphasis is placed on excellent durability. They represent moderately good money value. They can also be used for other industrial finishes.

Maroons of other types have been used in the past, and are being used in limited amounts at the present time (example: Helio Bordeaux). The organic pigment technologist can be counted on to develop new and better maroons in the future.

Oranges

Inorganic (Chrome Oranges). This family of pigments is the most widely used and most important of the orange pigments in the paint industry. Actually, chrome orange is basic lead chromate. The lighter shades of chrome orange will contain approximately the equivalent of 85 per cent of lead chromate and the balance lead oxide, whereas the very deep shade will probably not contain more than 60 per cent of lead chromate and the balance 40 per cent lead oxide. From this it is evident that the basicity of chrome oranges increases as the shade goes deeper. The deep shades of chrome orange (basic lead chromates) have considerable value as rust-inhibiting pigments and are widely used for this purpose. Chrome oranges are non-bleeding in water, oils and solvents, grind easily, and are much better in alkali-resistance than the chrome yellows. They show very little darkening on exposure in masstone shade and are quite permanent in tint shade. They represent good money value. The shades vary from an extra light orange to an extra deep shade, which approaches a red. The hiding of the darker shades is not as good as of the lighter shades. They have good baking characteristics at 250°F and are used for manufacturing a wide line of paints, enamels and lacquers.

Molybdated Oranges. These pigments are mixed crystals of lead chromate and lead molybdate. They have much greater brilliancy and are approximately two to three times stronger than any chrome oranges. Unfortunately, they show pronounced darkening on outside exposure when used for straight masstone work and the tint shade tends to fade. This means that they are unsatisfactory and not generally used for finishes where maximum permanency is essential.

They do find wide application for making interior finishes and also for finishes where darkening is of no significance. They are non-bleeding in all the oils and solvents used in the protective coating industry. They have some resistance to mild alkalies, but are destroyed by concentrated alkalies. They have good baking characteristics at 250°F, are easy grinding and have exceptionally good opacity. These pigments are a valuable contribution within the past decade to pigment technology. Because of the brilliancy and strength, they are finding wide acceptance in the paint industry.

Organic Orange Toners. There are several organic orange toners which have limited application in the paint field. One of the most important of this family is the so-called dinitroaniline permanent-type orange. This pigment is non-bleeding in oils and mineral spirits, although it shows some bleed in solvents. It has sufficient permanency in masstone to be used for manufacturing brilliant store front enamels and paints. It bakes satisfactorily at 250°F, has good opacity, is easy grinding and has good resistance to acids and alkalies. The pigment is relatively expensive and this limits its use.

Another organic toner sometimes used is Orthonitroaniline, commonly referred to as "Para Orange." This pigment bleeds in linseed oil and has practically all the characteristics of Para Toners. It has good permanency in masstone shade, has some resistance to acids, but is destroyed by alkalies. Because of its exceptional brilliancy, it is used to a limited extent in the paint industry, one of the principal uses being in the manufacture of striping paints for awnings.

Reds

Inorganic. *Synthetic Red Iron Oxide.* Mention was made of natural iron oxide in the paragraph on earth colors. The synthetic red iron oxides have to a very large degree replaced the natural oxides because of their greater strength and better uniformity. Synthetic iron reds are made by several processes, and are available in various shades. They are non-bleeding in water, oils and solvents, have excellent hiding, good heat and alkali resistance, are fast to acids and represent excellent money value. Generally, they are more brilliant than the natural oxide but less brilliant than the red organic toners or cadmium reds. They have wide application in the paint industry and are used for making freight car, barn and roof paints, as well as undercoatings, and many other important finishes.

Cadmium Reds. This is a family of permanent non-bleeding reds ranging in shade from a light red (or dark orange) to a deep maroon. They are fire process pigments consisting of cadmium sulfide (CdS) with varying amounts of cadmium selenide (CdSe). Some pure cadmium reds are available, but their main use is in lithopone-type pigments containing large percentages of blanc fixe ($BaSO_4$). Cadmium sulfide (Yellow) is the light shade component, and selenium is the dark component. The light red will carry approximately 10 per cent of cadmium selenide, 32 per cent of cadmium sulfide, and the balance blanc fixe. The medium shade will carry a higher percentage of selenium and a correspondingly lower per cent of sulfide; the maroon will be the highest in selenium content and the lowest in sulfide content. These reds are non-bleeding in water, oils and solvents, are fast to acids and alkalies, grind easily, are non-reactive, and have excellent permanency in masstone and tint shades.

Because of the high percentage of blanc fixe, they have only fair hiding and approximately three pounds per gallon should be used for satisfactory hiding. They bake at 400°F and represent poor money value. An interesting side light is that, so far as is known today, cadmium is found only as an impurity in lead and zinc ores and is present in very small amounts, so the world's supply of cadmium is limited. In the recent war, cadmium metal is reported as having been used in the atomic energy program. Cadmium reds are used chiefly in making permanent non-bleeding automotive enamels and lacquers. They also find application in specialty finishes where the characteristics they impart are more important than the high cost.

Organic. *Toluidine Toners.* Toluidine Toners are the most brilliant and most permanent organic reds available today. They are the measuring rod for permanency of organic reds and the masstone shade shows less change on prolonged outside exposure than any other family of reds in durable vehicles. The tint shade is not satisfactory for outside exposure. The shades vary from light to dark, but the range is not as great as in the para or lithol family. The pigments are fast to acids, reasonably fast to alkalies, and in the early days were referred to as non-bleeding reds to differentiate them from paras, which bleed badly. The pigment shows only a moderate bleed in linseed oil, with pronounced bleed in solvents. It is a soft, easy grinding pigment and bakes at 300°F. About three-quarters of a pound per gallon gives good hiding. This is the pigment used for making the familiar fire-engine red and gasoline pump red enamels.

It finds wide application in truck, architectural and industrial finishes. There is no substitute for toluidine where permanency of masstone shade and brilliancy are of primary importance.

Para Red Toners. This family of brilliant red pigments stands second only to Toluidine in permanency and brilliancy. The great difference between Para and Toluidine is in the bleeding characteristics. Paras bleed badly in oil and solvents and have slightly less acid- and alkali-resistance than toluidines. The shade range is wider than for toluidine—from light to dark. The light shades grind easily and are non-bleeding in water, but the darker shades are hard grinding and bleed in water. They bake at 200°F. Tint shades are fugitive to light. Money value is better than for Toluidine but not as good as for Lithol. Use about 12 ounces per gallon for satisfactory hiding. These pigments find application where bleeding is unimportant and are used for such purposes as manufacturing drum enamels, as well as many architectural and industrial enamels and paints.

Chlornitraniline Red Toners (Chlorinated Para). This red is commonly referred to as Chlorinated Para. It is a very brilliant yellow red which is lighter in shade than Toluidine, but with only slightly less brilliancy of masstone and slightly less permanency than toluidine. The cost is approximately 30 per cent less than Toluidine. It bleeds only slightly in oil, is non-bleeding in water, bleeds less in mineral spirits than Para, and bleeds badly in solvents. It bakes at 225°F. It has fair acid-resistance but is deficient in alkali-resistance. The tint shade is fugitive. The color has exceptional merit and is used where a lighter shade permanent red is required than can be secured with Toluidine. It is very easy grinding and 12 ounces per gallon gives good hiding. The pigment is used for gasoline-pump enamels and for making many industrial and architectural finishes.

Lithol Red Toners. This represents the largest family of red pigments. Shades vary from light red (dark orange) to a deep maroon. The pigments are made by coupling Tobias Acid and Beta Naphthol and there are today Sodium (Light), Barium (Medium) and Calcium (Dark Lithol). Each group can be resinated or not.

The resinated Lithols are more brilliant and generally more reactive than the non-resinated pigment. The sodium Lithols find only limited application in the paint industry because they are not as lightfast as the Barium and Calcium Toners, and tend to darken on baking.

Barium (medium shade) and Calcium (dark shade) lithols are more widely used than any family of reds because of their low cost, good brilliancy and good baking characteristics. Though their properties vary from pigment to pigment, generally speaking, lithols are less brilliant than Toluidines or Paras, and are not quite as good hiding as Paras or Toluidines. The masstone shade darkens on exposure and is not generally acceptable for outside use. Tint shade fades prematurely. The color will bake from 225 to 250°F or higher. The colors are non-bleeding in oils and mineral spirits, with only moderate bleed in other solvents, and find wide application because they bleed less than paras or toluidine. They bleed somewhat in water. The medium and some of the darker shades grind easily, but the very dark lithols and also the lithol maroons grind considerably harder than the light medium shades. Hiding can be secured with approximately 12 to 20 ounces per gallon. Money value is the best of the widely used reds. The colors are used for making a wide line of industrial and architectural air-drying and baking finishes. They find wide application in toy enamels and other similar finishes.

There are a number of other reds which have limited application in the paint industry. Among these can be mentioned Pigment Scarlet, English Vermillion, Scarlet Lakes and a few other specialty reds.

Violets

Violet pigments are relatively unimportant in the paint industry. This is probably due to a combination of circumstances: (1) violet is not a popular shade, (2) the pigments are expensive, and (3) they do not have maximum lightfastness. The basic dye methyl violet is precipitated with phosphotungstic or phosphomolybdic acid to produce brilliant organic pigments. These pigments are high-priced, bleed in solvents and are not sufficiently permanent for outside exposure, although they are used for inside finishes. Violet pigments are practically never used alone but in combination with opaque white pigments. Some inorganic violets, such as manganese and ultramarine violets, have been made but they never gained commercial acceptance.

Yellows

Inorganic. Chrome Yellows. Chrome Yellows and Oranges represent the largest tonnage chemical pigments used by the paint industry. Metallic Lead or a lead salt is first dissolved in acid such as acetic acid (to make acetate yellows) or nitric acid (to make nitrate yellows). Normal lead chromate is the precipitate formed by combining a solution of sodium dichromate with the lead solution.

C. P. Medium Chrome Yellow. This is probably the most widely used color in the chemical pigment industry. It is normal lead chromate. To manufacture the lighter shades, such as light yellow and primrose yellow, lead sulfate is usually co-precipitated with lead chromate. Chrome yellows are available in a wide range of shades from a very light greenish shade yellow known as primrose yellow, on through to the reddish shade medium yellow, followed by the chrome oranges, which have been described. The best and most widely commercially acceptable medium yellows will contain approximately 95 per cent of normal lead chromate.

The primrose shade may contain as little as 50 per cent of lead chromate, the balance being mainly other insoluble lead salts, such as lead sulfate. The so-called lemon or light chrome yellow will contain approximately 65 to 70 per cent of lead chromate, the balance being other insoluble lead salts, such as lead sulfate. Normal lead chromate, or Medium Yellow, hides very much better on a per pound basis than lead sulfate. This gives rise to a situation where all the c. p. chrome yellows sell for the same price, but have a pronounced difference in hiding power due to their chemical composition.

Actually, the c. p. chrome yellow medium is the best money value. Chrome yellow or orange is available primarily because it carries a maximum amount of normal lead chromate. Chrome yellows are non-bleeding in all the oils and solvents used in the protective coating industry. They are fast to acids but are sensitive to alkalies. They are easy grinding, bake satisfactorily at approximately 225°F and have reasonably good opacity, but this varies with the shade of the pigment. All chrome yellows darken in masstone shade when exposed outside for long periods of time. Tint shades darken and fade somewhat. They represent excellent money value pigments and are widely used throughout the paint industry for practically all types of finishes.

Cadmium Yellows. The most commonly used cadmium yellows today are of the lithopone type and vary in shade from primrose to orange. Cadmium sulfide content is approximately 26.5 per cent for the primrose shade to 32 per cent for the orange shade, the balance being mainly blanc fixe plus a small amount of zinc sulfide. The pigments are non-bleeding in water and all oils and solvents used in the protective coating industry. They have the unique characteristic of being fast to alkalies but not to acids. They have reasonably good lightfastness in tint shade but are not acceptable in permanency of masstone shade for the most severe outside exposure conditions. They are much poorer money value than the chrome yellow pigments. They are relatively low in hiding power and the high cost per pound means poor money value. Usage is limited to cases where a particular property, such as alkali resistance, etc., is essential. Because of their alkali-resistance, they are used in tinting casein and other water-thinnable paints where alkali is present. They are non-reactive, easy grinding and have good baking characteristics at 300°F.

Barium and Strontium Chromate. These two pigments have been known for a considerable time, but they have never achieved much commercial importance. During World War II both of these pigments were used to a degree for manufacturing rust-inhibiting primers, but they have nowhere near the commercial importance which zinc chromate enjoys. Barium chromate is reported as having excellent lightfastness in tint shade and good chemical resistance.

Zinc Yellow. This is a permanent type, sulfide-resistant, greenish yellow which has many unique characteristics. It is a complex salt of zinc and potassium chromate, made by reacting potassium or sodium dichromate, zinc oxide and sulfuric acid. The pigment is non-bleeding in oils and solvents but it does show a progressive bleed in water. This water bleed has to a degree been pointed out as one of the factors contributing to its excellent rust-inhibiting characteristics. The pigment is not affected by sulfide fumes, whereas chrome yellows are. The material is seldom used as a straight color pigment because it has a rather dirty greenish masstone shade, which tends to go greener and dirtier on exposure. However, when used for tinting work, it has excellent stability of tint shade. The main use for this pigment is in the manufacture of rust-inhibiting primers. As far as is known, this pigment is superior to all others in general use at the present time for making rust-inhibiting paints.

During World War II it achieved wide usage for manufacturing metal protective coatings which were used on all kinds of war equipment, both of the ferrous and non-ferrous type. Approximately 40 million pounds per year were produced during the war years. The pigment is somewhat reactive and suitable vehicles must be selected to avoid unsatisfactory finished products. It is not fast to alkalies but does have some resistance to acids. It is relatively easy grinding but is weak and has poor opacity and is not as good money value as the corresponding shade of chrome yellow. It is used in combination with opaque white and a small amount of phthalocyanine green or blue to make the permanent type trim and trellis paints which are so popular today. It can also be used in combination with iron blue for making greens, which are weaker than chrome green but which have excellent permanence.

Iron Yellows. These are synthetic hydrated yellow and orange iron oxides made by precipitating the hydrated ferric oxide from a solution of ferrous salt with alkali and then oxidizing. Composition is approximately 86 per cent Fe_2O_3 with 12 per cent water of hydration. The best synthetic iron yellows have about the same tinting strength as medium chrome yellow, but are much dirtier in masstone and tint shade. They are non-bleeding in water, oils and solvents, have good resistance to acids and alkalies, and represent the best money value pigments of the yellow family. When baked at too high temperatures water is driven off and the color tends to redden. They are widely used in combination with other pigments for making olive drabs. During the war the pigment industry was hard put to produce sufficient iron yellow for the war effort. They have largely replaced ochre for tinting work. They are excellent pigments and find wide application in the paint industry, particularly for making stains and for tinting work.

Organic. *Hansa Yellows.* This is an interesting family of organic yellows designated by their greenness of tone, namely, G, 5G, 10G, 13G and for the red shade 4R; 13G is the lightest shade and 10G corresponds to the primrose shade in chrome pigments. The masstone shade of this family of yellows is exceptionally permanent, but the addition of opaque white destroys the excellent permanency and the tint shades are not sufficiently permanent to permit use where maximum permanency is essential. Hansa Yellows are more permanent than Benzidine Yellow in both masstone and tint.

Unfortunately, these pigments have the unhappy characteristic of migrating to the surface, and this more than anything else limits their use in paint work. Hansa Yellows are non-bleeding in oil and water, bleed badly in solvents, are fast to acids, have good alkali-resistance, bake at 250°F, and are easy grinding. Hansa Yellows are several times stronger than chrome yellows. They are used for specialty paint manufacturing and also for tinting casein paints and other water-thinnable paints where alkalies are present.

Benzidine Yellows. This is a family of very strong organic pigments which has approximately 10 times the tinting strength of chrome yellows and about twice the tinting strength of Hansa Yellows. The colors are non-bleeding in oils and water and show only a slight bleed in solvents. They have good resistance to acids and some resistance to alkalies, but are not as good in this respect as the Hansa Yellows. The tint shade is less permanent than Hansa but they do not migrate. They only find limited use in the paint industry for making toy finishes where the toxic properties of chrome yellows are undesirable.

Other Organic Yellows. When making tint decorating colors and other similar transparent finishes, limited amounts of highly transparent, fugitive type yellow lakes are used. These transparent yellow lakes have various dyestuffs as their base, such as tartrazine, naphthol yellow, etc. They have good baking characteristics and are used to make imitation gold and bronze finishes, which are so popular on candy boxes, bottle caps, can closures and other similar items.

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Chapter 7

Rosin and Rosin Derivatives

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Rosin is obtained from several species of the pine tree indigenous to our Southeastern states. Commercial rosin is of two types, gum rosin and wood rosin. When the living pine tree is tapped, a sticky mixture, called oleoresin, is exuded from the wound. The distillation of this material yields gum turpentine as the distillate and gum rosin as the residue. Wood rosin is obtained by the solvent extraction of pine stumps which have been in the ground for a number of years after the tree has been cut down. The crude wood rosin as extracted from the stumps is then refined by treatment with a pair of immiscible solvents such as furfural and a petroleum hydrocarbon. Such a process removes from the crude rosin all colored and oxidized material formed in the stump during its many years' contact with air and moisture. In this manner uniform and pale grades of wood rosin are obtained.

Rosin is composed of approximately 90 per cent acidic material and 10 per cent neutral material. The characteristics of rosin are determined largely by the acid fraction. An understanding of the chemical nature of the resin acids composing this fraction permits interpretation of the properties of rosin and leads to the fullest utilization of rosin as a raw material. The resin acids (Figure 27) are structurally similar in that they all contain a more or less saturated phenanthrene nucleus with a methyl group and a carboxyl group on the 1 carbon and an angular methyl group on the 4a carbon. They differ in the nature of the substituents on the 7 carbon and in the amount and position of the unsaturation. The largest portion of the resin acid fraction, about 50 per cent, consists of abietic acid, levopimaric acid, and neoabietic acid, in which the substituent on the 7 carbon is an isopropyl group containing two ethylenic groups in conjugation. The members of this group differ only in the position of the conjugated system. Approximately another 20 per cent is made up of two stereoisomers, dextropimaric and isodextropimaric acids, which carry a methyl and a vinyl group in the 7 position. The remainder of the resin acid fraction comprises tetrahydroabietic acid which is devoid of ethylenic unsaturation, dihydroabietic acid which contains one double bond, and dehydroabietic, the unsaturation of which consists of an aromatic ring.

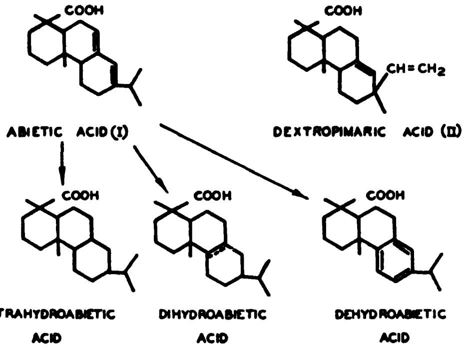

FIGURE 27. Resin acid types.

The chemical properties of rosin revolve chiefly around the carboxyl group and the unsaturation of the resin acids. While the carboxyl group of rosin is capable of undergoing the usual reactions of organic acids, such as salt formation and esterification, the reactivity of the group is greatly influenced by the fact that it is attached to a tertiary carbon. This steric hindrance factor is particularly enhanced by the fact that the tertiary carbon is a member of the bulky ring system. As a result, for example, esterification is difficult, high temperatures being required, and the esters are correspondingly resistant to saponification. The existence of most of the unsaturation in the form of a conjugated diene is of particular interest in that it permits a wide variety of reactions such as the addition of maleic anhydride, hydrogen, oxygen, or phenolformaldehyde condensates, as well as rendering the resin acids susceptible to polymerization and isomerization.

The most important resin-forming reaction of rosin is esterification. By the appropriate choice of the alcohol, the products can be varied from liquids, through balsamic resins, to hard resins (Figure 28). The melting points of the esters increase with the functionality of the alcohol and decrease as the chain between the hydroxyl groups lengthens. In evaluating these facts, one must consider that resins are amorphous materials and, therefore, do not possess true melting points as do crystalline substances. Resins are very viscous liquids; their "melting points" as determined by the various methods applied to resins are more nearly a measure of the temperature at which the resins attain a certain viscosity, that viscosity being dependent upon the method used. The harder resins, then, are in reality more viscous liquids. The correlation of the melting points of rosin esters with their composition can be understood since the relation of molecular shape, size, and complexity to viscosity of melts is known.

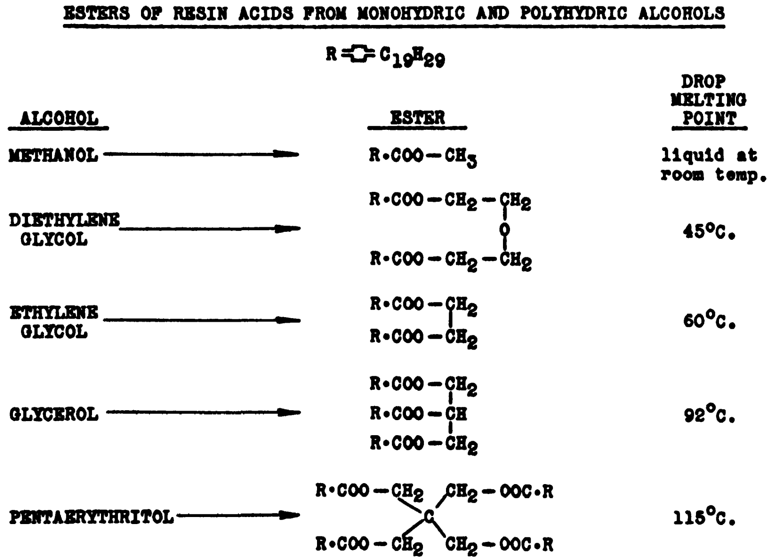

FIGURE 28

The molecular complexity, and hence the melting point, of rosin esters may be increased by the addition of maleic anhydride. This reaction takes advantage of the ability of the resin acids to isomerize as well as their ability to undergo the Diels-Alder reaction. Abietic acid, the major component of the resin acid fraction, will not react readily with maleic anhydride, whereas levopimaric acid, which is present only in small amounts, reacts at room temperature (Figure 29). If the temperature is raised so that isomerization takes place at a reasonable rate, then the isomerization equilibrium, ordinarily greatly in favor of abietic acid, can be displaced toward levopimaric acid by the adduct formation. In this manner, almost all the conjugated diene components may be converted to the levopimaric adduct. Since this adduct is a tribasic acid, esterification with alcohols of a functionality of two or more than two leads to a three-dimensional polymeric molecule. The increase in melting point attainable by this method is limited by the ratio of tribasic acid to monobasic acid (unreacted resin acids) which may be used without encountering gelation.

Another method of converting rosin to a polybasic acid is by treatment with phenol-formaldehyde condensates. Methylol phenols, prepared by the addition of formaldehyde to phenols in alkaline media, are known to add to ethylenic linkages. Although the exact nature of the reaction is not yet known beyond dispute, evidence points to a structure of the type represented in Figure 30. In some such manner two or more resin acid molecules are tied together to form polybasic acids.

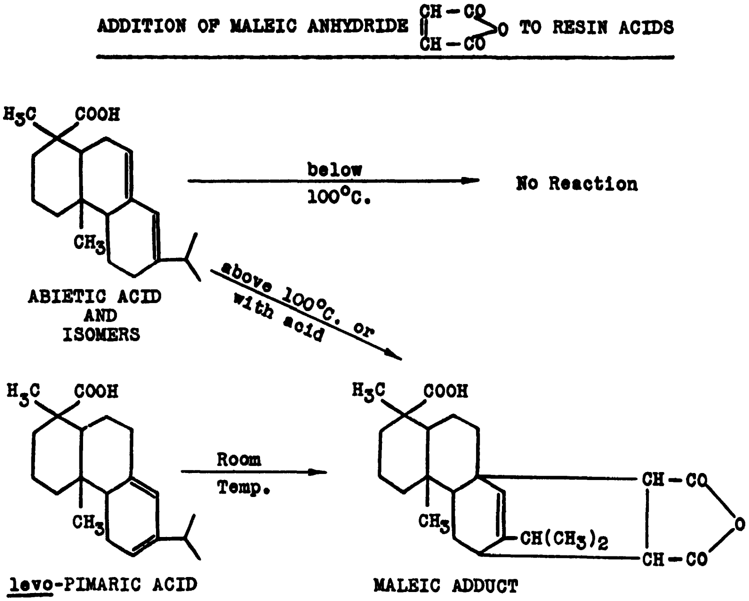

FIGURE 29

All the foregoing techniques have been employed to produce, commercially, rosin esters with a wide variety of properties and uses. The simplest member of this series is "Abalyn,"* the methyl ester of rosin. The distinctive characteristics of "Abalyn" are, first, its physical form, a heavy, viscous liquid, which at −40°C becomes pasty and mushy, but does not solidify; second, its reactive unsaturation; third, its wide range of compatibilities and solubilities; fourth, its wetting power, especially for cellulosic fibers; and fifth, its excellent resistance to saponification. These properties lead to wide use of "Abalyn" in such applications as mastic compositions, in asphaltic impregnants, as a tackifier in adhesives, and as

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* Reg. U. S. Patent Office by Hercules Powder Company.

a drying oil extender in the linoleum industry. Advantage of its reactivity has been taken in the preparation of varnishes by the reaction of Abalyn with alkaline-catalyzed phenol-aldehyde condensates in the presence of small quantities of drying oils. They are well adapted to baking on metal, and develop exceptional resistance to alkali. It is notable that the flexibility of a 10-gallon "Abalyn"-phenolic varnish is roughly equivalent to that of a 25-gallon varnish in which hard resins are used.

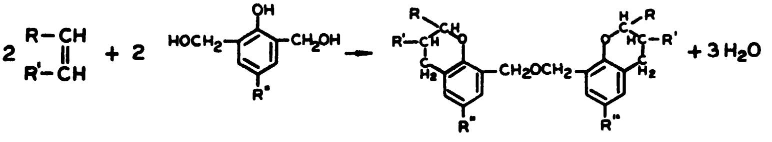

FIGURE 30. Reaction of methylol phenols with unsaturated compounds.

The glycol esters are typified by "Flexalyn,"* the diethylene glycol ester of rosin. It has a melting point of about 45°C and is balsamic at room temperature. It has found its chief use as an adhesive binder together with starch, dextrin, casein, and other water-soluble film-formers. Concentrated solutions of "Flexalyn" in organic solvents may readily be dispersed in water solutions of these film-formers; films cast from these mixed dispersions are clear and strong, showing good miscibility of the ester and the film-former, and preventing dusting of pigmented coatings.

The glycerol ester of rosin is commonly known as ester gum. This material together with the modified ester gums, such as the "Lewisols,"* are well known and have long been used extensively in the lacquer and varnish industries. A significant advance in the technology of protective coatings has resulted from the availability to industry of the pentaerythritol ester of rosin and a number of modified resins based on it known as the "Pentalyn"* resins.

By esterifying rosin with pentaerythritol instead of glycerol, two outstanding differences are achieved: first, an increase of some 25°C in melting point; second, much greater resistance to heat and saponification. The former is understandable in the light of the increase in functionality of pentaerythritol over glycerol. The latter may be deduced from the differences in the structural design of glycerol triabietate (Figure 31) and pentaerythritol tetraabietate (Figure 32). The glycerol ester has a relatively open structure, laying open the vulnerable ester groups to hydrolytic attack. In addition, this ester possesses an esterified secondary hydroxyl group with available hydrogen atoms on the alpha carbons; the

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* Reg. U. S. Patent Office by Hercules Powder Company.

result is a tendency to deacylate upon heating, accompanied by decomposition and increase in acid number. Similar tendencies have been observed upon heating fatty acid glycerides. In contrast, the ester groups of pentaerythritol tetraabietate are protected on all sides by the bulky rosin nucleus. In addition, pentaerythritol possesses only primary hydroxyl groups with no hydrogen atoms on the carbon attached to the carbinol groups.

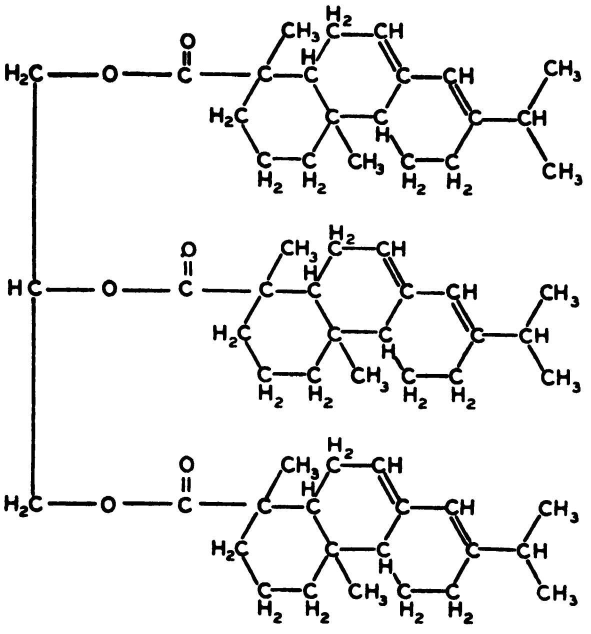

FIGURE 31. Glycerol triabietate.

It can be demonstrated that linseed oil cooked with pentaerythritol tetraabietate into a varnish yields, in comparison with an analogous preparation using ester gum, films which dry strikingly more rapidly and show greater resistance to both water and alkali. The stability of the pentaerythritol ester permits varnish preparations at 575°F or higher, at which temperatures soft oils will polymerize fairly rapidly in the presence of the ester. The resulting complex mixture of varnish polymers with the "four-spoke" pentaerythritol ester gives a film of greater mechanical rigidity than the less complex analogous ester gum varnish. The result is a film that requires less oxidation of the oil to bring it to a usable condition of dryness.

The wide selection of resins from the "Pentalyn" series is typified by those in Table 18. A variety of "Pentalyn" resins are available, graded in

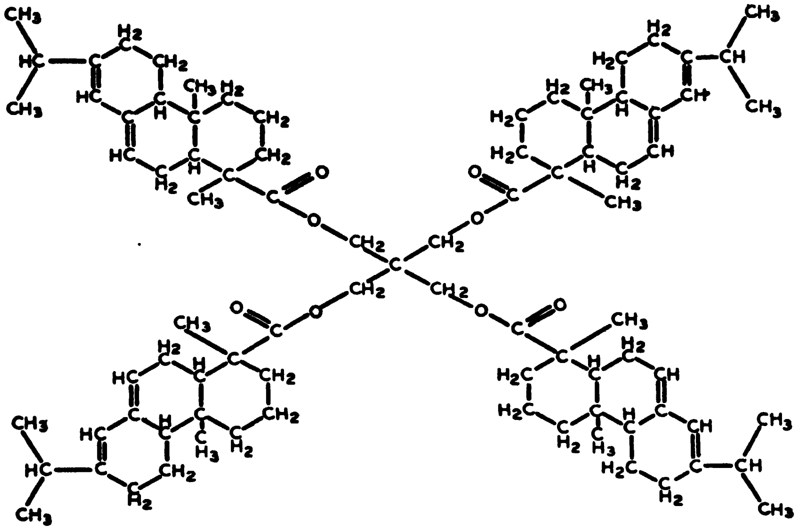

FIGURE 32. Pentaerythritol tetraabietate—*graphic formula.*

Table 18. Chemical and Physical Properties of "Pentalyns" (Typical Analyses)

	Pentalyn A	Pentalyn G	Pentalyn M	Pentalyn X.
Color (Lovibond)	35A	35A	80A	35A
Acid Number	14	15	20	15
Melting Point				
(Hercules Drop Method)	115	135	170	160
(Ball and Ring Method)	106.2	123	152	149
Specific Gravity	1.08	1.10	1.10	1.10
Hydroxyl Content	0.57	0.64	1.8	0.82
Thiocyanogen Value	43.5	42.0	40	31.5
Iodine Number	178	169	167	142.5
Refractive Index	1.544	1.544	1.545	1.545
Viscosity (50% in Mineral Spirits) Gardner-Holdt	A–	B	Z_2	U–V

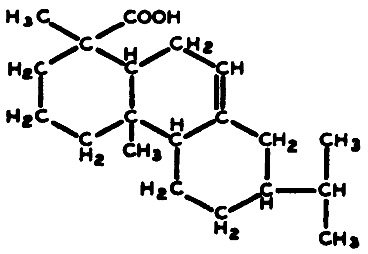

FIGURE 33. Dihydroabietic acid. *(Major constituent of staybelite resin)*

melting point and viscosity characteristics permitting varnish makers to adopt formulations using both soft and hard oils for many types of vehicles.

The reactive unsaturation of the rosin nucleus has been highly desirable in some of the applications already mentioned and of no disadvantage in others. For many uses, however, this reactivity, particularly with atmospheric oxygen, is detrimental. Since the chief offender in this respect is the conjugated diene portion of the resin acids, marked improvement is obtained by the utilization of hydrogenated rosin esters. The nature of

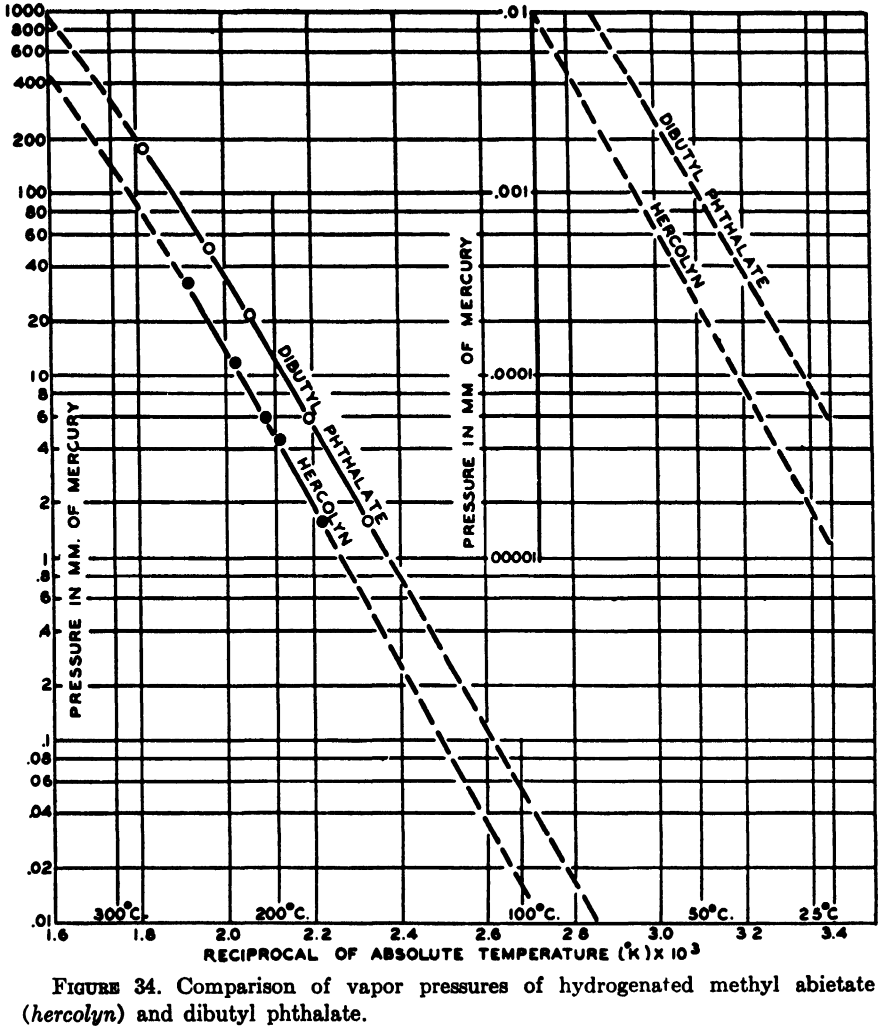

FIGURE 34. Comparison of vapor pressures of hydrogenated methyl abietate (*hercolyn*) and dibutyl phthalate.

the resin acid content of hydrogenated rosin esters may be exemplified by dihydroabietic acid (Figure 33).

"Hercolyn,"* the hydrogenated methyl ester of rosin, is very similar to "Abalyn" in properties, except that it has greatly improved retention of properties on aging. Its stability coupled with its wide compatibility (Table 19) and its low vapor pressure (Figure 34) make it useful as a resinous plasticizer. The pigment wetting characteristics, the low spewing tendency, and the excellent gloss and adhesion contributions of "Hercolyn"

Table 19. Compatibility of the Hydrogenated Methyl Ester of Rosin With Various Compounds

Compatible

Nitrocellulose
Ethyl Cellulose
Chlorinated Rubber
Vinyl Acetate-Chloride Polymers
Vinyl Chloride Polymers
Polymerized Olefin Hydrocarbons
Rubber & Latex Films
Asphalt
Coumarone-Indene Resins
Urea-Formaldehyde Resins

Incompatible

Cellulose Acetate
Vinyl Acetate Polymers

Partially Compatible

Cellulose Acetate Butyrate
Cellulose Acetate Propionate

Casein

(Compatibility of unhydrogenated methyl ester same as hydrogenated material.)

Table 20. Properties of "Staybelite" Esters

Physical State	No. 1 Tacky plastic	No. 2 Balsamic	No. 3 Viscous liquid	No. 10 Hard, brittle resin
Melting Point °C (Hercules Drop Method)	55–58	38–45	—	83–86
Acid Number (Max.)	12	10	10	10
Refractive Index @ 20°C	1.5277–1.5283	1.5225–1.5230	1.5177–1.5183	1.5319–1.5324
Specific Gravity @ 25°C	1.055–1.065	1.045–1.050	1.080–1.090	1.080–1.090
Color—(Lovibond)	25–40A	35–60A	20–60A	Max. 40A
—(Rosin Scale)	N Max.	N Max.	N Max.	N Max.
Bromine Number	85–95	85–95	85–95	85–95
Flash Point °C (Cleveland Open Cup)	244	246	226	280
Flame Point °C (Cleveland Open Cup)	276	262	263	287
Viscosity in Sec. @ 25°C—5/16 in. Falling Ball	—	—	100–125	—
Vapor Pressure @ 225°C	—	—	2.5 mm. Hg	—
Oxygen Absorption* after 160 hours	<0.1%	<0.1%	<0.1%	<0.1%
Bulking Value Lbs./Gallon (Approx.)	8.82	8.73	9.03	8.85

* Continuous film exposed to 300 lbs./sq. in. pressure of oxygen

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* Reg. U. S. Patent Office by Hercules Powder Company.

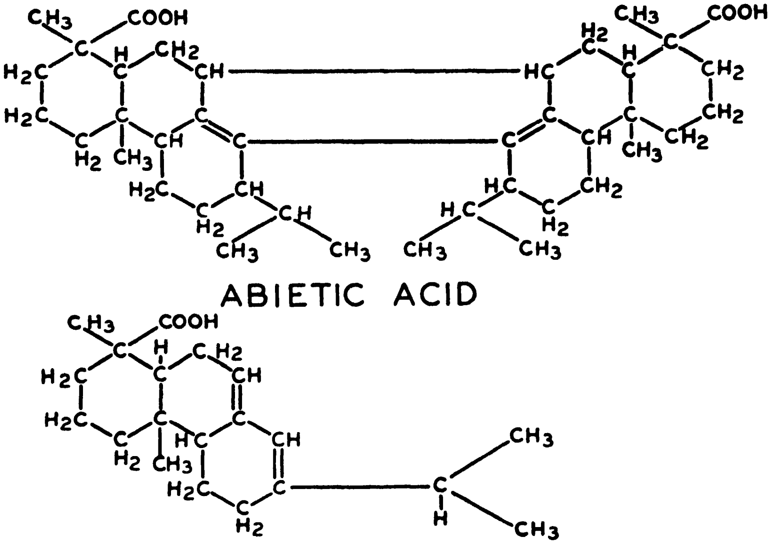

FIGURE 35. Suggested structural formulas of the dipolymer of abietic acid.

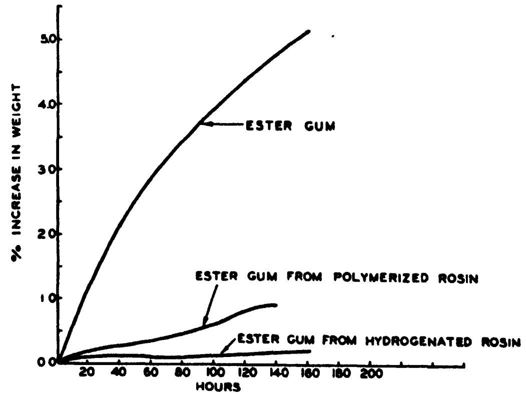

FIGURE 36. Relative oxygen absorption of various ester gums.

are particularly evident in artificial leather formulations. "Hercolyn" is also used extensively in transparentizing paper, as a tackifying plasticizer for adhesives, and in mastic compositions.

The higher melting esters of hydrogenated rosin are known as the "Staybelite"* esters (Table 20). Their physical characteristics parallel closely those of the rosin esters previously discussed with the notable exception of an exceedingly low oxygen absorption. Their stability to

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* Reg. U. S. Patent Office by Hercules Powder Company.

oxidation permits their successful use in adhesives based on natural and synthetic rubber and ethyl cellulose.

Another modification of rosin having interesting properties is polymerized rosin. Certain of the resin acids may be polymerized to yield dibasic acids. A proposed structure for the dimer of abietic acid is shown in Figure 35. Dimers of this type are present in "Poly-pale,"* and the esters of this material have higher melting points than the corresponding rosin esters. Thus, "Poly-pale" Ester No. 1, the ethylene glycol ester, melts at 80°C, which approaches ester gum in melting point, while "Poly-pale" ester gum melts at 110°C. Another interesting and predictable property of "Poly-pale" esters is the increased resistance to oxidation due to the elimination of a large portion of the conjugated diene content of rosin by polymerization (Figure 36).

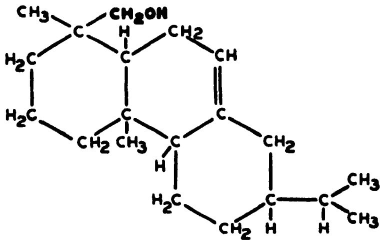

Figure 37. Hydroabietyl alcohol—*typical formula.*

Perhaps the most radical commercial use of chemical operations to modify the nature of rosin lies in the conversion of rosin to hydroabietyl alcohol. Here the carboxyl group has been replaced by a primary carbinol group. Its structure may be exemplified by one of its constituents, dihydroabietyl alcohol (Figure 37), although it also contains dehydroabietyl and tetrahydroabietyl alcohol. Hydroabietyl alcohol is an almost water-white, very viscous liquid with low vapor pressure and good color stability. The alcohol group permits a new wide variety of derivatives that promise to greatly extend the fields of application of rosin derivatives.

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Chapter 8

Natural Resins and Kindred Products

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Natural resins and their use as coating materials, as in paints and varnishes, go back to ancient times. The known natural resins are, in general, exudations of various types of trees and are collected in different parts of the world. These secretions or exudations may be either from living trees or the fossilized products of trees long dead. Some of the fossilized types of resins have almost disappeared (such as amber) and others have been gradually disappearing, for example, Kauri resin, obtained in New Zealand. There was a scarcity of these resins during the war, due to the upset conditions, but they are now appearing again.

Natural resins may be divided into two classes: (1) *fossil resins,* which are found buried in the ground; these resins are hard and friable, most of the essential oil having evaporated. They provide the bulk of the harder resins used in oil varnish making. The fossil resin group includes amber, Kauri, Congo, Boea, Manila, and Pontianak. (2) *Recent resins,* which are collected as oleo resins from the trees and harden rapidly on exposure; these are for the most part soft resins used in spirit varnishes and lacquers.

Resins are highly complex substances, and their exact composition is still a matter of uncertainty. By analysis all resins consist mainly of carbon and hydrogen, with a small proportion of oxygen. The combination of compounds which may comprise them may be listed as:

(1) Complex aromatic acids of high molecular weight.
(2) Essential oils such as terpenes.
(3) Resenes (complex saturated organic compounds.)

The resins generally exist, or have existed, in the tree in the form of a solution of the acids and resenes in essential oil. These solutions exude as viscous liquids or oleo-resins. This solution gradually hardens to form the resin on exposure to the air, partly by evaporation of the essential oil, partly by oxidation and polymerization. An example in the United States is the formation of rosin from pine trees in the South; however, we do not let the rosin cling to the tree until it hardens, but collect it and remove the turpentine.

Natural resins are characterized by great chemical stability and inertness and are not readily attacked by either acids or alkalies.

Fossil Resins

Congo Gum. Of the fossil resins at the present time, the one most generally used for varnish making is Congo gum. This product comes from the east coast of Africa, the Belgian Congo, and the surrounding territory. It is collected by natives, who walk around the swampy ground with a steel rod, poking it into the ground in the hope that it will strike a piece of resin, which is then dug out. This resin can be sorted into a great many grades, depending on hardness, color, cleanliness, and the size of pieces. There was no general grading of these resins during the war or since; they are received in a mixture of hard and soft resins, containing small and large pieces.

Congo gum does not dissolve in any organic solvent in its natural state, but will soften in some alcohols and hot solvents, giving a jelly-like mass. To make Congo gum soluble in oil, it must be cracked at moderate temperatures. This is done by the varnish maker by placing the resin in the kettle with or without rosin, as a flux, and heating to a temperature between 600 and 700°F. At this temperature, between 25 and 30 per cent of the resins is driven off, and it becomes compatible with the oil. The following is an example of a method of cracking Congo gum: 100 to 150 lbs. of Congo resin is heated in a kettle over a fairly hot fire up to 650°F, then cooled to about 575°F, run back to 650°F, and then cooled again to 600°F. It is then melted out again to about 650°F, either with or without a cover on the kettle. In this procedure the resin loses anywhere from 20 to 35 per cent of its weight, depending upon its hardness. The distillate which comes off the gum when it is being melted, if condensed, is an oily liquid, dark in color, with good solvency, but for which no particular use has been found.

It will be noted that when heat is applied to Congo gum it first swells into a more or less spongy mass, and gradually turns into a liquid as the heating continues. Eventually it becomes a thin liquid; but if allowed to cool to ordinary temperatures, it will be a hard, brittle resin, amber in color, of the same appearance as ordinary rosin, but harder.

Congo gum can be esterfied with Ester gum after it has been thoroughly cracked by treatment with glycerin, and can also be esterified in mixtures with rosin. Congo gum has been generally used in rubbing varnishes, floor varnishes, enamels, and also in baking finishes prior to the war.

Congo gum is still used to some extent and has some outstanding features; varnishes made from this resin have some characteristics which have not been duplicated in synthetic products. This is true also with other fossil resins, as in the rubbing and polishing properties of furniture varnishes, and the hardness and adhesion developed in some other applications. The success of Congo gum in varnishes has been due to a large extent to the use of China Wood Oil, and future use will depend upon availability and economic values.

Kauri Gum. Kauri gum comes from the north island of New Zealand. The trees which produced this resin are no longer in existence. Before the introduction of China Wood Oil and the use of Congo gum, Kauri was the principal fossil resin in use. It is found in the ground much the same as Congo, and in some cases excavation of the gum has gone down into the ground some 15 or 20 feet. Because of the cost of the resin and its gradually diminishing supply, its use has gradually decreased. The handling of this resin for export has been a government business with New Zealand for some time, and the grading is handled by the shippers in New Zealand.

Like Congo gum, Kauri must be cracked; it is handled in much the same way, as heat is required to crack it down. After heating, Kauri is compatible with all animal and vegetable oils. In its original form it is compatible with a wide range of solvents, such as alcohols, ketones, and other lacquer solvents.

Originally Kauri was used in varnishes for furniture. These old varnishes will be referred to often as piano, furniture and carriage-finishing varnishes, and were made with Kauri and linseed oil. They took much longer to dry than present materials, but they would polish to a much higher gloss than can be obtained with the latter.

There are Kauri trees in New Zealand now which give off a resin when tapped. This is of a very soft type, and is not generally used. Tapping is prohibited at present.

Manila Gum. There are a great many varieties of Manila. It is a fossil type, classified as Boea Manila, a light-colored resin, and is found where it has exuded from crotches of trees still standing. The amber and dark grades are found buried in the ground. This resin resembles Congo gum quite closely, but has a lower melting point and a slightly higher acid value. In melting in the kettle it does not take quite as much heat to process as does the average run of Congo resin.

Varnishes made from Boea resemble Congo varnishes. However, little of this resin is used in varnishes, because it generally costs more than Congo and finds better use in alcohol solutions as a spirit varnish.

Pontianak Gum. Pontianak is a semi-fossil copal of the Manila type, which comes from Borneo. The hard type resin in the bold form is used in making varnishes and has to be heat-treated before it becomes compatible with oil. It can be melted out much along the same line as Kauri, but it does not take quite as much heat as Congo resin. This resin, the same as Manila, is more generally used in alcohol solutions as a spirit varnish for various purposes.

When this resin was available it was plasticized with castor oil and used as a substitute for shellac.

Recent Resins

Damar. Damar is the most important of this class, as it enjoys the widest use. It comes from quite a variety of trees, and the type marketed takes its name from the region and shipping point where the collecting is done. Batavia Damar is obtained from Batavia, East Indies, while Singapore Damar comes from the port of Singapore, in the Malay Peninsula. The collecting and grading of Batavia Damar is supervised by the Netherlands government. The resin is pale in color, from straw color to water-white, and is graded from fair-sized pieces to dust. The grades run A, B, C, D, E and dust; grading depends upon the size of the pieces, the A grade being the largest pieces, and the E pieces the smallest.

Damar trees are tapped by cutting tap holes in them. The resin exudes from these holes, and is collected when it is hard enough to handle.

Damars are insoluble in alcohol, but are soluble in coal-tar and petroleum solvents, as well as in ethers and the like. Damar will dissolve in vegetable oil simply by heating. It has been used for a long time as a cold-cut resin in solvents blended with oils to make enamels and mill whites. In this case the Damar is cut in mineral thinner, turpentine or mixtures thereof. When used in this way, Damar has very good color; it imparts excellent gloss and has good color retention. Solutions of Damar, when pigmented, make good fume-proof whites, especially resistant to discoloration from sulfur. Naturally, when it is used in enamels of this type, no oil is added.

Damar is a most excellent resin for use in lacquer, especially if the lacquer is to be polished and if color is also a factor. To be suitable for this use, the Damar must first be dewaxed, as it contains between 10 and 12 per cent of wax. As this wax is not soluble in the regular lacquer solvents, using the Damar without removing the wax would give a cloudy lacquer. The dewaxing consists of dissolving the Damar in coal-tar petroleum solvent, and then precipitating the wax with alcohol. By allowing the solution to stand, the wax and alcohol separate from the gum solution, and then the two layers can be separated by decanting. After the wax is removed, the Damar is soluble in almost all solvents; as a result it can be used in lacquers without any separation. The use of Damar in lacquer imparts good rubbing and polishing properties, giving a brighter polish than most of the synthetic resins. Since it is a very pale resin, it gives lacquers a paler color than can be obtained with the other hard types of synthetic resin.

East India. This is a resin of the Damar family which is semi-fossil. The resin comes from the bold form down to smaller pieces. It is graded according to how much dirt is included in the resin, and on the size of the pieces.

The resin is quite compatible with other resins and also with asphalt, and is soluble in hot oils. Consequently, it is not necessary to use the usual melting procedure, as with Congo gum. However, it is handled in two ways. Some varnish makers prefer to melt the resin out in the kettle, while others melt it in the oil.

Prior to the war a considerable quantity of East India was used for grinding varnishes. These varnishes have good wetting properties. Cold-cut solutions of East India have been used as coating materials. If the resin is melted in oil to about 250°F (this temperature is not high enough to melt the wax included in the East India) the product is suitable for use in flat varnishes.

Black East India. Black East India is another variety of the Damar family. It is a dark-colored resin, almost black, related to Damar by similarity of origin, and closely allied to the paler grade. It has a higher melting point than Pale East India, but exhibits similar solubility and characteristics.

Batu. Batu is a semi-fossil East India resin related in a way to the Damars, and to the East Indias. It is soluble in coal-tar solvents and in petroleum solvents when about 15 per cent of coal tar is present. Batu gum contains considerable wax—more than is present in the East India. Like East India it can be used to make a flat varnish if the resin is heated with tung oil or with a varnish to a temperature which is not sufficiently high to dissolve and melt the wax.

Batu is readily soluble in oil when heated to a temperature above 500°F. It has also been used as a cold-cut solution for various purposes. One of these is a coating such as is applied to drawers and the like in furniture. In this case the inside of the drawer is either dipped in or sprayed with a solution of Batu.

Manila Gum. Some of the softer grades of Manila can be cooked into oil at ordinary temperatures without prerunning the resin, but most of these resins are relatively soft, and they find their place chiefly in alcohol solvent solutions. There are wide varieties of these resins of the spirit type which are obtained by tapping the trees and bleeding the resin. The older the resins are before they are collected, the harder they are. This is due to the loss of the volatile constituent. Resins which are not collected immediately after tapping the trees are generally hard enough so that when they are packed they do not mat together; but those that are collected immediately generally come on the market fused into one lump because of their low melting point.

The names of the various grades depend upon the regions from which they come as well as upon the sorting.

One of the particularly large uses for the softer Manila has been for making gloss finish on paper. The resin is dissolved in alcohol and then roller-coated onto the paper and run through a drying oven. It comes out with a high gloss finish, and gives practically no discoloration. This successful use is due to its rapid solvent release and to its pale color, with consequent freedom from discoloration. These resins are also used for adhesives, and when combined with pigments and other materials give excellent adhesion for such purposes as sticking down linoleum and kindred products.

The harder grades of Manila, Pontianak and the like can be used quite successfully for shellac substitutes, which have been previously mentioned.

Rosin

Rosin has been considered in detail in Chapter 7 and therefore will be mentioned only briefly in this chapter. Rosin is an annual crop, which comes from the pine trees in the southern states of the United States. These trees are tapped in a V-shaped cut; the rosin exudes from the tree and is collected. As the rosin is collected it is called "gum-thus." This is a combination of turpentine and rosin. It is then placed in stills where the turpentine is distilled off and the rosin which remains is run into packages. Originally most of the rosin came onto the market in wooden barrels, and later in metal packages; it is now marketed in paper bags.

Raw rosin as such is not generally used in finishing materials, but by various methods of treatment and as a raw material for synthetic resins, it finds its way into a wide variety of finishing materials.

Rosin can be melted in the kettle at moderate temperature (450 to 500°F), treated with lime, lead, zinc and other metallic oxides, and hardened. In this way the melting point is raised. Rosin is the basis of ester gum, where it is esterified with glycerin to form a simple ester of glycerin and rosin. It can also be esterified with other polyhydric alcohols, such as pentaerythritol. It is also the basis for the hard resins of the modified phenolic and maleic type.

Shellac

Shellac can be considered as one of the natural resins and is used extensively in the coating field. Practically the entire supply of this resin comes from certain parts of India. It is an excretion of small insects, mainly from the female of the species. These little insects, which are from $\frac{1}{20}$ to $\frac{1}{40}$ inch in length, attach themselves to trees and suck the sap from the branches. They then deposit the lac on the branches and in the course of time, live, die and produce a new generation of insects. The lac is removed from the trees by cutting off the twigs or by twisting the branches so that the resin falls from the trees. It is then taken to a central place where the wood is removed. It is washed to remove the wood pulp, refuse and dye which float to the top, and then is ground up into seed-lac. It is then placed in cloth bags, heated and strained. The melted shellac is flowed onto a flat surface where it is picked up before becoming solid and stretched into a thin sheet. Finally the sheets are broken up into flakes, in which form shellac usually comes onto the market. This is known as "orange shellac."

Bleached shellac is made from orange shellac by dissolving it in a sodium carbonate solution and then bleaching with hypochlorite and again precipitating the shellac from solution with dilute sulfuric acid. If it is desirable to remove the wax from the bleached shellac, this is done while the shellac is in solution, before the addition of the bleaching agent or sulfuric acid, as the wax is not soluble in the sodium carbonate solution. Bleached shellac is marketed with between 5 and 20 per cent of water, generally around 6 to 8 per cent. It is quite necessary to keep a certain amount of moisture in bleached shellac because it becomes insoluble when dry.

Shellac is used for a wide variety of purposes as a coating material—as a clear sealer coat under varnish or as a finishing coat on wood and similar materials. With the aid of soda, borax or ammonia, shellac can be dissolved in an alkaline water solution, used in stiffening felt hats, in the manufacture of shoe polishes, playing cards, leather sizings, etc. Shellac, white and orange, is perfectly soluble in alcohol, and in this form is used as a finishing material. Engravers coat the backs of zinc plates with shellac before dipping them in acid. In this way the strong acid dissolves the zinc from the face of the plate, but it does not attack the back. Shellac is also used as a dressing for leather and an ingredient of polishes, a glaze for paper, a stiffener for both wool and felt hats, a binder in shoe soles and leather work, the adhesive in gasket cement, nonconducting dielectric insulating coatings, a molding material for dielectric parts, an ingredient of ink, rubber, match heads, the principal constituent of sealing wax and for phonograph records.

The question remains, "What is Shellac?" Many attempts have been made to imitate shellac with synthetic material or with other resins, but at no time has anyone been able to develop a product which has all the qualities exhibited by shellac.

Asphalt

Natural asphalts are used in the manufacture of protective coatings. Of these the most important one in this country is Gilsonite, an asphalt mined in the states of Utah and Colorado. It appears in vertical veins from a fraction of an inch to 18 feet wide, several miles in length and up to 200 feet deep. This asphalt has been pushed up between the rock formations by great pressure.

There are three grades of Gilsonite: Jet, Select and Second. The Jet grade comes from the middle of a certain vein called "Cowboy" and it is more or less free from mineral matter. The "Second" includes all that is not suitable for the previous two grades, and may also contain some mineral matter, because it generally comes from the sides of the vein next to the rock and shale.

Gilsonite is used in the manufacture of black varnish, and is either heated alone or melted in oil. It answers the same purpose in these black varnishes as natural gums and other resins do in the clear varnishes, in that it is used as a hardening agent for the oil. There is generally a brown tone to a Gilsonite varnish, although the color is black.

Gilsonite has a fusing point of about 240 to 320°F depending upon the grade of the material. The Selects are the softest and the Jet grade is the hardest.

There are other natural asphalts which are used in the same manner as Gilsonite, and these come from various parts of the world. They occur generally as glance pitches and grahamite.

Chapter 9

Alkyd Resin Technology

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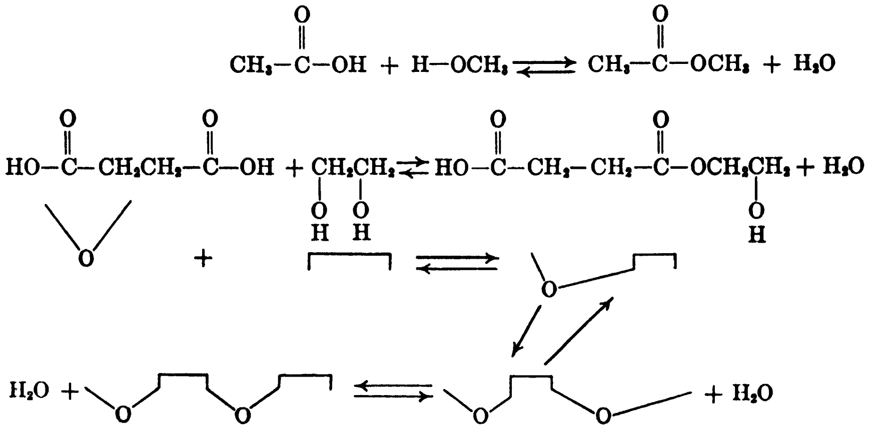
Alkyd resins are, by definition, polymeric esters prepared by the condensation of a polyhydric alcohol and a polybasic acid. They are therefore based upon one of the simplest of organic reactions, esterification. In spite of this seeming simplicity, the method of formation of alkyd resins was not truly understood until long after the resins themselves were known. The first polyester resin was prepared accidentally in 1847; yet in a standard text on synthetic resins published as late as 1927, the mechanism of the polymerization of a polyester resin was definitely stated to go through the formation of an intermediate aldehyde. It was not until the publications of Kienle and of Carothers in the late 1920's that the basic simplicity of the polyesterification reaction was truly recognized.

Let us look at some of the fundamental chemistry involved. Simple esterification is typified by the reaction of acetic acid and methyl alcohol to give methyl acetate and water (Figure 38). This is, of course, a reversible reaction and some method of removing the water is necessary to drive it to completion. We note that both the acid and the alcohol in this reaction have only one functional group, and the ester resulting from the reaction is a small monomeric molecule. If instead of methyl alcohol, ethylene glycol with two functional groups is used, the result will be essentially the same, although ethylene diacetate, the ester produced by this reaction, is a somewhat larger molecule. If both the acid and the alcohol involved in the esterification have two or more functional groups, simple monomeric molecules will no longer be produced in most cases. In Figure 38 is the equation for the reaction between succinic acid and ethylene glycol, both with a functionality of two. Again the reaction involved is simple esterification with the formation of water; again it is reversible. However, note that the primary product formed still contains one carboxyl group and one hydroxyl group.

Now, passing from the detailed structural formulas to these simpler line representations, let us follow the reaction through the succeeding steps. After the first reaction to form the monoester, we can see that a second molecule of succinic acid can esterify the remaining hydroxyl of the ethylene glycol. Then a second molecule of ethylene glycol can react with the free carboxyls at either end of the intermediate molecule. This series of reactions can, of course, be continued, with alternate glycol and acid groups adding on to the chain and the chain growing progressively longer and longer to a thread-like molecule of infinite length.



$$CH_3-\overset{\overset{O}{\|}}{C}-OH + H-OCH_3 \rightleftarrows CH_3-\overset{\overset{O}{\|}}{C}-OCH_3 + H_2O$$

$$HO-\overset{\overset{O}{\|}}{C}-CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH + \underset{\underset{H}{\overset{|}{O}}}{CH_2}\underset{\underset{H}{\overset{|}{O}}}{CH_2} \rightleftarrows HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OCH_2\underset{\underset{H}{\overset{|}{O}}}{CH_2} + H_2O$$

FIGURE 38

If one of the reactants has a functionality greater than two, the course of the reaction changes markedly. Let us consider the reaction between succinic acid and glycerol instead of ethylene glycol (Figure 39). The glycerol has three hydroxyls in place of the two in ethylene glycol. When equivalent amounts of succinic acid and glycerol are allowed to react, the first stage of the reaction is presumably very similar to the one we have already seen. The succinic will react with the primary hydroxyls of the glycerol to form rather short linear polyesters. As the reaction proceeds, however, the secondary hydroxyls of the glycerol come into play. Molecules of succinic acid will react with these secondary hydroxyls and connect the short chains, forming a branched or network type of structure. If this reaction is allowed to proceed, it is evident that very shortly a large number of these molecules will become joined by primary chemical valences. When such a state is reached the whole mass is essentially one molecule. Hence, it is no longer soluble nor fusible, in the usual sense, and reaches a state which we call a gel. Carothers was the first to analyze this condition mathematically and he derived a number of equations for predicting the extent of reaction at which gelation would occur. The calculations in the case of the reaction between succinic acid and glycerol predict that gelation will occur when approximately ⅘ of the groups have reacted. This is in fairly close agreement with experimental results.

Now, to complicate things a little further, let us replace part of the succinic acid in this last reaction by a monofunctional acid such as acetic acid (Figure 40). Let us assume that the first reaction which takes place is between the acetic acid and one hydroxyl of the glycerol molecule. The resulting ester, or monoglyceride, may now be regarded as a glycol, since it has only two free hydroxyls. If we allow the succinic acid to react with this modified glycol a linear polymer should result, since the functionality of each reactant is now only two and cross-linking, with its subsequent gelation, should not occur.

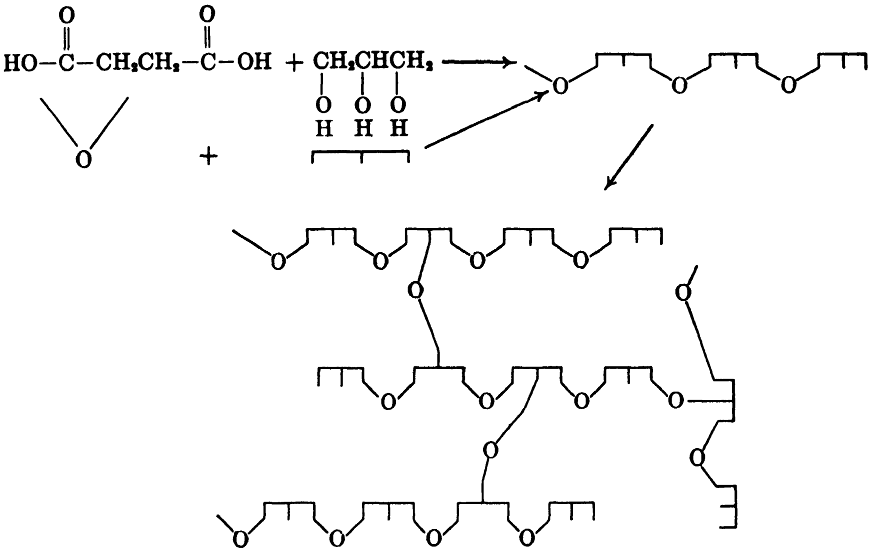


Figure 39

If we increase the amount of monobasic acid beyond the single mole illustrated, we can see that certain of the glycerol molecules must combine with two moles of acetic acid, leaving only one hydroxyl group. When these glycerol molecules react at the end of a chain there will no longer be any reactive functional group through which the chain can grow. Terminated molecules, such as those indicated as II in Figure 40, will be formed. The so-called "terminal molecular weight" will be a function of the ratio of monobasic to dibasic acid. It is possible to develop equations to calculate what this molecular weight should be; experimental results check these calculated values rather closely. Of course, if there is insufficient acetic acid to react with all the secondary hydroxyls of the glycerol, some of these will still be available for cross-linking, so that while gelation of such a system may be postponed beyond the ⅚ reaction point, it must inevitably occur if the reaction is carried sufficiently far.

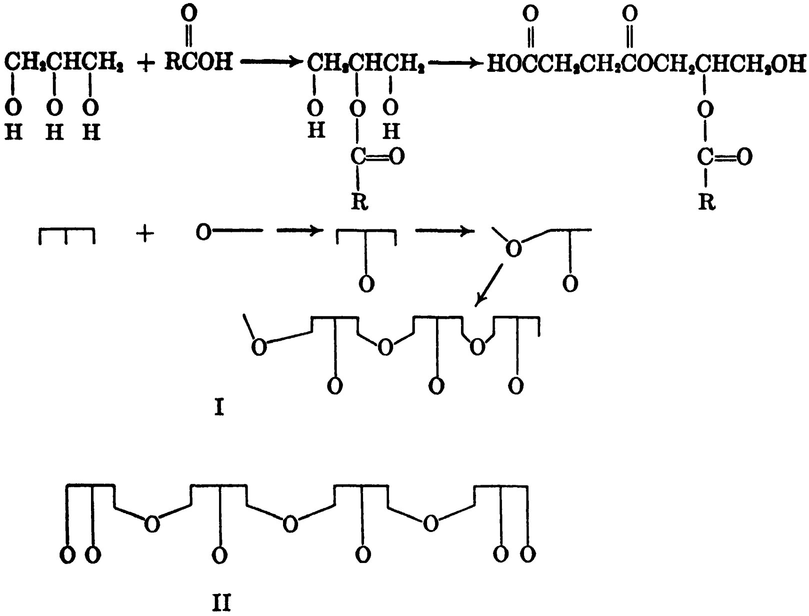


FIGURE 40

It should be pointed out that these reactions have been idealized for the sake of simplicity. Actually, in almost any system containing a dibasic acid, a monofunctional acid, and glycerol, there would be some formation of branched chains, since molecules tend to go their own sweet way, and acetic acid is not so amenable as to react with only the secondary hydroxyls of the glycerol.

Turning now, briefly, to the history of alkyd resin development, it has been mentioned that the first polyesters were prepared in the middle of the last century. Berzelius reacted tartaric acid and glycerol in 1847, and obtained a light-colored, brittle mass. Von Bemmelen in 1856 reacted succinic acid and glycerol and obtained a gelled polyester. In those days, no self-respecting organic chemist would have anything to do with such weird "gunks" which could be neither crystallized nor distilled. A few hardy souls continued to experiment with these materials, however, and in 1901, Smith reported the reaction between glycerol and phthalic anhydride. Between 1910 and 1915, Callahan recognized the commercial possibilities of some of these polyesters and prepared and patented a number of variations on the basic alkyd reaction.

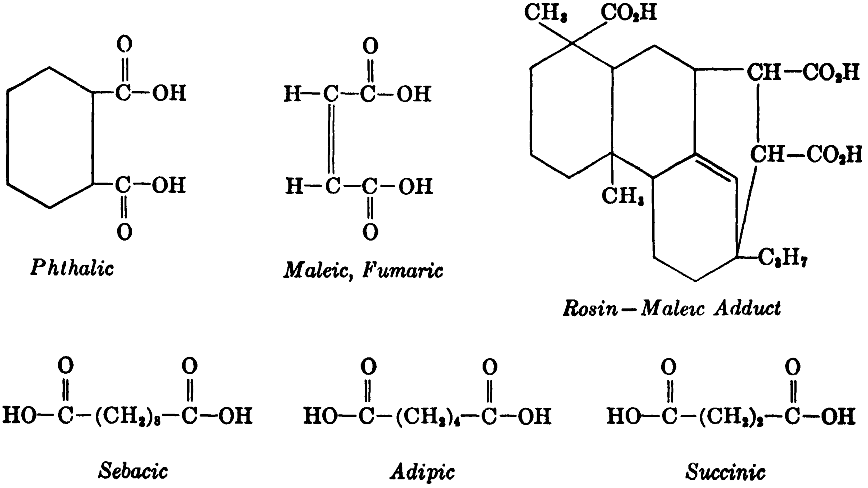
The development of these resins was enormously stimulated by the introduction around 1918 of the Gibbs and Conover process for the production of phthalic anhydride from naphthalene. This produced for the first time a pure dibasic acid at a reasonable price. A great many empirical experiments were performed with alkyd resins, substituting all sorts of mono- and polyfunctional reactants for the primary polybasic acid and polyhydric alcohol. As a result of this work, it was found that resins prepared by reacting phthalic anhydride, glycerol and oleic acid were excellent permanent plasticizers for nitrocellulose. They imparted to the hard nitrocellulose film a very desirable fullness and gloss which withstood weathering remarkably well. In addition, the adhesion and flexibility of the film were improved. This development formed the basis for the well-known Duco finishes for automobiles.

Around 1927, it occurred to a number of people that if fatty acids from drying oils were used in an alkyd resin, instead of oleic acid, a "coreacted varnish" might result which would be an excellent air-drying vehicle. This was indeed the case, and the field was opened for the tremendously large and varied expansion of alkyd resins in the coatings field.

The raw materials available for use in alkyd resins are many and varied, though they generally fall into three classes: Polybasic acids; polyhydric alcohols; monobasic acids. Because of this wide choice of starting materials, there is perhaps no other class of resins which is capable of such wide variations in physical properties and uses.

Let us look at some of the polybasic acids which are available (Figure 41). By far the most important is phthalic acid, usually, of course, sold in the form of its anhydride. Another important acid is maleic, also usually sold as the anhydride, and its isomer, fumaric acid. In addition to their reactivity as acids, maleic and fumaric contain an active double bond, which can combine with unsaturated fatty acids, terpenes, rosins, etc. These two acids are often used combined with rosin by bonds formed along the dotted lines (the Diels-Alder reaction), forming a tribasic acid, the rosin-maleic adduct. In a somewhat different class are the aliphatic dicarboxylic acids, sebacic, adipic, and succinic.

The fundamental properties of an alkyd resin are very markedly affected by the choice of the dibasic acid used. The glycerol esters of phthalic acid, maleic acid, and of rosin-maleic adduct are hard, brittle resins. On the other hand, the corresponding esters of sebacic and adipic acids are soft or in some cases almost liquid materials. The reason for this difference is rather easy to see. The two carboxyl groups in phthalic acid, for example, are quite rigidly attached to the benzene ring. They cannot change their spatial relationship to each other. The same thing is true in maleic and fumaric acids and in the rosin-maleic adduct. In the case of sebacic and adipic acids, however, the two carboxyl groups are separated by a long flexible chain of carbon atoms; thus the two carboxyl groups can assume almost an infinite number of positions with respect to each other. Succinic acid falls between these two classes. Although there is some degree of flexibility between the two carboxyl groups, it is markedly less than in sebacic or even adipic. If any of the more rigid acids is reacted with a polyhydric alcohol of a functionality greater than two, the network which results will be a very rigid one, since the cross-linking acids have little or no flexibility. On the other hand, when sebacic or adipic acid is substituted, the cross-linking acids are flexible; consequently a soft or even fluid product results. As might be expected, succinic esters are midway between the two classes. We might compare glycerol phthalate or glycerol maleate to a three-dimensional network made from rigid wire. On this analogy the sebacate or adipate would be a network woven from flexible threads. Polar attraction between the carboxyl groups exaggerates these differences.



Phthalic *Maleic, Fumaric* *Rosin—Maleic Adduct*

Sebacic *Adipic* *Succinic*

FIGURE 41

A rather wide variety of materials is also available for use as the polyhydric alcohol component (Figure 42). By far the most important of these is glycerol. Other polyfunctional alcohols of interest are pentaerythritol and, to a lesser extent, sorbitol and mannitol. Glycols are of some value for certain speciality resins, particularly ethylene glycol and propylene glycol. Both of these glycols also form ether-glycols, a class of which diethylene glycol is typical.

The dependence of the physical properties of the final resin upon the polyhydric alcohol used is quite similar to that found in the case of the polybasic acid. Glycerol phthalate, pentaerythritol phthalate, and ethylene glycol phthalate are hard, brittle materials; diethylene glycol phthalate is a very viscous liquid. This difference between diethylene glycol and the other materials is again undoubtedly due to the long, relatively mobile chain between the hydroxyl groups in diethylene glycol. As might be expected, most of the sebacic esters of these alcohols are viscous liquids or soft gums such as propylene sebacate. In the case of ethylene glycol, however, the product is a hard, tough, waxy material. This unusual behavior is due to the fact that ethylene sebacate is a rather homogeneous material and hence actually crystallizes. Above its melting point, approximately 72°C, it is a very viscous fluid, quite similar to propylene sebacate at room temperature.

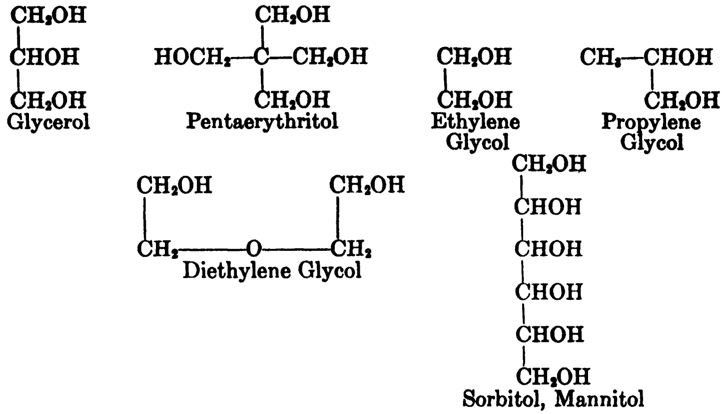
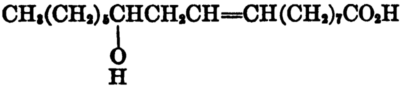


Figure 42

By far the greatest number of alkyd resins manufactured are not simple esters of polyhydric alcohols and polybasic acids, but are modified with varying amounts of monobasic acids. With the exception of rosin, almost all of these monobasic acids are derived from the vegetable oils or animal fats which are glycerol esters of these acids. In Table 21 are listed the more important fatty acids which are available from these sources. All of them are derivatives of stearic acid, the straight-chain 18-carbon atom aliphatic acid. The three acids following stearic acid, oleic, linoleic, linolenic, are the major components of the common vegetable drying and semi-drying oils such as linseed, soya, cottonseed, peanut and olive oil. They differ from stearic acid by increasing amounts of unsaturation. Oleic acid has one double bond, linoleic two double bonds, and linolenic three double bonds, each of these double bonds being separated from its neighbor by a methylene group. We are all familiar with the drying properties of linseed oil. If a film of linseed oil is exposed to the air, it gradually thickens, then gels and finally forms a hard coherent film. This drying to a hard film is accelerated by the addition of oil-soluble salts of certain multivalent metals such as cobalt, manganese, and lead. The chemistry of this change is quite complex. This has been considered in Chapter 3. It is found that if an oil has an iodine number of approximately 135 or more, it will undergo drying. This is equivalent to about 1.5 double bonds per fatty acid residue. Below this range, the oils either do not dry or take extremely long times to form a film.

Table 21

		I. No.
Stearic	$CH_3(CH_2)_{16}CO_2H$	0
Oleic	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$	90
Linoleic	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$	180
Linolenic	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$	273
Eleostearic	$CH_3(CH_2)_3CH{=}CHCH{=}CHCH{=}CH(CH_2)_7CO_2H$	273
Ricinoleic	 $CH_3(CH_2)_5\underset{\substack{\vert\\ OH}}{CH}CH_2CH{=}CH(CH_2)_7CO_2H$	85
Dehyd. Ricin.	$CH_3(CH_2)_5CH{=}CHCH{=}CH(CH_2)_7CO_2H$	180

Most of the common oils are glycerol esters of the first four fatty acids. However, there are two very important oils which are based upon quite different fatty acids. Tung oil, containing about 90 per cent of eleostearic acid ester, is the most rapid drying oil known. Its films are extremely alkali-resistant. This rapid drying and good resistance are due to the fact that all three double bonds in eleostearic acid are conjugated, making them very much more reactive than the so-called isolated double bonds in the linseed series of acids. Ricinoleic acid is the main fatty acid in castor oil. The hydroxyl group in ricinoleic acid is responsible for many of the unusual properties of castor oil, such as its solubility in alcohol, its high viscosity, and its purgative properties. Since ricinoleic acid has only one double bond, and an iodine number of only 85, the oil derived from it is not a drying oil. However, like most aliphatic hydroxylic materials, ricinoleic acid can be dehydrated, introducing another double bond. The acid so produced is an isomer of linoleic acid. The formula given for it shows the two double bonds conjugated. Actually, only about 25 or 30 per cent of dehydrated ricinoleic acid will have this formula; the other 75 per cent has its double bonds in the isolated position similar to linoleic. With two double bonds and an iodine number of about 160, the esters of dehydrated ricinoleic acid or dehydrated castor oil are excellent drying oils. Most of the properties of these oils carry over into alkyds modified with their fatty acids.

Table 22

Oil	I. No.	Speed	Color	Gloss Ret.
Tung	170	↑	│	↑
Linseed	180	│	│	│
Dehyd. Castor	155	│	│	│
Soya	135	│	│	│
Cottonseed	110	│	│	│
Peanut	108	│	│	│
Olive	85	│	│	│
Castor	85		│	
Coconut	9		↓	

In Table 22 are the more common vegetable oils whose fatty acids are used in the manufacture of alkyd resins. Tung, linseed, soya and dehydrated castor are used in drying type alkyds; cottonseed and peanut oil are used in non-drying or semi-drying alkyds; coconut and castor oil are used only in non-drying materials.

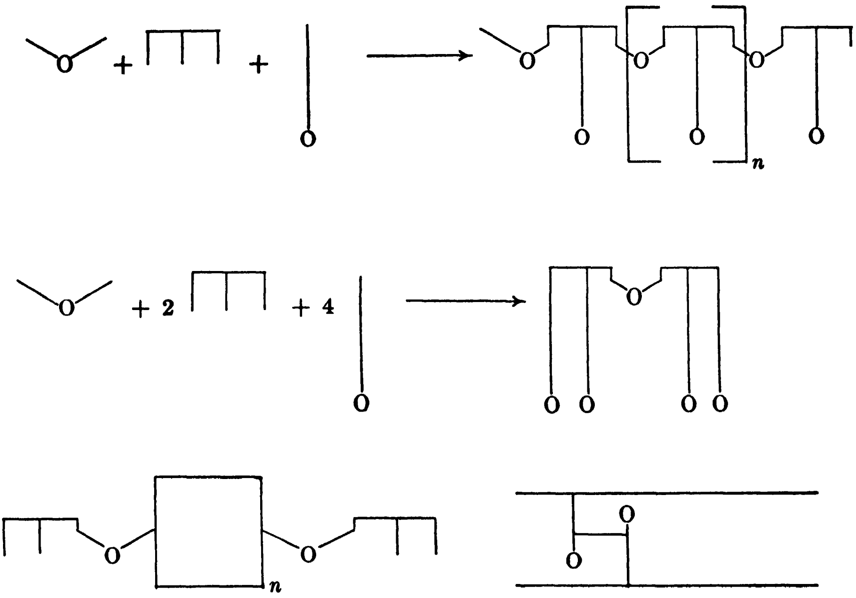
With the exception of stearic acid, which tends to give waxy alkyd resins, the physical appearances of alkyd resins modified with different fatty acids are quite similar. The important thing from a *physical* point of view is the proportion of fatty acid to polybasic acid. This proportion may be expressed in a number of ways. Most useful is the "alkyd ratio." If one reacts, say, phthalic anhydride, glycerol and a fatty acid to obtain a resin of relatively low acidity, any individual molecule of that resin is a very mixed ester. A certain glycerol unit in the resin molecule may have one or two of its hydroxyls esterified by phthalic, and one or two of its hydroxyls esterified by monobasic fatty acid. Consequently, there is no glyceryl phthalate or glycerol ester of the fatty acid present as such. However, it is convenient to speak of the glyceryl phthalate content, or the alkyd ratio, of such a resin. These two terms, glyceryl phthlate content or alkyd ratio, both refer to the weight per cent of glyceryl phthalate which could be obtained if the phthalic anhydride in the resin formulation had been reacted with the stoichiometrically equivalent amount of glycerol.

The physical appearance of a modified alkyd resin is largely a function of its alkyd ratio. Thus, if the alkyd ratio is 100, we have pure glycerol phthalate and the product is a hard, brittle material, soluble only in such strong solvents as ketones and esters. If the alkyd ratio is 0, we have pure oil and the product is usually a fluid of quite low viscosity and soluble in such poor solvents as mineral thinner and other aliphatic hydrocarbon mixtures. As the alkyd ratio decreases from 100 to 0, the physical properties of the product change continuously between these two extremes. At an alkyd ratio of 60, for example, the resin is a tough, gum-like material which is soluble in xylene and toluene, as well as the stronger oxygenated solvents. As the alkyd ratio falls to about 45, the product gradually changes from a soft gum to an extremely viscous liquid and begins to have solubility in the aliphatic hydrocarbons. As the alkyd ratio is reduced still further, the viscosity of the final product becomes lower and lower. The usual alkyd resins of the coatings industry range from alkyd ratios of about 65 to 18.

There are two rather critical points of alkyd ratio in any series of alkyd resins. In the glyceryl phthalate series, one of these is at 40 alkyd ratio and the other at 14. The reasons for these two points is shown in Figure 43. If we react a mixture of 1 mole of phthalic, 1 mole of glycerol and 1 mole of fatty acid, this combination, theoretically at least, would produce only a linear polymer. Such a resin would be capable of proceeding to a very high molecular weight, but would not be capable of gelling. This particular resin has an alkyd ratio of 40.

As the alkyd ratio is raised above 40, you can see that this is equivalent to replacing some of the monobasic acid by dibasic acid. When this is done, cross-linking of the chains becomes possible and the resulting resin is capable of gelation. If the alkyd ratio is decreased from 40, this is equivalent to replacing part of the dibasic acid by monobasic acid. The chains thus will ultimately become terminated, since some of the glycerin molecules must react with two fatty acid molecules. Hence, as the alkyd ratio is decreased below 40, the resin should reach a terminal viscosity beyond which it cannot go by simple esterification; this viscosity will be lower, the lower the alkyd ratio. The other critical point is indicated by the second equation in Figure 43. If we react one mole of dibasic acid, two moles of glycerol and four moles of fatty acid we should obtain on the average the product shown. This is a rather small molecule as resins go. If the alkyd ratio is decreased further, that is, if part of the polybasic acid is replaced by a monobasic acid, it will be necessary for at least some of the glycerol molecules to react with three fatty acid molecules. Such a molecule is not an alkyd resin at all. It is an oil. Consequently, any glycerol phthalate resin prepared at an alkyd ratio of less than 14 is actually the equivalent of a blend of an 14 alkyd ratio resin with an oil.

There are two other factors important in alkyd resin formulation which modify these statements. One is the fact that an excess of polyhydric alcohol over the stoichiometric amount is almost always necessary in order to reach a low acid number in a reasonable time. This, of course, has the effect of terminating some of the polymer chains by placing on the ends of the chain glycerol molecules for which there is no acid available. Such a molecule is illustrated in Figure 43 and is, of course, incapable of reacting further. This has the effect of producing a terminal viscosity in glyceryl phthalate alkyds at higher alkyd ratios than 40. The other effect is caused by the ability of unsaturated fatty acids with two or more double bonds, such as linoleic or eleostearic acid, to dimerize. Two such fatty acid molecules may unite to form a dibasic acid. Any such dimerized fatty acids can no longer be considered as part of the monobasic acid fraction, but rather as part of the alkyd fraction, since they can, of course, cross-link two polymer chains in the manner illustrated. Hence, when reactive fatty acids such as these are used in an alkyd resin, gelation is possible at alkyd ratios considerably lower than 40. In fact, in the case of tung oil, gelation is possible at an alkyd ratio of 0. As these two factors



I

II

FIGURE 43

tend to counterbalance each other, in practice as well as theory the two alkyd ratio values of 14 and 40 remain critical ones in the glyceryl phthalate series.

A few of the properties which make alkyd resins so useful, and how these properties vary as the formulation is changed will now be briefly considered. The most valuable property of alkyd resins as film-forming agents is their durability under a wide variety of trying conditions. By this is meant that a film comprising an alkyd resin will retain its protective value for a long time. In addition, it will also have excellent gloss and color retention, so that its decorative as well as its protective value is of long duration. This is true of both the two major types of modified alkyd resins, the drying oil modified resins, which are capable of forming films by themselves, and the non-drying oil modified alkyds which require the addition of a film-former such as urea-formaldehyde resin or nitrocellulose.

In Figure 44 is shown in a rather rough manner how some of the important film properties of alkyd resins vary with the alkyd ratio. The speed of set and the ultimate hardness of the resin are directly proportional to the alkyd ratio, since they are both dependent upon the hard resin content, which is to say the glyceryl phthalate content. The through-dry or through-hardness and the durability will vary differently, depending upon whether the resin is simply air-dried or baked. In an air-dried film, hardness and film integrity are obtained by the oxidation and polymerization of the fatty acid portion. Consequently, the more fatty acid the formulation contains up to a certain point, the better will be the through-dry and the durability. In a baked film, on the other hand, continued polymerization of the alkyd portion is an important process in obtaining the ultimate properties. Consequently, in films of this type, the through-dry and the durability increase with the alkyd ratio.

Since the discoloration of an oil-modified alkyd is due to the unsaturated fatty acid portion, the color retention will be better as the oil fraction is decreased, that is, as the alkyd ratio is raised. The tolerance of the resin for alcohol is greater as the alkyd ratio is increased. Compatibility with polar resins such as urea-formaldehyde and nitrocellulose follows the same trend. The tolerance for aliphatic hydrocarbons, on the other hand, is exactly the reverse of this, as might be expected. Compatibility with drying oils follows the same trend as the hydrocarbon tolerance. Ease of brushing, an important property for many coating compositions, is influenced by a number of factors, but in general it improves with decreasing alkyd ratio.

Of course, the character of the fatty acid in the modifying-oil portion of the alkyd also has a very marked effect on the film properties of the final resin (see Table 22). Generally speaking, it may be said that most of the properties vary with the iodine number of the oil fatty acid. Thus, resins modified with oils of high iodine number are very fast-drying and give hard, resistant films. Those with lower iodine number are slower drying and, of course, in the case of resins modified with oils of iodine number of 120 or lower, good films are formed only when some other component such as urea-formaldehyde or nitrocellulose is present. Since discoloration is due to the double bonds in the oil, color retention is improved as the iodine number is lowered. Gloss retention, on the other hand, is usually improved by using the higher iodine number oils.

The variation in film properties with the variation in dibasic acid or polyhydric alcohol content are those which might be expected from the character of the polyesters which the individual materials form. Thus, phthalic alkyds in general form hard films with a tendency toward brittleness, making them very suitable for applications in which the alkyd resin is used alone. Sebacic or adipic resins, on the other hand, give soft, flexible films, and hence they are usually used as plasticizers for other film-forming materials. Glycols are customarily used only in alkyd resins which contain no monobasic acid, since they are capable of forming only linear polymers with dibasic acids, and the addition of a monofunctional acid would mean a final product of very low viscosity. Pentaerythritol is coming into wider and wider use in place of glycerin in drying-type resins because resins made from it dry very much faster and harder than their glycerin counterparts and in general have markedly improved alkali resistance. The same thing is true to a lesser extent of mannitol and sorbitol. There are good theoretical reasons for this difference, but they will not be considered in this discussion.

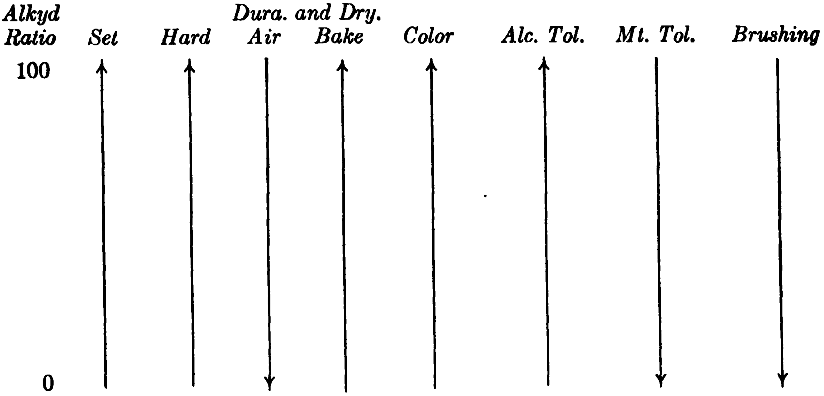


FIGURE 44

Fairly substantial amounts of alkyds are further modified with rosin, natural resins or phenolic condensates. In general, these alkyds have the advantages and drawbacks usually associated with the modifying resins when these are used in conventional varnishes.

A brief consideration will now be given to the manufacture of alkyd resins. In the laboratory this is usually done by one of two methods. In the so-called "fusion" method of manufacture, the alkyd components are charged to a three-neck flask, as shown in Figure 45. Carbon dioxide is introduced either over the surface of the batch or below the surface. The resin is heated to reaction temperature, usually in the range of 200–260°C, water is evolved, and the viscosity and acid number are followed until they reach suitable values. In the "solution" method of manufacture, a high-boiling solvent is added with the other components and the mass is heated to refluxing temperature. The refluxing solvent returns to the flask through a water separator. Viscosity and acid number are followed in a similar manner until the desired properties are attained.

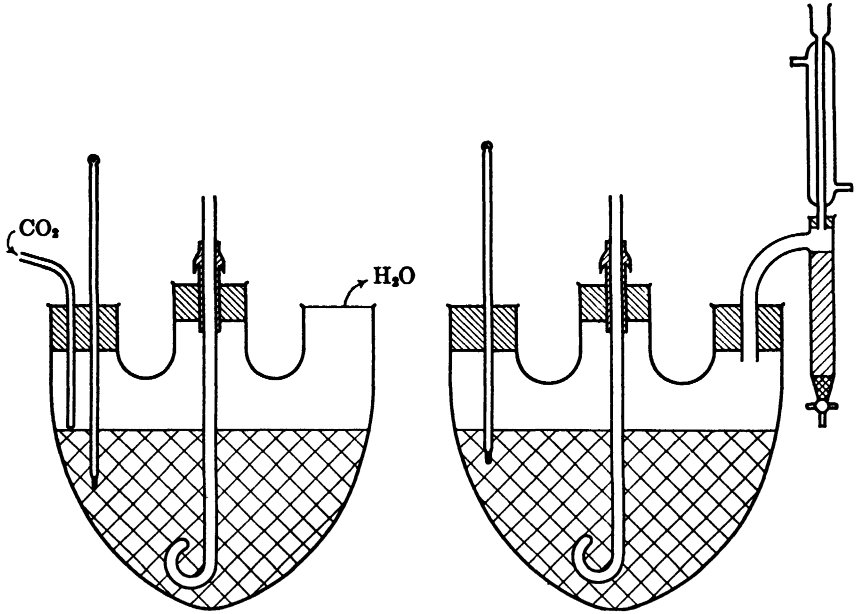


FIGURE 45

Viscosity and acid number curves are illustrated in Figure 46. The dotted line (I) represents a typical acid number curve. It falls very rapidly from an initial high value; then, as the concentrations of acid and hydroxyl groups diminish, the rate slows down and the acid number finally approaches a low value. The viscosity curves, illustrated by the solid lines, fall into three general classes. The lower curve (II) is that for a relatively low alkyd ratio resin which rises steadily for a while and then levels off at a terminal viscosity. The middle curve (III) represents an alkyd in the 40 alkyd ratio range, which continues to rise steadily and does not level off. The top curve (IV) is typical of resins in the ranges where gelation can occur. The viscosity rises steadily until gelation is imminent, and then at the gel point jumps rapidly to an infinite value.

For any given alkyd ratio, there is an optimum range in which the viscosity and acid number should lie. If the resin is stopped before this range is attained, poor drying, poor water resistance and generally inferior properties are found. If the resin is carried beyond this range, reactivity with pigments, poor gloss and other undesirable properties occur. The need for very careful control and uniformity of product in the manufacture of alkyd resins is obvious.

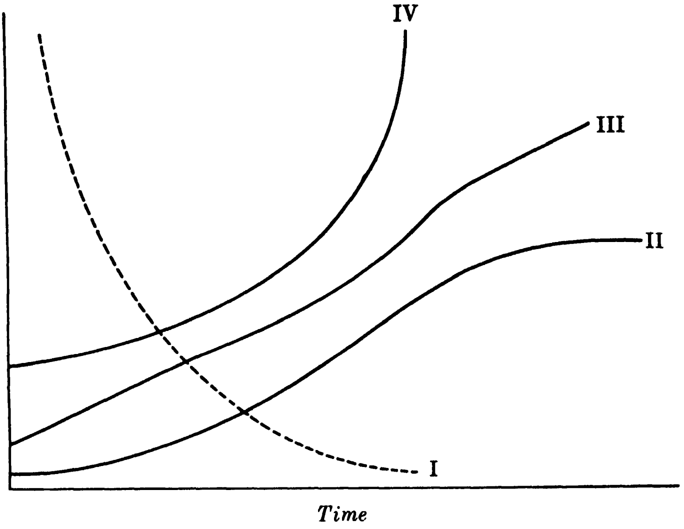


FIGURE 46

It often happens that the best formulation to give a desired combination of physical properties is difficult to obtain. Reactivity of the oil portion, alkyd ratio, the type of polyhydric alcohol and the amount of excess polyhydric alcohol must all be carefully balanced. Until recently this has been more of an art than a science. There has been accumulating, however, a good deal of fundamental information on this subject, so that a somewhat more scientific approach is now possible. Examples of this method of formulation are too complicated and lengthy to discuss in this chapter; however, anyone interested may find an excellent theoretical discussion of one approach in a paper by Wiederhorn given at the 1947 Chicago meeting of the American Chemical Society.*

So far modifying alkyd resins by the use of various monobasic fatty acids have been considered. Most of the fatty acids used are derived from vegetable oils. Since the vegetable oils are glycerol esters of these fatty acids, it is necessary to hydrolyze the vegetable oil, separate the fatty acids from the glycerol, purify each component and then, to make an alkyd resin, add the fatty acid and glycerol with phthalic anhydride to a kettle and re-esterify them. This seems like a rather wasteful process—to take the two ingredients of an oil apart and then just put them back together again. It would be much nicer if one could merely add the vegetable oil, some phthalic anhydride and excess glycerol to a kettle, heat them up and obtain the final alkyd resin. Unfortunately, when this is attempted, glyceryl phthalate forms very rapidly. Unmodified glyceryl phthalate is insoluble in vegetable oils and will merely float around in the reaction mixture in chunks.

$$CH_3CO_2CH_3 + HOC_4H_9 \rightleftharpoons CH_3CO_2C_4H_9 + CH_3OH$$

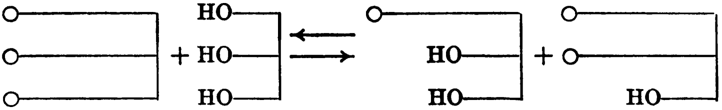


FIGURE 47

However, there is a device by which one may use a vegetable oil directly in the manufacture of an alkyd resin. The reaction involved is illustrated most simply by the equation at the top of Figure 47. If an ester such as methyl acetate is heated with an alcohol different from that in the ester, such as butyl alcohol, there is an interchange of the alcohol radicals, resulting in the production of butyl acetate and methyl alcohol. If such a mixture is heated, it will reach an equilibrium value which will contain methyl acetate, butyl alcohol, butyl acetate and methyl alcohol. A vegetable oil is an ester, and glycerol is an alcohol, so we may apply this reaction to these two components. If the vegetable oil is heated with glycerol, ester-interchange occurs and the products illustrated on the right of the second equation will be formed—monoglycerides and diglycerides. Actually an equilibrium mixture of all four components will result. This reaction is generally carried out at temperatures of from 200 to 260°C. Small amounts of alkaline catalysts, such as lime, sodium hydroxide or

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* This paper may be found on page 51 of the Division of Paint, Varnish and Plastics Chemistry reprints and will undoubtedly be published in some standard journal soon.

litharge, are generally used and the reaction is considered complete when this mixture becomes soluble in alcohol. When this equilibrium mixture, commonly called a glycerolized oil, has been prepared, phthalic anhydride may be added to it and the alkyd condensation reaction carried out. A homogeneous product will result which is essentially similar to that prepared by first saponifying the oil and obtaining the free fatty acid and the free glycerol. Alkyds prepared by this ester-interchange or glycerolysis process are suitable for many purposes. For the highest quality alkyds, however, it is still necessary, in most cases, to use the free purified fatty acid.

Manufacture of alkyd resins on a plant scale is generally carried out in 500 to 3000 gallon kettles which are essentially large-scale versions of the laboratory three-neck flask.

Most of this discussion has been directed to the fatty-acid or oil-modified type of alkyd resin, since these are of major interest to the coatings industry. In the last few years, however, there has been a remarkable amount of activity directed toward the utilization of unmodified alkyds, especially the linear polyesters obtainable from dibasic acids and glycols. At the present time there are available synthetic rubbers, laminating solutions, fibers, casting resins, plastics, caulking compounds and resinous plasticizers, to mention a few of the products obtainable with these versatile polyesters.

For example, a polyester prepared from propylene glycol, with an aliphatic dibasic acid such as adipic, and a little maleic, can be compounded and cured with a peroxide or sulfur to give a very respectable synthetic rubber. Some of these rubbers will withstand exposure at 400°F for days. They are extremely oil resistant, although being esters, they do not stand up well against steam.

Similar polyesters, containing somewhat more maleic than the synthetic rubber type, are dissolved in styrene to give laminating and casting solutions. Since the styrene serves as both solvent and polymer-forming ingredient, these are true "solventless varnishes" and can be used under simple contact pressures instead of the pressures of several thousand pounds needed with ureas or phenolics. Both the type and amount of polyester can be varied so that the final light-colored, thermoset resins range from very flexible ones used for fabric coatings and impregnants, to hard rigid materials suitable for table tops and structural members. Since the solutions are quite fluid, and can be cured at low temperatures, castings may be made in flexible molds which will reproduce the contours of the mold with an amazing exactness.

The polymerization of these styrene solutions is inhibited by the presence of air, and open surfaces must be covered by at least a sheet of cellophane during the curing cycle. For this reason they have not made much of a splash in the coatings field. However, progress is being made along these lines, and it appears to be only a matter of time until they become another member of the growing family of synthetic coatings.

Polyester plasticizers for polyvinyl chloride corrected a serious defect in the early radar installations. Because of their high molecular weight, these polyesters show a resistance to loss by volatilization or leaching that is not attainable with conventional monomeric plasticizers. With the added advantage of pale color, the rapid acceptance of these new plasticizers for high-quality PVC is not surprising.

These newer developments combined with the steady increase in quality of the more conventional alkyds, make one confident that the important position of alkyds in industry is assured for many years to come.

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Chapter 10

The Chemistry of Urea and Melamine Coating Resins[*]

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Thermosetting nitrogenous resins have won for themselves positions of considerable importance in a variety of industrial applications, among which may be listed coatings and enamels, the bonding of plywood, the manufacture of molded and laminated articles, improvement in the physical properties of paper, and the stabilization of textiles against shrinkage and crushing. So far the two most important examples of these versatile thermosetting resins have been the urea-formaldehyde and melamine-formaldehyde types. The urea resins have been produced in this country in considerable volume since the early 1930's, whereas the more recent melamine resins date back to approximately 1940. These resins as a class are characterized by their ability to form hard, brittle, colorless, chemically resistant products upon conversion under the influence of heat or of suitable catalysts, or more generally of a combination of both. They are classed as relatively rapid-curing, and are sensitive to small changes in temperature and catalyst concentration.

A consideration of the chemistry of these resins involves three reaction stages, which may be classified broadly as follows:

"A" Stage: Methylol derivatives, analogous to monomers.

"B" Stage: Intermediate stage in polycondensation. Resins soluble or dispersible in water or other solvents. Molecules doubtless of essentially linear type, probably branched.

"C" Stage: Final "cured" stage, following conversion by heat. Insoluble, infusible, hard products. Molecules considered as complex, two- and three-dimensional networks.

Urea-Formaldehyde Resins

The simplest known reactions of urea and formaldehyde are those which lead to the formation of the methylol ureas. Monomethylol urea

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[*] After presentation at Case Institute of Technology, this article appeared in *The Resinous Reporter,* 8, No. 3, 2–6 (May, 1947) and No. 4, 12–15 (July, 1947).

and dimethylol urea are the "A" stage intermediates referred to above. Under neutral or slightly alkaline conditions and at mild temperatures, equimolecular proportions of urea and formaldehyde react to form monomethylol urea, as shown in Figure 48.

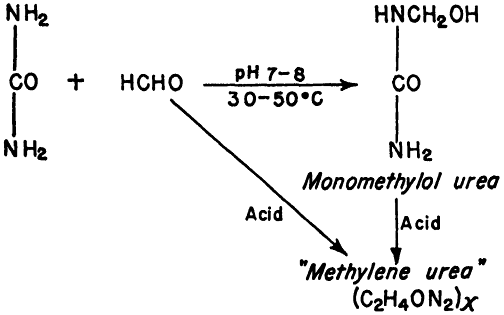


FIGURE 48

This product is a water-soluble, crystalline solid. Under similar reaction conditions urea can react with two moles of formaldehyde to form dimethylol urea, which is also a water-soluble, crystalline solid. This reaction is shown in Figure 49. Dimethylol urea or mixtures of dimethylol urea and monomethylol urea are valuable resin intermediates.

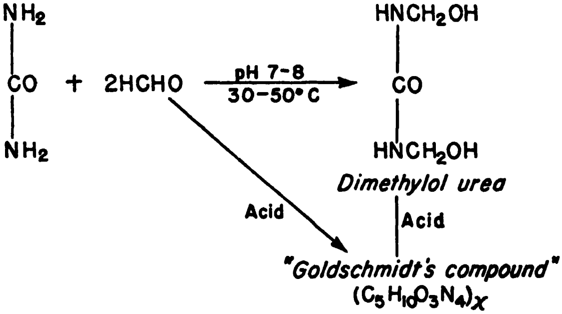


FIGURE 49

The amorphous, insoluble, infusible products, "methylene-urea" and "Goldschmidt's compound," are formed from urea and formaldehyde or from the appropriate methylol compounds, as shown, in the presence of strong acids. These products are complex and probably polymolecular in nature. Inasmuch as they are of little practical interest to the resin chemist, except as side-reaction products to be avoided, the complex problem of their chemical constitution need not be discussed.

The chemistry of the urea-formaldehyde condensation leading to the "B" stage is a rather complex problem and still a controversial one. It will be more convenient first of all to consider the "B" stage reaction of urea and formaldehyde in simple aqueous medium, even though the resulting resins are only of limited use in coatings. The preparation of the organic solvent-soluble types will be considered subsequently.

The "B" stage condensation is conveniently carried out at temperatures above 60°C and under carefully controlled, mildly acidic conditions. One or two important generalizations with respect to this condensation can be stated with some assurance. The reaction undoubtedly involves the linking of a plurality of urea units to form essentially linear molecules, which are probably branched but not cross-linked to any complex network. The linkages involved derive from formaldehyde and are generally considered to be methylene bridges. The polycondensation of monomethylol urea is the simplest possible example of this type, for which two possibilities are shown in Figure 50.

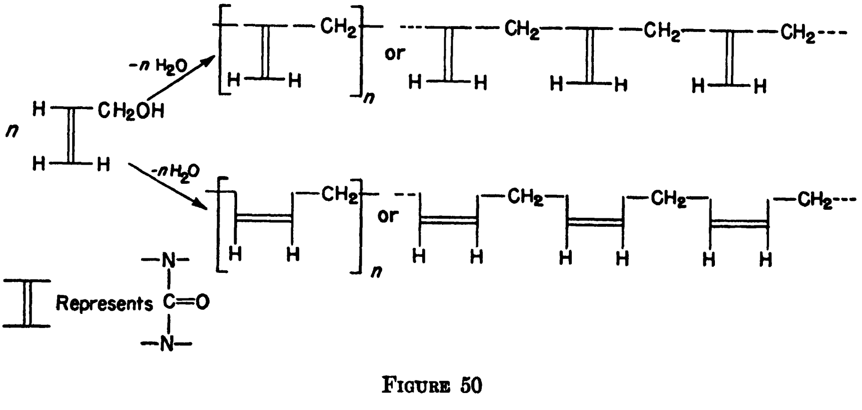


FIGURE 50

Of the two alternatives the one involving reaction between the methylol group of one molecule and the primary amino group of the other, *i.e.*, the one involving a "head-to-tail" structure, seems to be the more probable. In either instance linear molecules result which are probably not complicated by an appreciable branching, and which afford no opportunities for subsequent cross-linking and conversion to the "C" stage.

The formation of most useful urea-formaldehyde resins involves dimethylol urea, or a mixture of dimethylol and monomethylol ureas as important intermediates. Hence the "B" stage condensation of dimethylol urea is a matter of considerable importance. Unfortunately it is also a difficult question in terms of fine structural details, and one which is still controversial and unsettled. Figure 51 shows in a very general way how the type of polycondensation which has had the support of Walter and other leading investigators in this field might proceed.

The probabilities for "head-to-head" and "head-to-tail" configurations now seem to be about equal and a rather random distribution would be expected. Another manifestation of the random character of these resins would be a rather high degree of branching, a structural characteristic which is considered to be probable. At any rate, it seems quite certain that at this stage we are dealing with something less complex than a cross-linked two- or three-dimensional network.

The "B" stage condensates are soluble or dispersible in water. The resulting solutions or dispersions exhibit certain colloidal properties. For example, wide variations in hydrophobic or hydrophilic properties, directly relatable to composition variables, are exhibited. Viscosities are definitely higher than those of simple solutions and are rather sensitive functions of concentration, molecular size, and composition. Some of the hydrophils behave as protected colloids and deposit precipitates upon dilution with additional quantities of water. The question of average molecular weight is a difficult one and no completely satisfactory method for determination has yet been worked out. The best opinion, based on facts so far available, is that these "B" stage molecules probably contain not more than 10 or 20 urea units. Another important physical property of the "B" stage condensates is their relatively poor stability in solution. It is difficult to store these resins in a dilutable, reactive state for periods of more than a few months; after this time, either gelation or excessive deposition of insoluble fractions is encountered.

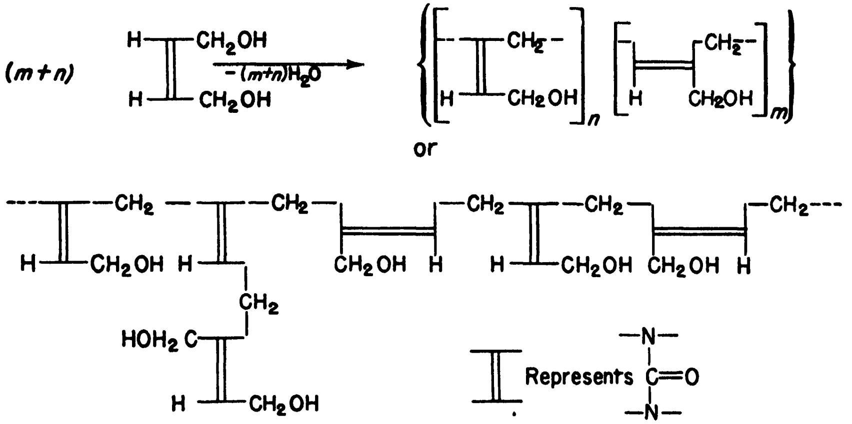


FIGURE 51

It can be seen in the type of structure proposed for the "B" stage molecules that ample opportunities exist for cross-linking by the interaction of a methylol group on one chain with a nitrogen-bound hydrogen on another. Figure 52 shows in a rough way how this process might occur.

The formation of such a complex, cross-linked network would account for the ready formation of "C" stage, hard, brittle, insoluble, infusible products by the conversion of the "B" stage resins under the influence of elevated temperature or acidic catalysts, or a combination of the two. The formation of some such network is in accord with modern theories relating to the behavior of thermosetting resins and the formation of insoluble, infusible end-products.

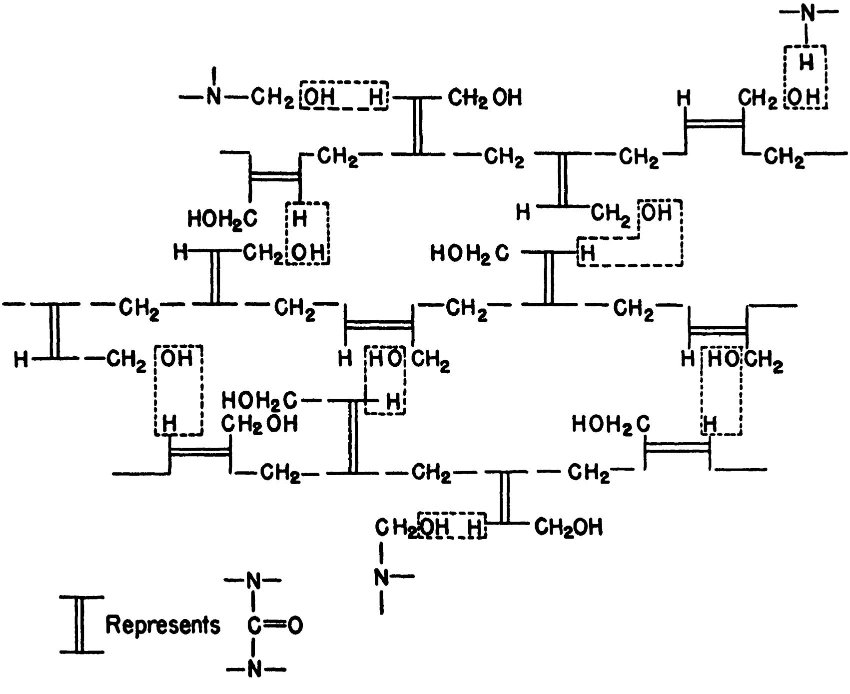


FIGURE 52

As has been mentioned previously, the nature of the urea-formaldehyde resin-forming reaction continues to be a matter of disagreement. Some chemists have been prone to consider this reaction as a type of polymerization along a double bond, similar to that involved in the polymerization of a vinyl or ethylenic compound. The principle illustrated in Figure 53 is fairly representative of such views.

Considered in this light, the analogy to the formation of linear polymers from styrene and to the formation of cross-linked polymers from divinyl benzene is quite striking and understandably tempting. There are a number of reasons why considerable caution should be exercised in drawing such a simple analogy. In our own work we have found the polycondensation mechanism discussed above to be a more useful guide. The particular type of polymerization mechanism illustrated in Figure 53 can be disproved very easily by gravimetric data.

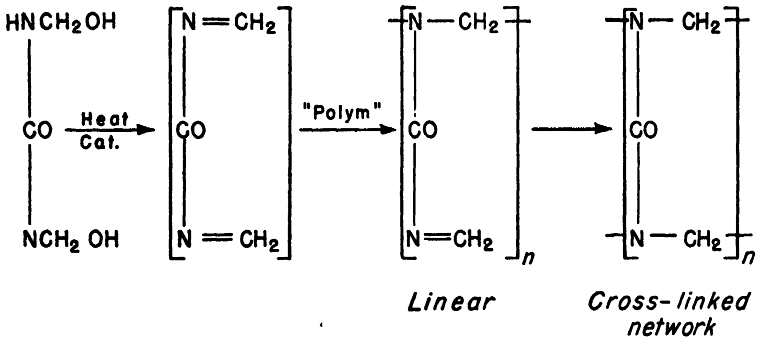


FIGURE 53

Figure 54, representing the Redfarn mechanism, should require very little discussion. The formation of such four-membered rings with nitrogen-nitrogen bonds, of course, is quite improbable in terms of any known analogous chemistry. Furthermore, hydrolysis of the resins fails to form any hydrazine or substituted hydrazines, as would be expected from such a structure. And finally, this mechanism allows for no subsequent cross-linking in the "C" stage conversion.

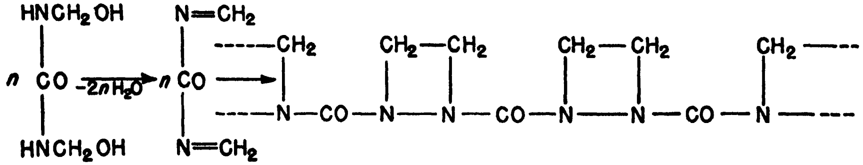


FIGURE 54

A theory which has lately come to the foreground is that proposed by Professor Marvel in extension of some of the ideas of Thurston. According to this concept, a methylol urea, or a corresponding mixture of urea and formaldehyde, reacts to form a resin by a process involving the formation of intermediate molecules with six-membered rings, as shown in Figure 55.

In a recent article in the *Journal of the American Chemical Society,* Marvel has given a clear and persuasive presentation of this theory. His reasoning is very interesting. In brief, Marvel has elected to consider urea as the first member of the homologous series of the amino-acid amides. He postulates that one end of the urea molecule behaves as a primary amine toward formaldehyde. This corresponds to the formation of a cyclic trimer with a six-membered ring structure, which is characteristic of many amine-aldehyde reactions. The other end of the urea molecule, then, is considered to exhibit the more sluggish behavior of an amide. The formation of bridges between these relatively less reactive amide groups is held to account for the formation of linear or cross-linked macromolecules containing a plurality of the six-membered ring units. Amides are known to be able to form methylol derivatives and compounds with methylene bridges between a pair of amide groups. According to the Marvel theory, some aspects of the geometry of the cured resin are different from those presented previously; however the essential idea of a complex cross-linked structure persists.

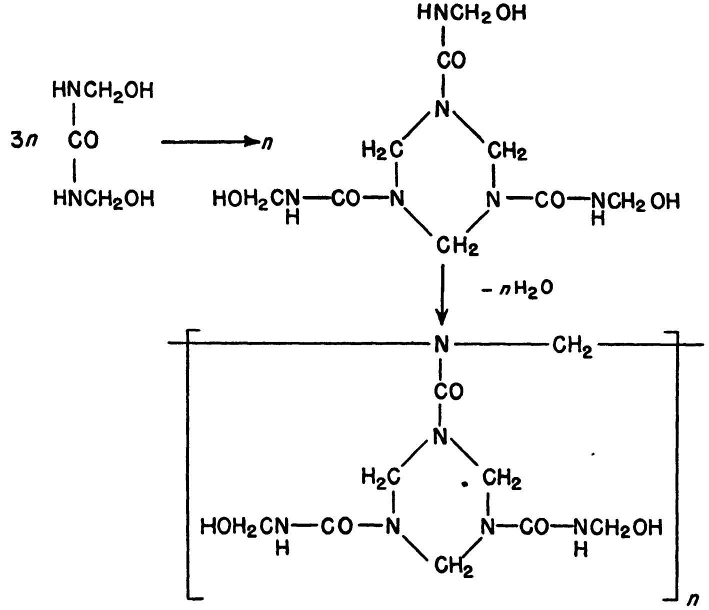
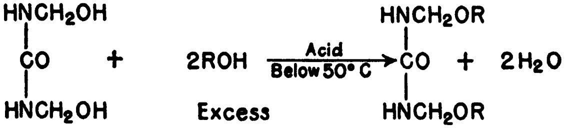


FIGURE 55

Marvel and his co-workers have studied the reaction of formaldehyde upon representative amides of amino acids and have shown that the behavior is actually essentially as outlined. Direct proof by the study of the urea-formaldehyde reaction itself, however, is not so easy, and the matter cannot yet be considered definitely settled. The different types of urea-formaldehyde products which can be prepared are difficult to account for in terms of any picture as simple as that just described. No one has yet isolated and clearly established the existence of the cyclic trimer postulated by Marvel. However, some sort of ring formation probably does play an important role in the complex urea-formaldehyde reaction. It is to be hoped that additional fundamental reaction studies, similar in nature to the excellent work of Marvel and his associates, will be forthcoming from the academic world.

Some brief mention has already been made of the general properties of the aqueous types of the urea-formaldehyde types of resins. Being water-dispersible, they find use in a variety of adhesive, paper, molding, laminating, and textile applications. However, they tend to be brittle and stand in great need of the help of plasticizers. Such plasticizers are difficult to find, however, because of limitations of compatibility and water resistance. Also the unmodified urea-formaldehyde resins are not suitable for modification of any of the organic-solvent-soluble coating resins. These stumbling blocks of solvent insolubility and incompatibility with plasticizers were tantalizing to men in the coating field because of several of the attractive properties of the urea resins. Among these might be mentioned again excellent hardness, rapidity of cure, chemical resistance, and freedom from discoloration.



$$\begin{matrix} \mathrm{HNCH_2OH} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{HNCH_2OH} \end{matrix} + \underset{\text{Excess}}{2\mathrm{ROH}} \xrightarrow[\text{Below } 50°\text{ C}]{\text{Acid}} \begin{matrix} \mathrm{HNCH_2OR} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{HNCH_2OR} \end{matrix} + 2\mathrm{H_2O}$$

FIGURE 56

A number of ethers of dimethylol urea are known. These are crystalline compounds soluble in alcohol and in some instances in other common organic solvents as well. Figure 56 illustrates a general method of preparation. The introduction of the alkyl groups contributes greatly to the solubility in organic solvents.

This same type of reaction can be combined with polycondensation to yield a modified linear or branched linear molecule with a number of solubilizing alkoxy groups. The general idea is presented in Figure 57.

Here we have considered the reaction as a polycondensation of dimethylol urea, much after the manner of the "B" stage condensation previously shown, together with a supplementary etherification reaction resulting in the introduction of the alkoxy groups. Thus we are dealing with a problem in competing reactions, and the preparation of a suitable product is very largely a matter of controlling the relative rates of the two types of reactions. Of course it is not necessary to commence with solid dimethylol urea as starting material; a corresponding mixture of formaldehyde and urea may be used instead, but conditions during the first stage of the process must be controlled to give dimethylol urea as the first intermediate. The coefficients shown in the general type of equation presented in Figure 57 are selected somewhat arbitrarily and may be varied over considerable ranges. The average number of alkoxy groups per urea unit may be varied; and the total yield of water removed is also a variable subject to control.

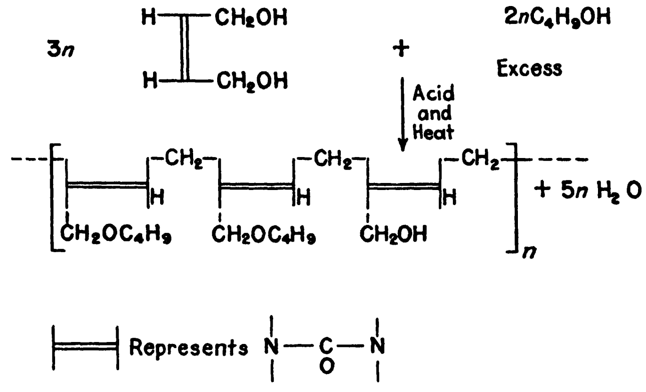


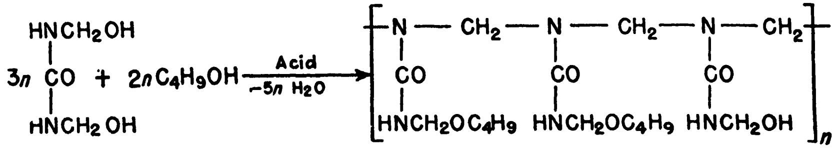
FIGURE 57

It has been proposed that the alkoxy groups present in such a resin are introduced by the reaction of urea amino groups with a formal, *e.g.*, dibutyl formal, formed by the previous reaction of formaldehyde with the alcohol. However, this sequence is much less probable than the one just presented, inasmuch as formals are quite sluggish toward urea under the conditions employed. Furthermore, it is easy to show that reaction of the formaldehyde with urea takes precedence over formal formation. Hemiformals, on the other hand, are possible reactive intermediates, particularly if an anhydrous solution of formaldehyde in the alcohol is employed.

It has been possible to isolate the "B" stage alkoxy-modified urea-formaldehyde resins by precipitation with a non-solvent. In the solvent-free condition these prove to be solid resins. The following data show the results of elementary analyses carried out on just such a precipitated sample.

	Calc for $(C_{17}H_{34}O_6N_6)_x$	Found (Micro Combustion)
%C	48.80	48.72
%H	8.13	7.90
%N	20.10	20.2 (Dumas)
%O	22.97	23.18 (By Diff.)

The analyses agree very well with a postulated structure containing two butoxy groups for every three urea units. It will be noted that the two pertinent figures illustrate both "head-to-head" and "head-to-tail" configurations. Actually a random arrangement is probably involved. It is to be emphasized again that this ratio of alkoxy groups to urea units can be varied over a considerable range and that the rather striking two-to-three ratio exemplified here is fortuitous. Gravimetric studies established another fact of considerable importance, namely that most of the alkoxy groups remain in the molecule during the curing operation. Cross-linking appears to take place at positions unblocked by alkoxy groups.



$$3n\,\begin{matrix}\mathrm{HNCH_2OH}\\|\\\mathrm{CO}\\|\\\mathrm{HNCH_2OH}\end{matrix} + 2n\,\mathrm{C_4H_9OH} \xrightarrow[-5n\,\mathrm{H_2O}]{\text{Acid}} \left[\begin{matrix} -\mathrm{N} & -\mathrm{CH_2}- & \mathrm{N} & -\mathrm{CH_2}- & \mathrm{N} & -\mathrm{CH_2}- \\ | & & | & & | & \\ \mathrm{CO} & & \mathrm{CO} & & \mathrm{CO} & \\ | & & | & & | & \\ \mathrm{HNCH_2OC_4H_9} & & \mathrm{HNCH_2OC_4H_9} & & \mathrm{HNCH_2OH} & \end{matrix}\right]_n$$

FIGURE 58

This finding is in excellent agreement with the fact that the properties of the cured film depend in large measure upon the type of alkoxy group originally introduced.

The change in properties accompanying the introduction of the alkoxy groups is strikingly great. Whereas the unmodified aqueous "B" stage urea-formaldehyde types show very little solubility in or tolerance for nearly all organic solvents, the alkoxy-modified "B" stage modifications are soluble in nearly all common organic solvents, including aromatic hydrocarbons, and may be dissolved in mixtures of alcohol and petroleum solvent. Furthermore, the modified resins are compatible with a wide variety of other organic-solvent-soluble resins. The most important example is the excellent compatibility with alkyd resins. As might be expected, the speed of cure is retarded somewhat as a consequence of the blocking influence of the alkoxy groups. This effect is not serious, however, and the resulting resins are still among the fastest of the solvent-soluble types known. Alkyd-urea combinations based on resins of this type may be satisfactorily baked in a matter of 20 minutes or less at 300°F, sufficient speed to render them attractive in a large number of applications. Fortunately enough the blocking effect seems to be manifest to a highly desirable degree in improving the stability of the resins at ordinary storage temperatures. Instead of only a few months, these alkoxy-modified resins, when properly prepared, may be stored for years without deleterious effect. They also show greater stability in the presence of curing catalysts at room temperature. Whereas the aqueous urea-formaldehyde "B" stage resins are gelled in a matter of hours by most acids and ammonium salts, the alcoholic types are stable for long periods of time in the presence of appreciable concentrations of carboxylic acids and acids of comparable strength. This is of considerable practical importance, since the presence of suitable acid curing catalysts is very advantageous. As might be expected, the introduction of the alkoxy groups effects some improvement in toughness and chemical resistance. However, the resulting thermosetting resins still require plasticizing to overcome deficiencies in toughness and adhesion.

The effect of variation in number of carbon atoms in the introduced alkoxy group is a matter of considerable interest. Qualitatively the effects are in general what one might predict from simple fundamental considerations. However, the magnitude of the effect obtained by the addition or subtraction of one carbon atom is quite striking. In the industrial resins produced in any appreciable volume so far, the normal butyl and isobutyl groups have predominated. Resins of this type are particularly attractive in terms of ease of manufacture and resulting properties. Research has naturally been directed toward a study of groups with fewer than four carbon atoms on the one hand, and larger numbers on the other. As the number of carbon atoms is reduced, the speed of cure tends to be enhanced at some sacrifice in toughness, adhesion, and water resistance, as might be supposed. Likewise the tolerances for hydrocarbon diluents and compatibilities for other resins tend to be reduced. In general, opposite effects are observed as the number of carbon atoms in the alkoxy groups is increased above four. The solubilities in and tolerances for the poorer hydrocarbon solvents become improved in striking degree. The rate of cure is retarded somewhat and the resistance toward aqueous reagents, alkali for example, is improved. Resins containing octyl groups, or mixtures of butyl and octyl groups, have found general industrial acceptance for certain applications, notably for formulations with petroleum thinners and for the fortification of oleoresinous varnishes.

A few aspects of the manufacture of urea-formaldehyde coating resins may be considered briefly. It is possible to start with either a mixture of urea and formaldehyde or previously isolated dimethylol urea. In other words, the dimethylol urea may be prepared either in the presence of or in the absence of the alcohol, which serves both as a reactant and as a component of the reaction solvent. The formaldehyde employed may be either aqueous formaldehyde or, in order to reduce the amount of water to be removed, an anhydrous solution prepared from paraformaldehyde and the alcohol. The matter of reaction catalysis is of prime importance. The dimethylol urea, of course, must be prepared under neutral or slightly alkaline conditions. The co-reaction with the alcohol, together with the polycondensations, is favored by an acid catalyst. A variety of acids has been used successfully. Phthalic anhydride and phthalic acid, for example, have been mentioned frequently in the patent literature, as have been some phosphoric acid types. The use of too strong an acid is dangerous from the standpoint of precipitation or gelation. The problem of removal of reaction water is of prime importance, as one might expect from mass action considerations, inasmuch as water is a product of both the polycondensation and the alcoholic co-reaction. Processes are usually designed to yield products dissolved in a mixture of the alcohol in question, usually butanol, together with some cheap aromatic hydrocarbon, usually xylol. This is natural in view of the fact that xylol is a solvent commonly used by the enamel formulator. The metal used in the construction of the plant equipment may be any one of several commonly used metals resistant to attack by formaldehyde or the acid catalyst employed.

Several of the foregoing remarks have touched upon the varied uses of the urea coating resins. Of these the most important continues to be the hardening of alkyds in pigmented enamels. These two types of resins supplement one another to an admirable degree. The toughness, adhesion, fullness, gloss, and durability of the alkyd are advantageously retained; while marproofness, baking speed, color, and chemical resistance are improved by the urea-formaldehyde component. The urea/alkyd ratio may vary over a wide range, depending upon the properties desired and the type of alkyd used. Usually the urea component is held below 50 per cent of total resin vehicle to avoid excessive embrittlement and loss of adhesion; the range 20 to 35 per cent is particularly interesting and may be considerably lower in some formulations, such as automotive finishes, for which a relatively slight degree of hardening is desired. The fast-baking alkyd-urea enamels are used as surface coatings for a variety of objects, among which may be mentioned refrigerators, washing machines, stoves, kitchen cabinets, and hospital equipment.

Melamine-Formaldehyde Resins

With the exception of urea, melamine is by far the most important amino type of raw material to find its way into the industrial resin field. Figure 59 shows the structure of melamine, more precisely named 2,4,6-triamino-1,3,5-triazine. The triamino-triazine structure is the one more commonly accepted for this compound, although there is good reason to believe that it also exists in equilibrium with the imino tautomer shown side by side with the other structure.

The sequence of reactions diagrammed for the synthesis of melamine shows the use of a relatively cheap starting material, calcium cyanamide. Dicyandiamide, or perhaps more properly cyano-guanidine, is an easily prepared and important intermediate in the melamine synthesis. Dicyandiamide is also of potential value as an intermediate in the preparation of other related heterocyclic compounds. A number of patents have been issued to describe the final step for the conversion of dicyandiamide to melamine; the conditions shown in the figure are simply illustrative and do not necessarily pertain to those in actual use today.

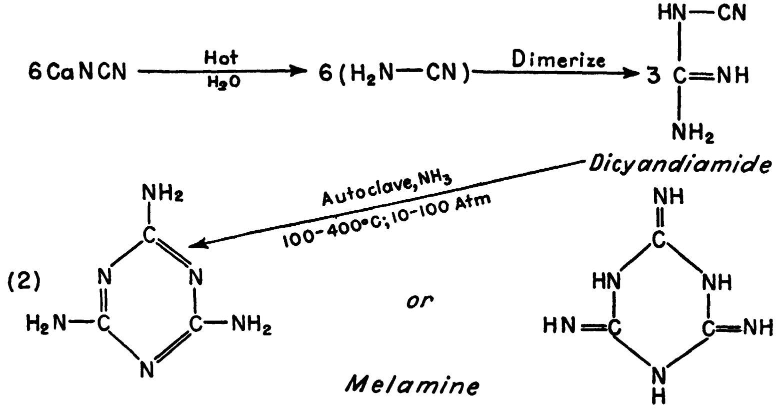


FIGURE 59

Melamine is much more resistant to hydrolysis than urea and also exhibits superior heat stability. In fact it is stable almost up to its melting point, which is usually given as 354°C. Melamine turns out to exhibit a maximum functionality toward formaldehyde of six, which is unusually high in a compound of such a relatively low molecular weight. All these basic aspects of melamine seem to be reflected in the resulting resins prepared by reaction with formaldehyde. For example, these resins show outstanding chemical resistance and heat stability. The higher functionality toward formaldehyde is undoubtedly responsible for the more rapid cure, greater hardness, and more pronounced brittleness of the resulting resins.

With the exception of the significantly greater functionality toward formaldehyde, the general chemistry of the melamine-formaldehyde reactions seems to parallel rather closely that already presented for urea. As for the "A" stage condensation, the formation of analogous methylol compounds is easily achieved. Here the maximum functionality of six may be exhibited. Figure 60 shows, first of all, the formation of trimethylol melamine.

Here again it is very important to observe generally mild reaction conditions with careful control of pH. In general the melamine-formaldehyde reactions are even more sensitive to traces of acid and small variations in pH than are the analogous processes involving urea. Although the introduction of only three methylol groups is shown in this figure, it is easily possible to introduce as many as six. This is one reason for suspecting the presence of the imino tautomer previously shown, inasmuch as such a molecule contains six hydrogens evenly distributed over as many nitrogen atoms. Hence it is unnecessary to assume the presence of more than one methylol group on a nitrogen atom, a structure that has usually been found to be unstable.

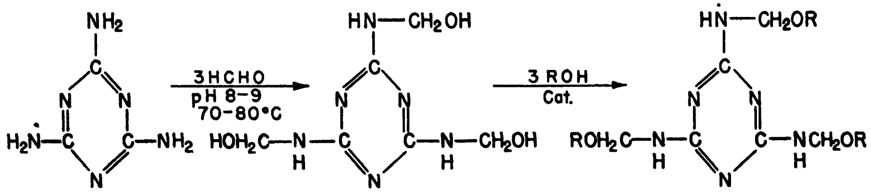


FIGURE 60

There are, of course, greater opportunities for complexities in the structure of the polycondensate molecules obtained by reaction with formaldehyde. As already noted, careful control of catalytic conditions is of paramount importance. The general principle of formation of linear and branched linear "B" stage molecules by linkages derived from formaldehyde seems to obtain in this instance also. The methylene bridge is again possible here, and it is of interest to note that recent work has shown that dimethylene-ether linkages play a particularly important role in the formation of the melamine-formaldehyde polycondensate molecules.

The concept of co-reaction with an alcohol to introduce solubilizing alkoxy groups applies here as well. This principle and the polycondensation are shown in Figure 61.

Here the use of a noncommittal symbol is preferred to illustrate the symmetrical, hexafunctional nature of melamine without restriction to either of the two tautomeric forms previously shown. Two types of linear polycondensation have been illustrated here also, namely, by means of methylene bridges, and in the second case, by means of the formation of dimethylene-ether linkages. It has been found possible to introduce alkoxy groups to the extent of about one per melamine nucleus. This ratio may be varied; the one shown has been selected for simplicity and is not necessarily representative of any standard product now on the market. The solubilizing improvements and effects on compatibility are every bit as striking here as in the corresponding modification of the urea-formaldehyde resins. A very attractive combination of storage stability and speed of cure can readily be attained.

These melamine resins are manufactured by processes generally similar to those mentioned for the urea coatings. Consideration must be given to the special solubility properties of the intermediates and to the characteristic sensitivity to catalysis.

The melamine coating resins are superior to the urea analogs with respect to speed of cure, hardening efficiency, resistance to high bake and overcure, and alkali resistance. At normal baking temperatures of 250 to 300°F, the melamine resins require approximately one-third less conversion time than the ureas. The speed advantage is particularly important in the range of 180 to 225°F, whereas the resistance to discoloration and general degradation at higher temperatures is most advantageous above 300°F. Because of superior hardening efficiency, more pronounced brittleness, poorer adhesion, and higher cost, the melamine content of the enamel formulation is often lower than the urea concentration which would be selected for any given application. Specifically, melamine/alkyd ratios are usually held down to 30/70 or below. Combinations of alcohol-modified melamine resins with non-drying alkyds are particularly suitable for high-bake applications and for stove enamels.

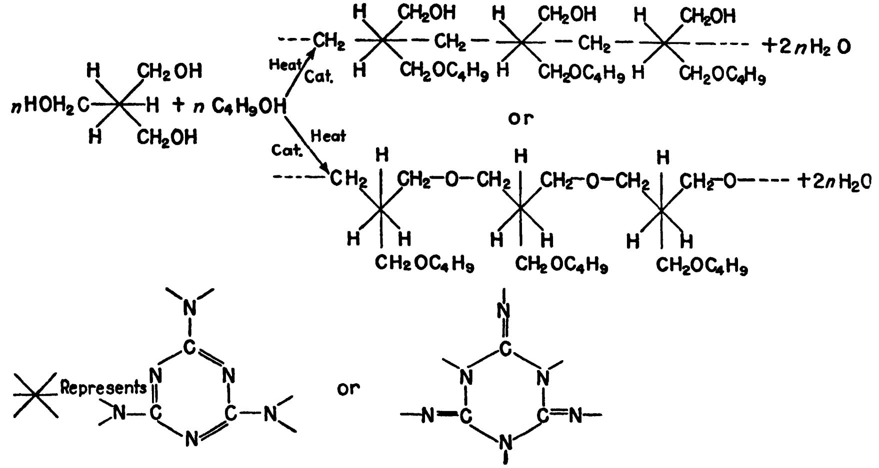


FIGURE 61

In some instances attractive combinations of cost and performance values can be achieved by the conjoint use of melamine and urea coating resins.

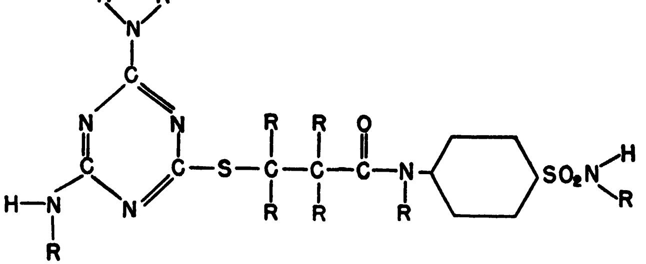
New and Future Developments

During recent years progress has been achieved with respect to refinements in the control and manufacture of the urea and melamine resins, with consequent important improvements in uniformity and quality.

There have also been advances in improving the conditions for use and in uncovering new applications for which the thermosetting resins can be used to advantage. The use of infrared as a convenient means of rapid cure (*e.g.*, in 3 to 10 minutes) is an example of an advance in use technology. Important new and recent applications include force-dry furniture finishes, the thermosetting of polyvinyl butyral, and the modification of cellulose nitrate. For the force-dry furniture finish application, a strong acidic catalyst, for example an acidic phosphoric acid ester, is used to permit drying at temperatures in the range of 140°F, which are not harmful to the wood. It should be emphasized that as new outlets are found it is frequently possible to "tailor-make" new types of nitrogenous resins to fulfill in enhanced degree the new requirements involved. There is probably more flexibility in regard to possible properties than is commonly realized.

From the chemist's standpoint the possibilities inherent in the use of new raw materials are of perhaps greater interest. It is immediately apparent that the study of other modifying alcohols is a large potential field in itself. The use of aldehydes other than formaldehyde offers some interesting potentialities, but it is probable that the most interesting advances will come from the exploration of other nitrogenous reactants and other modifying reagents of the alcohol type.

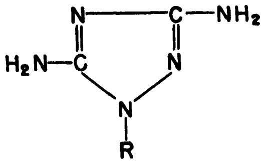
A quick glance at some of the possibilities among the nitrogenous compounds may be of interest, even without detailed discussion. The use of monoalkyl ureas, particularly in combination with urea, has already been mentioned in the patent literature. The use of thiourea has also been reported, although it is probable that this reactant will not play a very great role in the future development of this field. The polyaminoheterocyclic compounds offer a wide variety of interesting possibilities. Some of the attainable modifications of the melamine pattern are tempting. For example, it is possible to prepare analogous compounds with



hydrocarbon radicals on either the nitrogen or the carbon atoms, thus achieving interesting variations in solubility and reactivity properties.

The patent literature on the thioammeline derivatives is particularly extensive. This triazine contains, in addition to two amino groups, a mercapto group. As might be expected, it is possible to prepare a wide variety of "S"-substituted derivatives. The formula on page 160 is an example, selected at random, to illustrate the possibilities.

There is no intention to imply, however, that it has been or will be selected for extensive development. Some heterocyclic compounds with five-membered rings are also of interest; among these may be mentioned the guanazoles:



A somewhat different approach has been considered by the Germans in their use of diisocyanates for the modification of coating resins based upon vegetable oils and characterized by the presence of hydroxyl groups capable of reacting with isocyanate groups to form urethane linkages.

Many possibilities in the field of nitrogen chemistry remain to be explored. The search is continuing actively and there is every reason to believe that as a result the coatings industry will benefit still further by the efforts of the resin chemist.

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Chapter 11

Phenolic Resins in Protective Coatings

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More people are aware of the use of phenol-formaldehyde resins in molding compounds used for common household items, such as telephone hand sets, than they are of the types of resins which are to be considered in this chapter. This undoubtedly is because the oil-soluble phenolic resins are relatively new as compared with phenolic condensation products used as molding resins, laminating resins, or abrasive bonding. For instance, phenolic molding or laminating resins have been in use in one form or other since the early part of this century, dating back to Dr. Baekeland's early work.

About 1913 there appeared the first rosin-modified phenolics, popularly called "albertols." These were generally made by reacting phenol with rosin and formaldehyde and esterifying with glycerin to reduce the acidity. Such products found favor in varnish manufacture because of their ease of solubility in drying oils and they were a distinct advantage in many respects over the natural resins, which had been used literally for centuries. The unsubstituted phenol used was not suitable for making a formaldehyde reaction product which would be oil-soluble in itself without considerable modification. Thus it is obvious why acidic natural resins were used as modifiers.

A brief review of the chemistry of the phenol-formaldehyde reaction will be given. This reaction is exceedingly complex and much of it is based upon supposition. There are certain definite factors, however, which should be pointed out, inasmuch as they concern the type of product under consideration, that is, varnish resins.

Unsubstituted phenol is the parent substance from which the substituted phenols are derived by addition of alkyl, aryl, carboxyl, hydroxyl, halogen or other groups. The position in the phenol nucleus of this substituent group is the most important factor determining oil solubility. It was not until 1928 that 100 per cent phenolic oil-soluble resins were commercially available; and they demonstrated the importance of this theory.

The three most reactive positions in the phenol ring structure are the para and the two ortho positions. When any one of these positions is occupied by a substituent group, the tendency to form cross-linked or "three-dimensional" insoluble polymers is lessened. It is interesting to compare this with an analogous situation explained by Dr. Albert in Chapter 7 when he demonstrated the insolubility of rosin maleates because of their three-dimensional pattern if too much maleic anhydride is used. In meta-substituted phenols such as *m*-cresol, all three reactive positions are unoccupied; thus it acts very much like unsubstituted phenol in producing insoluble resins.

The most important substituting groups for making oil-soluble resins are the alkyl *p*-tertiary butyl, the *p*-tertiary amyl or the aryl type *p*-phenyl phenol. The type of product obtained depends upon such factors as type and amount of catalyst, proportions of phenol and formaldehyde as well as temperature, pressure and reaction time.

Alkaline catalysts favor formation of oil-insoluble materials on continued heating unless the reaction is stopped at an unfinished or intermediate stage. These latter resins, however, are commercially important, and are the so-called heat-reactive, oil-soluble materials. During subsequent heating in varnish making they continue to polymerize without separation and produce favorable properties of drying, especially in thick films such as in insulating varnishes.

Acid catalysts, on the other hand, yield resins which are permanently fusible or thermoplastic and are used perhaps for the largest volume of varnish resins. The reaction can be carried to completion and still produce satisfactory oil solubility. This is the type of resin which is generally used in undiluted form in varnishes.

A question which is the subject of much debate is what happens when phenolic resins are cooked into oils. There is strong evidence that certain types at least react chemically with oils, especially those containing conjugated double bonds. Furthermore, the greater activity of the phenyl group suggests that in the case of phenyl phenol the greater unsaturation may provide more active points for combination with the oil.

In Figure 62 are shown the cooking times for a linseed oil and for the same oil at 75-gallon length with ester gum, with a *p*-phenyl phenol resin (BR-254) and with a rosin modified phenolic resin (BR-2963). Figure 63 gives the comparison with sardine oil and Figure 64 with soybean oil. In all cases it can be seen that the cooking time is decreased considerably when the phenolic resins are present.

The non-heat-reactive type resins were early found to have superior properties in varnishes; these properties are generally in direct proportion to the amount used—that is, they are most pronounced in short oil varnishes. Before the advent of these 100 per cent phenolics, varnishes were considered good if they would pass a 15-minute boiling water resistance test or 30 minutes in dilute alkali. These limits were easily changed in properly cooked tung oil varnishes to 7 hours boiling water resistance and 24 to 48 hours in 5 per cent sodium hydroxide.

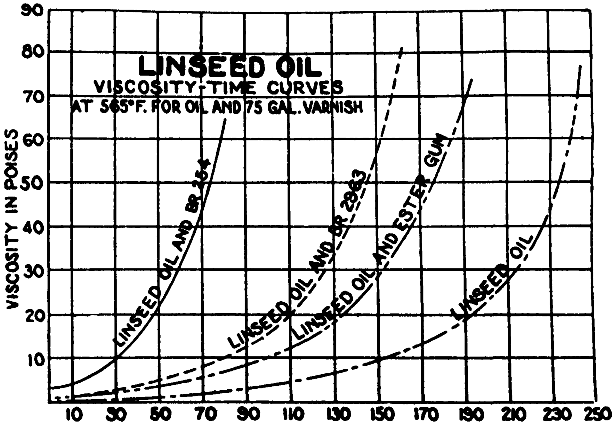

FIGURE 62

The following advantages were obtained with these resins:

(1) A marked accelerating effect on the polymerization of oils, which is evident not only in a more rapid increase of viscosity during cooking

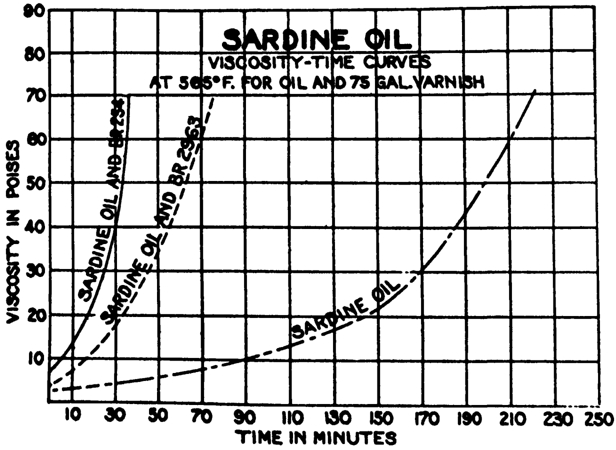

FIGURE 63

but also in more rapid drying of the film. Other hard varnish resins very often impart increased viscosity to varnish because of their inherent high viscosity, and the procedures used very often involved cutting them into bodied oils.

(2) An inhibiting effect upon oxidation after the initial drying cycle. This tends to prolong the life of a film, as a long, slow oxidation period invariably causes film failures in coatings. This drying more by polymerization than by oxidation also allows the use of lower metallic drier content.

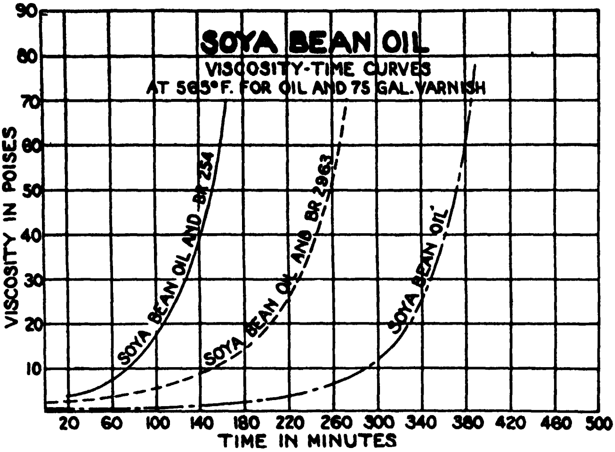

Figure 64

In the decade before World War II the 100 per cent phenolic resins became so predominant because of their chemical and water resistance and outdoor durability that they were often specified in finishes for bridges, locks and dams, steel freight cars, gas and oil storage tanks, structural steel and marine parts. They also gained favor in trade sales varnishes and vehicles, spar varnishes for station wagons, yachts and industrial coatings and primers for trucks, automobiles and home appliances.

Many of these varnishes or vehicles used 100 per cent tung oil or a very high per cent of this oil. The elimination of China as a source of tung oil imports, even before World War II, caused the varnish industry to turn to the softer oils, many of which clearly demonstrated their value and in some cases actual superiority.

The U. S. Navy specified substituted 100 per cent phenolic resins during World War II to be used in a wide range of ship and marine finishes. These ranged from 100 per cent tung oil in a few applications to 50–50

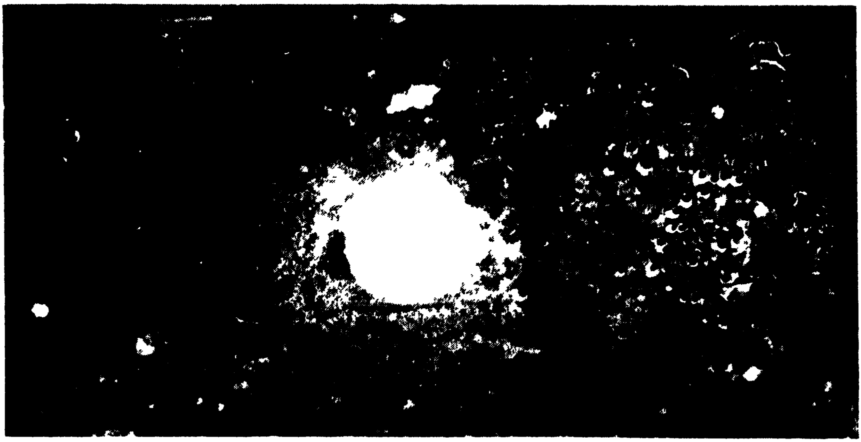

Figure 65

mixtures of tung and linseed to 100 per cent linseed. One definite point which has been demonstrated repeatedly by metal primer exposures at Miami, Florida, and elsewhere in tide level racks, is the excellent freedom from blistering and better adhesion of these finishes made from linseed oil or dehydrated castor oil. These changes to softer oils required modifications in processing and in formulation, including cooking at high temperatures (560 to 585°F) in order to obtain practical speed of bodying. The best results are obtained with the lowest possible viscosity oil, although faster cooks can be made with heavier-bodied oils at a considerable sacrifice in drying time, durability and resistance to moisture

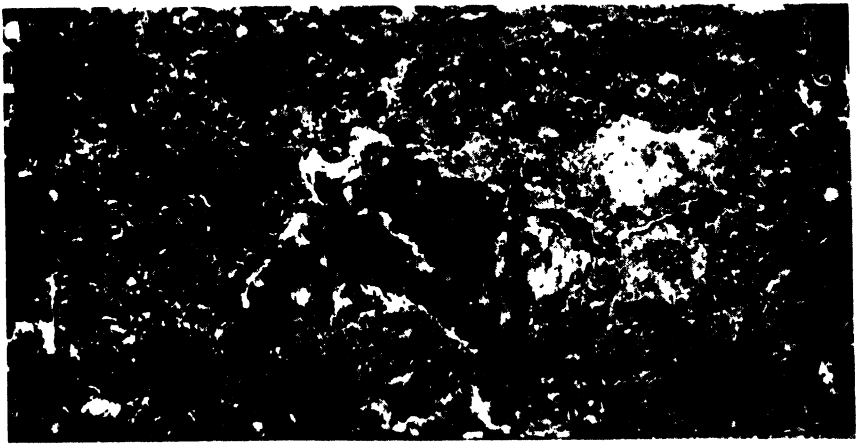

Figure 66

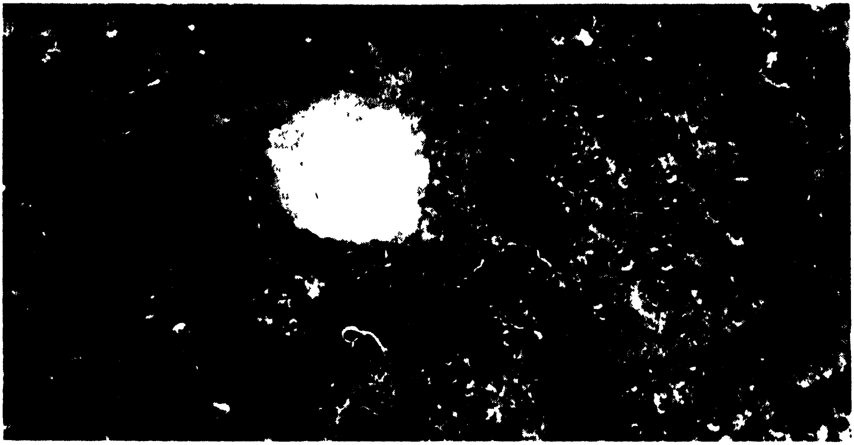

FIGURE 67

and chemical attack. As a matter of fact, the alkali resistance of linseed oil varnishes is almost exactly parallel to the degree of polymerization. This ties in with the previous discussion on reaction of substituted phenol resins with oils.

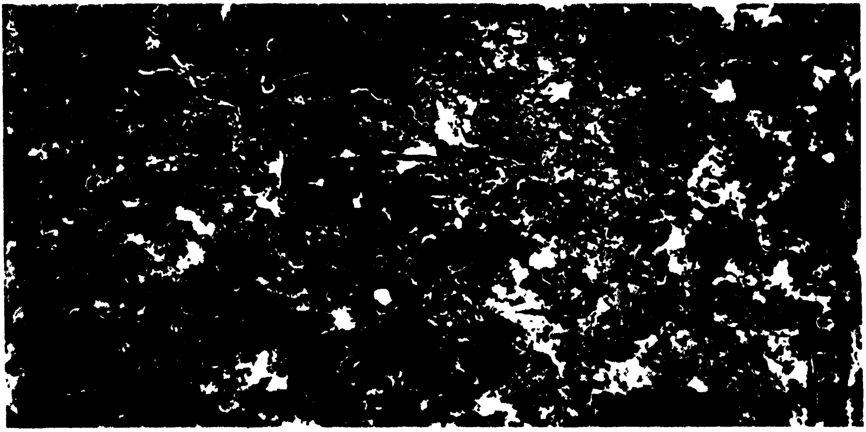

FIGURE 68

A very interesting comparison of the effect of salt-water exposure on 100 per cent phenolic coatings and on other varnishes is shown in Figures 65, 66, 67 and 68. These are photographs of panels which had been completely submerged in sea water for twelve months. Figure 65 is the photograph of a panel coated with a paint in which the vehicle is a 100 per cent phenolic containing varnish (25-gallon BR-9432—linseed varnish), whereas Figure 66 shows a panel coated with a paint whose vehicle composition is 66⅔ per cent 25-gallon BR-9432—linseed varnish and 33⅓ per cent of an alkyd varnish (Navy alkyd 52-R-13).

Figure 67 shows a panel which has a coating in which the vehicle is again a 100 per cent phenolic varnish (25-gallon BR-9432—dehydrated castor oil varnish). The vehicle used in the coating of Figure 68 is a 100 per cent alkyd varnish (Navy alkyd 52-R-13).

An inspection of the above-mentioned figures shows the superiority of the films of 100 per cent phenolic vehicles under salt-water exposure conditions. The vehicles mentioned were all pigmented (according to the Navy's 52-P-18 specifications) as follows:

Zinc chromate	55%
Titanium dioxide	15
Raw Sienna	5
Magnesium silicate	25
	100%

Most of this material thus far has been on the acid-catalyzed, non-heat-hardening types of phenolics. We shall now consider the alkaline-catalyzed, oil-soluble, heat-hardening, substituted phenolic resins.

These are generally used in either one of two different applications. The first instance is in short-oil varnishes with no diluting resins for industrial baking, such as deep-curing, insulating varnishes. The electrical properties of these resins are excellent in contrast for instance to the poor electrical properties of rosin and other rosin-modified resins. This is advantageous for insulating rotors and stators of high-speed motors and it can sharply reduce the curing time of these impregnating varnishes from a matter of approximately 48 hours at times to a fraction of an hour. This was of utmost importance during the war when speed of manufacture was important for electric motors for Army and Navy equipment.

The other prevalent use of the heat-reactive, oil-soluble resins is with lower cost diluting resins, where it is desired to harden these resins in order to give more durable, resistant films. The advantage of adding this type of resin is demonstrated in Figure 69. Figure 70 shows the variation in acid number and melting points for blends of rosin and a heat-reactive, oil-soluble phenolic (BR 3360).

Varnishes which contain a relatively small amount of the heat-hardening 100 per cent phenolic resin are of value not only in industrial baking finishes but in vehicles for use in trade sales items. One very recent application is the use of this type of resin in tall oil varnishes where it greatly decreases the kettle time. This oil is so very slow that some means must be found to make it more usable in practical varnish formulations. The heat-reactive resin, when used in amounts from 2 to 10 per cent, based on the tall oil, will not only speed up reactivity in the varnish kettle but also decrease drying speed and increase water resistance and durability. The trend in this kind of phenolic resin is toward more reactivity with better oil solubility. New developments along these lines may increase interest in many other industrial applications.

The next classification of phenolic resins to be mentioned is the modified material. Reference was made previously to production of rosin-modified phenolics before the 100 per cent resins were ever available. Since that time these resins have found uses in trade sales products and wherever cost may be a limiting factor. Furniture varnishes have used large quantities of such resins. With the present high cost of glycerin, rosin-modified phenolic prices are almost as high as some of the 100 per cent resins.

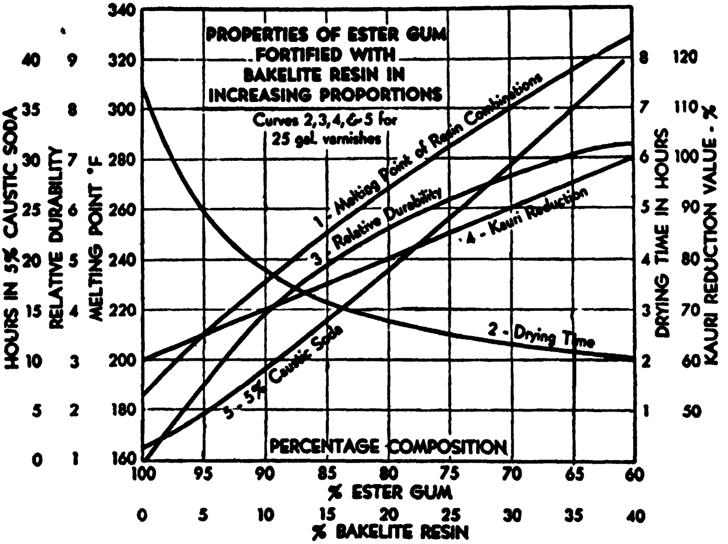

FIGURE 69

Another group of resins which are modified, this time with oil, are sufficiently different to warrant separate treatment. These are the dispersion resins, which may be regarded as almost completely polymerized phenolic resin-oil complexes dispersed in a volatile organic solvent. Earlier mention was made of minimizing oxidation in phenolic varnishes, especially when the *p*-phenyl type of resin is used. Since this oxidation mechanism is to be avoided in film curing, why not eliminate it entirely? The dispersion resins were designed with this in mind; they are the only oleoresinous, air-drying types that most nearly meet these demands. It is only reasonable to assume that such compositions would exhibit different properties than other oleoresinous types, and this has been found to be the case.

Certain of these properties are common to all the dispersion resins, but the various members of this family have their own individual characteristics. To a large extent, as with the oleoresinous varnishes, these properties depend upon the kind of resin and drying oil employed, although the conditions under which the materials are polymerized and dispersed have a considerable influence on the performance of the resulting composition.

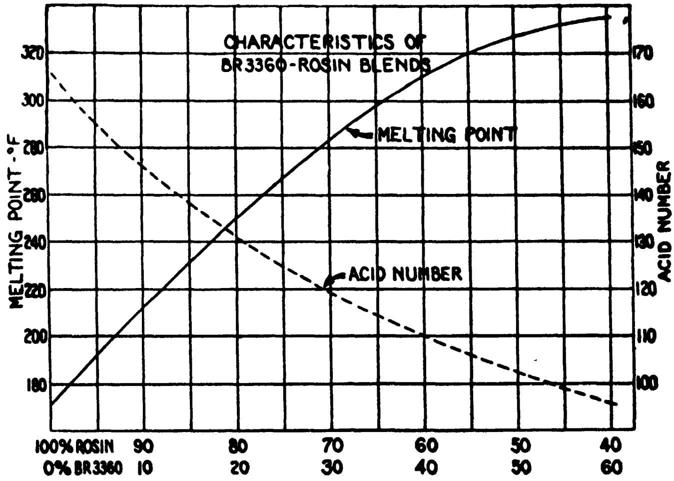

FIGURE 70

Speed of drying, inertness on aging, high impermeability to moisture, good adhesion to metal surfaces, resistance to strong solvents, and excellent durability are perhaps their chief properties of practical interest to the formulator of protective coatings.

(1) Speed of Drying

The dispersion resins are dry as soon as the solvent used with them evaporates. When used alone in pigmented coatings the drying time of a sprayed film may be as short as one minute. In considering the speed of air-drying, these resins may be compared to nitrocellulose lacquers as they are very fast-drying by themselves, but this property is modified by other materials which may be added to them. For example, they are often used as additives to alkyds or varnishes to speed up the initial setting of the film. The final drying of such blends to a tack-free condition will depend to a considerable extent upon the alkyd or varnish employed. The use of the dispersion resins in blends with varnishes, oddly enough, is a comparatively recent development and promises to be a most important one. Air-drying or quick-baking primers based on such blends are remarkably resistant to blistering when subjected to high humidities or prolonged immersion in water, and should find a considerable service in industrial applications. Addition of the dispersion resin also contributes better "hold-out" and gloss to subsequent coats of enamels or lacquers.

(2) Inertness on Aging

Since the dispersion resins do not cure by oxidation, it is not surprising that they show excellent durability on exposure. Single thin coats of primers containing dispersion resins have shown no sign of failure after exterior exposures of two to three years in an industrial atmosphere. In addition to being inert and very durable by themselves, the dispersion resins markedly improve the toughness and retention of flexibility on aging of varnishes and alkyds when blended with them. This may be obtained with as little as 25 per cent of dispersion resin, based on the total vehicle solids.

(3) Impermeability to Moisture

These resins have shown a higher degree of impermeability than top quality spar varnishes and lacquers in comparative tests. This property has made these resins useful in sealing absorbent materials, such as pressed fiber composition wallboards. In a series of tests on one such type of wallboard, it was found that the area near the cut edges of the uncoated wallboard showed an increase in weight of 33 per cent, and the center section which was six inches away from the edges showed an increase of 18 per cent after a 24-hour immersion in water. The same wallboard with one normal coat of a thinned dispersion resin showed an increase of only 4.4 per cent in the edge area and 0.5 per cent in the center section after the same immersion. The sealing of such porous materials probably will be one of the chief uses for dispersion resins.

(4) Good Adhesion to Metal Surfaces

Coatings based on these resins have been used successfully for years on steel, aluminum, magnesium, copper and zinc surfaces.

(5) Resistance to Strong Solvents

Since the dispersion resins are soluble to only a very limited extent in alcohols, ketones, esters, and ethers, they have found considerable use in air-drying primers for use under nitrocellulose and ethylcellulose lacquers and some vinyl finishes. Some of these dispersion resin primers may be recoated with nitrocellulose lacquers within five minutes after application with no danger of lifting, wrinkling, or bleeding. They may likewise be coated with lacquers at any time thereafter without danger.

(6) Durability

This property stems directly from those previously mentioned. The fact that these resins have been an essential ingredient in the formulation of aircraft primers for the past ten years is certainly a tribute to the durability of these resins under all sorts of climatic conditions.

Some of the markets for these resins are for quick-drying industrial undercoats used for product finishing, in order to speed up production lines; shopcoats for structural steel and fabricated steel parts; auto refinishing primers; traffic marking paints; non-slip deck and floor coatings; and sealers for paper, cardboard and wallboard.

The last type of phenolic coating resin to be considered is the non-oil-soluble thermosetting or "one-step" phenolic resin. Although these resins were available for many years before the advent of 100 per cent oil-soluble phenolic resins, it has been only in the last few years that they have reached prominence in the protective coating industry. They are related closely to the type of thermosetting resin commonly used in laminating operations, *i.e.*, impregnating paper or cloth under pressure to form hard, durable laminates or sheets.

Recently there have been many references to plastic coatings, with the implication that these are something very mysterious and most noteworthy in properties. Some of these can in no sense of the word be rightfully called "plastic coatings." A plastic coating is a coating based entirely on a resin. In other words, it is a thin film of a material, which in the form of a molded product would be called a plastic. The resin baking finishes, by this concept, are plastic coatings. They are solutions of partially polymerized phenol-aldehyde resins which convert with heat to give completely polymerized, insoluble, and highly resistant films. Most of these are not modified with drying oils or other film-forming materials, but they may be modified and pigmented to fit certain applications. During the years prior to the war they found their chief usage in coatings for the inside of cans, drums, tanks, and tank-cars where resistance to corrosion, solvents, chemicals, and food products was required. For example, drums for strong solvents such as ethyl acetate and turpentine, tank-cars for transporting beer and wines, milk cans, sea food cans, and chemical vats were lined with these materials. These and many other uses led to an increasing interest and demand for these resins.

When we became involved in the war, we were suddenly confronted with alarming shortages of many corrosion-resistant metals and alloys which were considered essential in our armament program. Since the metals were in limited supply, it was necessary to use steel, and the coatings industry was faced with the problem of supplying finishes which would protect the metal and would also meet many other specialized requirements. This shortage of corrosion-resistant metals resulted in such items as cartridge cases, Army food containers, and portable gasoline tanks made of steel. The phenolic resin baking finishes were chosen as the only suitable organic coating material to use for these applications, and in each instance these coatings did an excellent job. In addition to the applications mentioned, these resins have been used on buckles and webbing strap ends, ammunition boxes, certain parts of several types of bombs, propellers, portable water tanks, aircraft engines, and many other products used by our Armed Forces.

The resin baking finishes were chosen in each case because of their distinctive properties, which may be summarized as follows:

(a) *Mineral Acids.* Excellent resistance to all but high concentrations of strong oxidizing acids, of which nitric acid is the most corrosive. Recent developments have, however, made improvements here. Table 23 shows the acid resistance of a new type of phenolic resin (VF-1124).

(b) *Organic Acids.* Excellent resistance to all organic acids. Concentrated acetic acid, formic acid, and oxalic acid solutions are the most corrosive.

(c) *Organic Solvents.* Excellent resistance. This type of reagent provides no corrosion problem to resin baking finishes.

(d) *Inorganic Compounds.* Excellent resistance to all but alkalies and compounds which break down to produce alkalies. Here again new developments have markedly increased alkali resistance. Table 24 shows the alkali resistance of the new type of phenolic resin (VF-1124).

Table 23. Phenolic Resin Baking Coatings: Acid Resistance.

	VF-773	VF-775	VF-774	New Type VF-1124
95% H_2SO_4 @ 25°C	0.25	.20	.05	1000 plus
50% "	200.00	—	—	1250 plus
70% HNO_3 @ 25°C (commercial con.)	0.25	0.25	0.10	2.5
Glacial Acetic Acid	200.00	50.00	20.00	2000 plus

Table 24. Phenolic Resin Baking Coatings: Alkali Resistance.

	VF-773	VF-775	VF-774	VF-1124
10% NaOH @ 25°C	0.80	40.00	50.00	3500
50% "	28.00	48.00	56.00	4300
Refluxing 5% NaOH	0.01	0.13	0.40	35.0
10% NH_4 @ 25°C	150.00	48.00	96.00	4300 plus

(e) *Flexibility.* Most of these materials are not highly flexible. However, they can be plasticized to produce films which possess good flexibility and shock resistance. These specially plasticized finishes also retain their original excellent corrosion-resistance properties.

(f) *Abrasion Resistance.* Good.

(g) *Weathering.* Good retention of gloss, and minimum disintegration of film, either in prolonged atmospheric weathering or accelerated weathering tests.

(h) *Electrical Properties.* Good electrical insulating properties.

(i) *Thermal Resistance.* These finishes can withstand short periods of exposure to dry heat as high as 600 to 700°F. Exposure to high temperatures darkens and embrittles the film and eventually causes charring.

(j) *Color.* These finishes may be pigmented to produce various colored finishes. Pigmented coatings retain the excellent corrosion resistance properties of clear solutions.

The high degree of resistance of these resin baking finishes to corrosion, abrasion, and chemical attack may be illustrated by some of the severe tests of the various Army and Navy specifications which they meet. Some of these unusual test requirements are given here in abridged form: "The films shall withstand 1 hour's immersion in boiling toluene, 1 hour in glacial acetic acid at room temperature, 1 hour in 10 per cent ammonium hydroxide, 1 hour in ethyl alcohol, and 1 hour in ethyl ether without softening or other evidence of deterioration."

"Coated panels, having diagonal cuts through the film, shall be exposed to 24 hours of continuous salt spray at 65–80°F. At the end of this exposure, there shall be no evidence of rusting other than within ⅛ inch distance from the scribe marks on edges of the panel."

"Coated panels, at a 45° angle, shall withstand the abrasive action of 5 liters of Ottawa sand (20 to 30 mesh) dropped through a vertical tube 3 feet long."

"Films of 0.3 to 0.5 mil thickness on steel shall withstand 10 days' exposure in an atmosphere of 100 per cent relative humidity at 100 to 120°F with no evidence of corrosion or spread of corrosion beyond that in scratches in the finish, and the film shall show no softening, peeling, blistering, chipping, or loss of adhesion."

"Films of 0.3 to 0.5 mil thickness on steel shall withstand exposures of at least 10 days to salt spray and show no corrosion or spread of corrosion beyond that in the scratches in the finish and there shall be no other evidence of deterioration."

"Coated steel panels, having a film thickness of 0.3 to 0.5 mil shall withstand immersion for not less than 7 days at 95 to 100°F in a two-layer liquid consisting of a 3 per cent solution of sodium chloride in water and 40 per cent aromatic hydrocarbon fluid with no evidence of film failure or corrosion."

Other specification tests call for 5000 hours' immersion in moving sea water, 5000 hours in lubricating oil at 200°F, 5000 hours in acetone, alcohol, boiling water, gasoline and toluene. The resin baking finishes are the only organic coatings that will withstand such severe treatment.

The metal surfaces must be especially prepared for these baking resins in order to secure best results. This may involve acid etching, solvent degreasing, or sand blasting. In general these resins are applied at between 18 and 30 per cent solids. The application may be slushing, dipping, roller coating, or spraying. After application, it is desirable to allow an air-drying period to permit most of the solvent to escape before placing the coated object in the oven. Satisfactory baking temperatures range from 275 to 400°F, and the following generalizations apply to all of the resins in this class.

There are several methods of baking these resin coatings. Convection ovens, infrared lamps, hot air blasts, and induction heating have all been used successfully. The induction heating method is an interesting development which has many advantages over the more conventional baking methods and it will probably find considerable use in the future. It is particularly good for the continuous coating of pipes. This process consists of passing the pipe through a tank of resin solution and then through an electromagnetic field actuated by low-frequency alternating current. The pipe may be heated almost instantly to the desired temperature and the coating is quickly cured. In one recent test it was found possible to heat resin-coated pipe from room temperature to 375 to 400°F in two minutes. One advantage of the induction heating method is that the heat is generated within the pipe and the resin coating is cured from the metal surface inward. This minimizes defects due to too rapid a surface hardening and solvent trapping.

There are several general rules governing the choice of proper baking schedule: (1) the corrosion resistance of a resin film increases with an increase in baking temperature or time; (2) short time, high-temperature bakes produce more resistant films than long time, low-temperature bakes; (3) an increase in baking time, or temperature, tends to darken and embrittle the resin film. Therefore, choice of the proper baking schedule to be used must depend on the properties required in the final baked coating. If the film is applied to a rigid object, where protection against corrosion is most important, and color and flexibility are of less importance, the film should be baked at as high a temperature and for as long a time as is practicable. On the other hand, if the coating is to be mainly decorative, for which light color and less severe corrosion resistance are required, lower baking temperatures and shorter baking times should be used.

In multiple-coat systems the best practice is to underbake the undercoats and then apply the full bake to the final coat. This promotes better adhesion between coats and reduces the total baking time.

An interesting test has been under way for many years which clearly demonstrates the value of this type of phenolic resin. In August, 1937, an extensive corrosion study was started by the National Bureau of Standards Dept. of Commerce involving testing coated and uncoated pipes for underground corrosion. Pipes were coated or wrapped in accordance with recommended procedures and buried in twelve test spots throughout the country to make an extensive study of the effect of various soils. The Milwaukee, Wisconsin, test pit was considered by the Bureau of Standards as the most severe, inasmuch as the specimens were laid in a bed of cinders prepared so that its top was roughly on a level with the Menominee River. Another bed of cinders was used to cover the samples, creating an ideal setup for electrolytic corrosion. In Figure 71 are samples of the various pipes that were used.in the test. It is easy to recognize the two very bright pipes which had been coated with resin-baking phenolics. These are in almost perfect condition after 9 years' exposure to these severe conditions.

FIGURE 71

In the future there should be considerable expansion in the use of these resins in the protection of machine parts, industrial storage tanks, wire screens, boiler tubes and other piping, the interior of drums and tank-cars, and for chemical equipment. With the improvements that have been made in flexibility and coating technique they should also be used for applications in which they have never heretofore been considered.

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Chapter 12

Miscellaneous Resins in Protective Coatings

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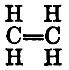
Petroleum Resins

Modern methods of producing gasoline have developed a large number of unsaturated hydrocarbons. These are known as olefins, diolefins and cyclo-olefins. They are the raw materials used in producing the petroleum or hydrocarbon resins. Examples of these compounds are:

OLEFINS

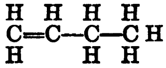
Ethylene



$$\begin{array}{cc} H & H \\ C & \!\!=\!\! C \\ H & H \end{array}$$

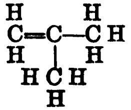
Acetylene $HC{\equiv}CH$

Butene or *Butylene*



$$\begin{array}{cccc} H & H & H & H \\ C= & C- & C- & CH \\ H & & H & H \end{array}$$

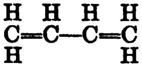
Isobutylene



$$\begin{array}{ccc} H & & H \\ C= & C- & CH \\ H & | & H \\ & HCH & \\ & H & \end{array}$$

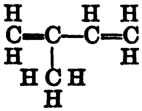
DIOLEFINS

Butadiene



$$\begin{array}{cccc} H & H & H & H \\ C= & C- & C= & C \\ H & & & H \end{array}$$

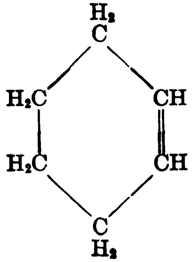
Isoprene



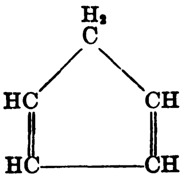
$$\begin{array}{cccc} H & & H & H \\ C= & C- & C= & C \\ H & | & & H \\ & HCH & & \\ & H & & \end{array}$$

CYCLO-OLEFINS

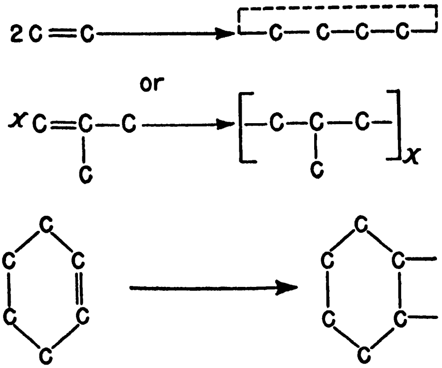
Cyclohexene



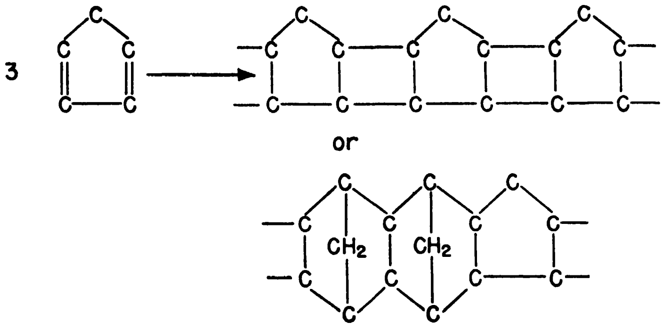
Cyclopentadiene



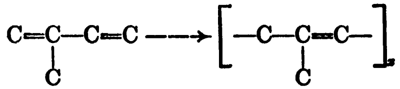
The one characteristic which causes these compounds to react to form resins is their unsaturation. Each of those shown above carries one or more double or triple bonds. For simplicity they may be considered to react as follows:



There are two structures considered for polymerized cyclopentadiene:



It should be noted that these reactions very closely parallel those encountered in the chemistry of synthetic rubber. Isoprene is considered the basis for natural rubber:

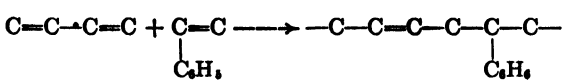


$$\underset{\displaystyle C}{C{=}C}{-}C{=}C \longrightarrow \left[-C-\underset{\displaystyle C}{C}{=}C-\right]_x$$

One of the first types of synthetic rubber to be produced was Buna, or polybutadiene:

$$C{=}C{-}C{=}C \longrightarrow [-C-C{=}C-C-]_x$$

A much more satisfactory grade was produced by co-polymerization of 75 per cent of butadiene and 25 per cent of styrene. This is known as Buna S. For simplicity it might be shown as follows:



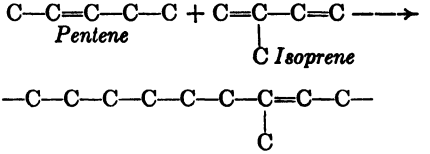
$$C{=}C{-}C{=}C + \underset{\displaystyle C_6H_5}{C}{=}C \longrightarrow -C-C{=}C-C-\underset{\displaystyle C_6H_5}{C}-C-$$

There are many other possibilities. Artificial polymerization of these compounds was accomplished experimentally as long ago as 1880.

Most of these hydrocarbons will polymerize alone or may be co-polymerized with other, similar compounds to produce desired characteristics. In a few cases aldehydes and aromatic compounds are used in conjunction with these unsaturated hydrocarbons in similar reactions.

In general these polymerizations take place very readily. Transformation to solid polymers will occur slowly at ordinary temperatures without the aid of a catalyst. For example gummy, resinous polymers are found in gas mains carrying coke-oven gas and water gas. These residues are from the unsaturated compounds occurring in these products. However, the reaction takes place more rapidly at higher temperatures and is aided by catalysts, such as $AlCl_3$, $SnCl_4$, and $SbCl_5$.

Although these individual compounds will polymerize with themselves, such products are of little commercial value, as they seldom have the desired properties. They are either too plastic or too insoluble. Usually, it is found desirable to co-polymerize two or more compounds. A common method is to react an olefin with a diolefin. Such mixtures are found in a material known in industry as "drip oil," which is collected as a condensate during the cracking of natural gas for certain organic syntheses. Similar mixtures of olefins and diolefins are found in unrefined cracked gasoline. As an example of this type of reaction, we may consider:



$$\underset{\textit{Pentene}}{C{-}C{=}C{-}C{-}C} + C{=}\underset{\substack{|\\ C\ \textit{Isoprene}}}{C}{-}C{=}C \longrightarrow$$

$$-C-C-C-C-C-C-\underset{\substack{|\\ C}}{C}=C-C-$$

As indicated by the formula of the finished product, some of the double bonds are unsatisfied. This is indicated by a relatively high iodine value, and it results in a resin that will react further with the unsaturated vegetable oils when cooked into a varnish. The larger the proportion of pentene used in this reaction the softer and more soluble the resin obtained.

Olefins and diolefins may also be polymerized with aromatic compounds such as toluene and xylene, as well as with terpene compounds, to produce oil-soluble resins.

As mentioned before, these unsaturated hydrocarbons are formed during the cracking processes for the production of gasoline. They are detrimental to the gasoline since they tend to polymerize and form gummy resinous deposits in tanks and lines. As a result they must be removed in the refining process. These furnish a low cost source of raw material to the resin manufacturer.

There are two possible methods for removing and utilizing the olefinic compounds in cracked gasoline. The first one polymerizes the unsaturated compounds in the gasoline by means of catalysts such as $AlCl_3$, and the second method removes these compounds by absorbing them in fullers earth, bauxite, finely divided clay, etc.

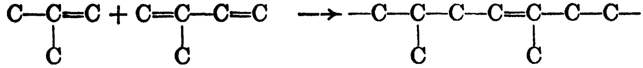
In the first method a cracked gasoline distillate is treated with anhydrous $AlCl_3$ catalyst with the evolution of considerable heat. After a reaction time of about 6 hours the mass is treated with sodium hydroxide to remove the $AlCl_3$, and the $Al(OH)_3$ is filtered off, together with a certain amount of insoluble resin. The filtrate containing the soluble resin is distilled, yielding a solid, amber-colored resin with a melting point from 110 to 115°C, and an iodine value of 130 to 160. It is practically neutral and is soluble in vegetable oils, petroleum and coal-tar solvents. Such a resin was produced by the Thomas and Hochwalt Laboratories at Dayton, Ohio, and was later produced by Monsanto Chemical Company under the name of "Santo" resin.

The second method aims at absorbing the undesirable unsaturated compounds rather than attempting to polymerize and form the resin directly in the gasoline. In some cases these compounds are thrown down with sulfuric acid. Apparently, a certain degree of polymerization is accomplished at the same time. When the absorbing agent becomes saturated the residues are removed by treating with a different type of solvent, filtering out the clay, and reclaiming it for repeated use. These many-colored residues are named Gray tower polymers, after the man who invented the tower and process for this treatment. They are treated in a variety of ways to produce pitches, resins, etc. They may be simply heated or blown with air to produce the black petroleum asphalts.

Other processors treat such residues to improve the color and separate the more unsaturated portions, after which they are polymerized with catalysts such as $AlCl_3$, yielding neutral, oil-soluble resins like those which are produced directly from the cracked distillate.

Cyclo-pentadiene, obtained from "drip oil" mentioned previously, is a very reactive hydrocarbon. It is readily polymerized in petroleum or aromatic solution by means of amphoteric chloride catalysts such as Al, Fe, Sb, or Bi chlorides. For example, 300 parts of cyclo-pentadiene, 450 parts of toluene, and ten parts of ferric chloride are agitated at 25°C. When well dispersed, ½ part of silicon tetrachloride is added as a secondary catalyst. Considerable heat is evolved. Cooling is required to hold the temperature around 25°C and to prevent the reaction from forming an insoluble resin. Time of reaction is approximately 1 hour. The resin may be precipitated by the addition of acetone or alcohol, or the solution may be used as a coating without further treatment. Best results are secured by baking. Solid resins produced by this process are of little value by themselves, since they have a high iodine value, and unless they are used immediately they will oxidize or continue to polymerize. Stable varnishes may be prepared by immediately cooking the resin with oil. A solution similar to the above may be blended with prepared oils to produce the desired composition.

To mention again the similarity of these resins to the synthetic rubbers, Butyl rubber—one of the most desirable forms—uses isobutylene and isoprene as the raw materials in a co-polymer reaction. For simplicity the reaction may be illustrated as follows:



$$\mathrm{C{-}\underset{\overset{|}{C}}{C}{=}C + C{=}\underset{\overset{|}{C}}{C}{-}C{=}C \longrightarrow {-}C{-}\underset{\overset{|}{C}}{C}{-}C{-}C{=}\underset{\overset{|}{C}}{C}{-}C{-}C{-}}$$

Isobutylene *Isoprene* *Butyl rubber*

Based on this or a similar reaction with higher molecular weight ingredients, the Standard Oil Company of N. J. has recently developed a new petroleum resin known as "Stanco A" resin. This resin differs from those produced by previous methods, using cracked gasoline or Gray tower polymers, in that it is much lighter in color and more uniform in quality. These characteristics may be attributed to the fact that the resin is produced from definite chemical compounds rather than from mixtures of by-products and left-overs.

The important characteristics of this resin are:

Softening point	90–110°C
Iodine value	120–150
Acidity	neutral
Saponification number	zero

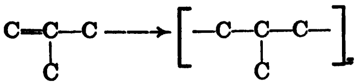
It is suggested that much less oil be used in manufacturing varnishes with this resin than is normally recommended for other resins. Oil lengths from 7 to 15 gallons are considered best for most purposes. Such vehicles are used in can coatings and metal primers and show excellent adhesion and good alcohol and chemical resistance. One disadvantage of this type of resin is its poor oil resistance.

A typical varnish or paint vehicle might be cooked in the following fashion:

100 lbs.	"Stanco A" resin
15 gals.	Dehydrated castor oil
34 "	Mineral spirits

Heat the resin and ½ the oil to 560°F. Hold to clear cold pill. Add remainder of oil and heat to 550°F. Cool and reduce. Non-volatile content 50 per cent, Viscosity E, Color 11 (Gardner).

Another resin or resinous type of material developed by the synthetic rubber industry is "Vistanex." Chemically this is polyisobutylene:



$$\mathrm{C{=}\underset{\underset{C}{|}}{C}{-}C \longrightarrow \left[{-}C{-}\underset{\underset{C}{|}}{C}{-}C{-}\right].}$$

Isobutylene is polymerized using boron fluoride as a catalyst. The degree of polymerization is controlled by varying the temperature. Lower temperatures give the more viscous polymers. The reaction is carried out in a solution of propane or butane and is very vigorous unless the solution is well diluted. Since there is only one double bond in isobutylene this is eliminated in all but one molecule at the end of the linear polymer, thus yielding a very saturated compound. As would be expected from its composition it is inert chemically and usually is used in solution as a softener or plasticizer.

To sum up the character of these petroleum resins, we should list the following points:

(1) Very low acid number.
(2) Good compatibility and solubility.
(3) Low melting point and corresponding low viscosity of solutions and varnishes.
(4) High degree of unsaturation as shown by high iodine value in certain types.
(5) Good water, alcohol, and chemical resistance.
(6) Good adhesion to metal.
(7) Poor oil resistance except on baked or converted films.
(8) Poor exterior durability.
(9) Poor color except those produced from pure chemical compounds.

Generally speaking, the petroleum resins are used in the shorter oil length varnishes, about 25 gallons being the maximum length. This is due to their low melting point and lack of hardness. Some difficulty is encountered in their use with large amounts of China wood oil since the resin is of no assistance in rendering this oil gas-proof. The resins of low iodine number show no reaction when cooked with the vegetable oils. In fact, they usually retard polymerization of any oils with which they are cooked. As a result it is common practice to pre-body the oil and add the resin at the end of the cook. Bodied linseed or dehydrated castor oil will work well in this manner.

On the other hand, the unsaturated resins do show reaction when treated with oils. However, due to the low average melting point of the resins, it is usually advantageous to start with oils of at least moderate viscosity in order to shorten the cooking time.

The varnish shown previously using "Stanco A" resin is an example of a varnish cooked with an unsaturated resin. A varnish produced from a saturated resin is exemplified by the following:

100 lbs.	Velsicol A-B-11-4
12½ gals.	Bodied linseed oil Z_6
12½ "	China wood oil
47 "	Mineral spirits .

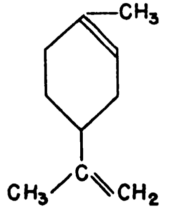
Heat both oils to 570°F and hold for short string off spade. Check with the resin, melt out and reduce. Non-volatile content 50 per cent and viscosity of F. A number of commercial grades with the suppliers are listed below:

"Velsicol"	Velsicol Corporation
"Stanco A"	Standard Oil of N. J.
T & H Resin (now discontinued)	Thomas & Hochwalt Lab.
"Santo" Resin (now discontinued)	Monsanto Chemical Co.
"Petro" Resin	R. J. Brown Co.
"Petropol" or "Petropon"	Pure Oil Co.
"Dutrex"	Shell Oil Co.

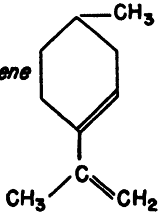
Terpene Resins

Turpentine, which is obtained from the resin of the pine tree, contains a number of compounds that are very similar in composition and chemical structure. These are known as terpenes. They are cyclic hydrocarbons and in most cases they carry two double bonds. These are the compounds that act as the basic raw material in the formation of the terpene resins. Turpentine consists of about 85 per cent of unsaturated compounds. Some examples of these compounds are:

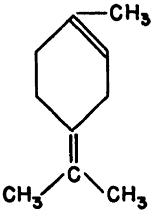
Dipentene



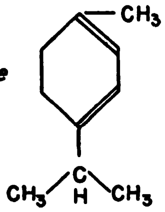
Menthadene



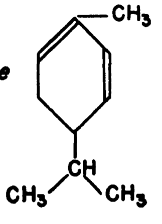
Terpinolene



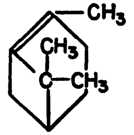
Terpinene



Phillandrene



α-Pinene



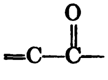
It might be interesting at this point to note the similarity of these compounds to abietic acid which also comes from the pine tree and is used in the form of rosin in similar resins (see Chapter 7).

These unsaturated hydrocarbons will polymerize by themselves under certain conditions. This is best illustrated by the fact that turpentine becomes gummy or fatty on standing. The reaction is greatly accelerated by the aid of catalysts. For example, 1,000 parts of turpentine are placed in a vessel with cooling coils, condenser, and agitator. Add slowly 50 parts of anhydrous $AlCl_3$ or other Friedel-Crafts catalyst. The reaction is strongly exothermic. The temperature may be held at 20 to 25°C, or allowed to rise as high as 100°C. The higher temperature results in a higher degree of polymerization and higher melting point resins. When the desired degree of polymerization is attained, 300 parts of mineral spirits or coal-tar solvent is added to dilute and stop the reaction. The solution is washed with 260 parts of 2 per cent HCl-water solution, and then with pure water to wash out the catalyst. The solvent is distilled off and the polymerized turpentine can then be separated by distillation into the following fractions:

150	parts	unreacted turpentine
175	"	dimer (viscous liquid)
40	"	trimer " "
635	"	polyterpene resin (M.P.—100°C)

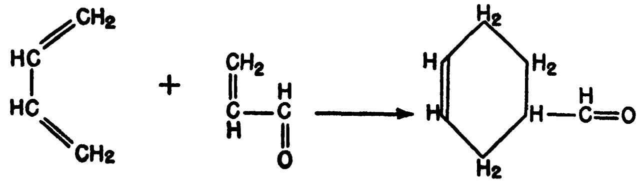
Many of the terpene resins in common use are formed by the reaction of a terpene with some other compound, such as maleic anhydride or one of the many phenols. A number of different type reactions have been observed.

Terpenes and maleic anhydride react in accordance with the diene or Diels-Alder reaction. In its simplest form this reaction consists of a combination between a compound containing conjugated double bonds and a second compound containing the group:



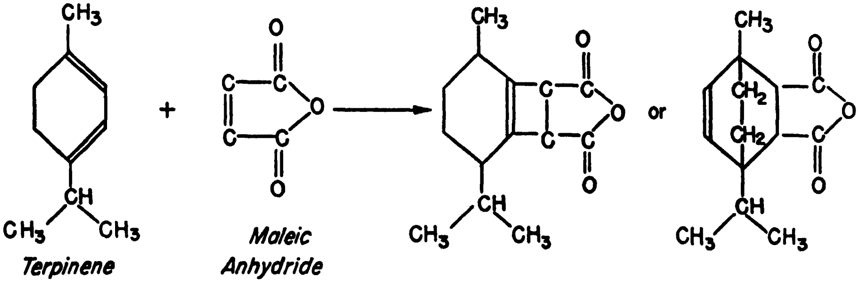
$$=C-\overset{\overset{\displaystyle O}{\|}}{C}-$$

A common example of this reaction is:



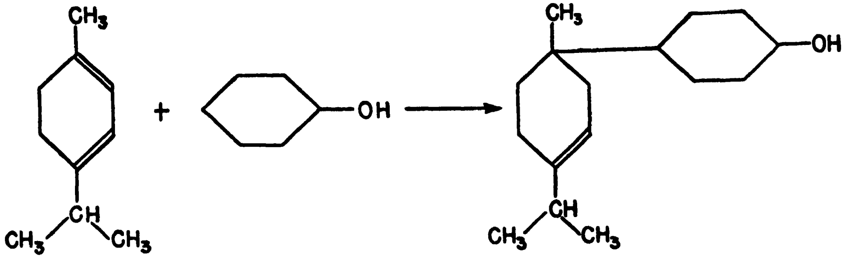
Butadiene *Acrolein*

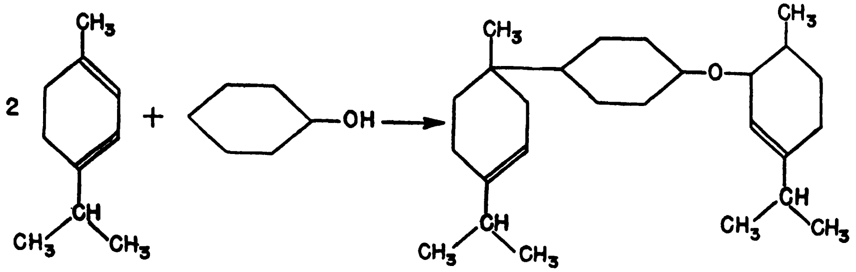
Terpinene and maleic anhydride combine in a reaction similar to the above:

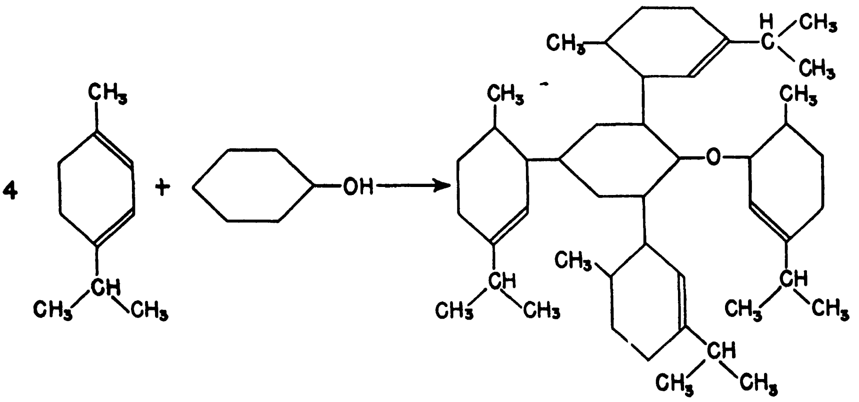


This product is an example of one of the resins known as "Petrex." It is usually used as a dibasic acid similar to phthalic anhydride, being modified with vegetable oils or fatty acids and esterified with polyhydric alcohols in the common alkyd reaction. Its high molecular weight results in relatively high melting points and its branched chain type molecule gives good solubility and compatibility with oils.

Terpenes and phenols may react together in several different ways. Possible examples of reactions are given below:







Polymerization of the terpene with anhydrous $AlCl_3$ as a catalyst may be carried out before or after the reaction with the phenol in order to give a large variety of types with much higher melting points.

A typical procedure for making a terpene phenolic resin may be as follows:

300	parts	pinene
75	"	phenol
300	"	petroleum naphtha
150	"	coal-tar naphtha

The reaction mixture is cooled and agitated, as 33 parts of anhydrous $AlCl_3$ are added gradually. Considerable quantities of HCl are liberated. The temperature is controlled between 70 and 80°C and agitation continued for 2 hours. The catalyst is removed by repeated washings with 5 per cent HCl solution. Volatile and unreacted materials are distilled off. The resin yield is about 60 per cent.

Mixtures of terpene and rosin have been used to react with either maleic anhydride or phenol. Such a let-down with rosin gives a resin with much lower cost. This also results in a higher acid number. It may be used as is, or esterified with poly alcohols if a lower acid number is desired. A resin of this type may be produced as follows:

200	parts	rosin
100	"	maleic anhydride
85	"	terpinene

This mixture is heated to 300°F for 3 hours. No catalyst is required. Volatile or unreacted material may be removed by placing the batch under reduced pressure. This resin will have a very high acid value (350 to 400). The addition of 100 lbs. of glycerin and esterification for 7 hours at 240°C yields a resin with a melting point of 100°C and an acid number of 40, which is quite suitable for use with nitrocellulose. It should be further esterified with more glycerin to an acid number of 25 when it is to be used as a varnish resin.

The terpene resins are produced commercially under the following trade names: "Piccolyte": 7 grades with melting point range from 10 to 125°C, produced by the Pennsylvania Chemical Corp. They are practically neutral and are evidently of the pure polyterpene type.

Durez Plastic Co. has 10 to 12 items ranging from liquid at ordinary temperatures to a melting point of 145°C. These are of the terpene phenolic type and range in acid value from 0 to 100.

"Petrex," produced by Hercules Powder Co., is offered in the form of dibasic acid to be processed into the alkyd; or one can purchase the resin in the alkyd composition in several melting points and acid numbers.

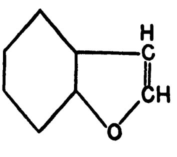
Newport Industries produce three varieties of limited use. These are known as "Varene," "Nubro" and "Bexin."

The pure terpene resins are characterized by their excellent color and color retention. They are very inert to the action of acids, alkalies, etc., but do not have particularly good exterior durability. In general they are low in melting point and are not inclined to be reactive when processed with vegetable oils. As a result they work better with the harder type drying oils.

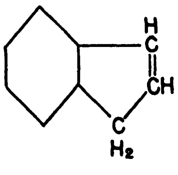
The phenolic derivatives of the terpenes tend to approach the let-down phenolics in performance. They are darker in color, more reactive in the varnish kettle and have better durability and drying than the pure terpenes.

Coumarone—Indene Resins

The group of resins popularly known as *cumars* is produced from the two compounds, *coumarone* and *indene*, or mixtures thereof. The structural formulas for these materials are:



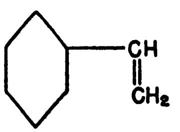
Coumarone



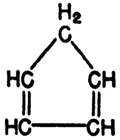
Indene

It is interesting to note the similarity of these two compounds with two other compounds previously mentioned under the petroleum resins, namely, styrene and cyclopentadiene.

Two homologs of coumarone also may be considered as raw materials

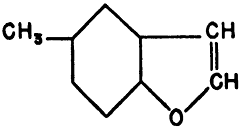


Styrene

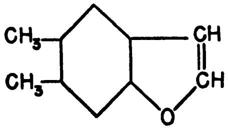


Cyclopentadiene

for this class of resins, namely, methyl coumarone and dimethyl coumarone:



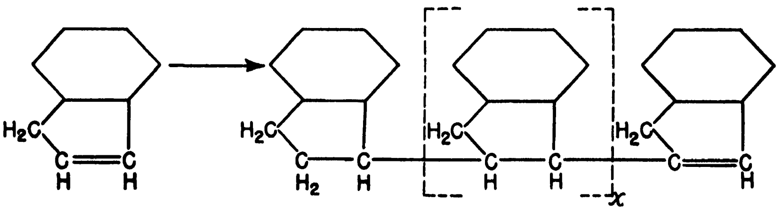
Methyl Coumarone



Dimethyl Coumarone

Here again we are considering a class of resins manufactured for the most part from by-products or residues. The compounds used as raw materials are found in crude coal-tar naphthas distilling between 155 and 185°C. Although the quantity varies within wide limits, it may be said that such naphthas contain about 35 per cent of the compounds that may be converted into these resins.

Note again from the structural formula that the characteristic function of these compounds is the double bond. The polymerizing reaction may be expressed as follows:



Most of the resins produced have a molecular weight indicating formulas from $(C_9H_8)_4$ to $(C_9H_8)_{12}$, although polymers have been prepared as high as $(C_9H_8)_{35}$. The reaction is carried out with the aid of catalysts such as H_2SO_4, $AlCl_3$, $SnCl_4$, $FeCl_3$, etc. H_2SO_4, however, is the one most commonly used on account of its low cost. $SnCl_4$ is more effective in attaining a high degree of polymerization. The melting point and solubility of the resulting resins may be varied by the amount of catalyst used. For example:

Amount of H_2SO_4	M.P.	Solubility
20%	210°C	Insoluble in ether
5%	165°C	Soluble in ether but insoluble in ether-alcohol
2% and diluted somewhat	100°C	Soluble in ether-alcohol

In producing the resins the naphthas are usually selected according to the type of resin desired. Considerable refining is necessary for the best quality product. The first step is to treat the materials with caustic soda to remove tar acids and then to neutralize any residual caustic with dilute H_2SO_4. Small amounts of more concentrated acid are then added to dry the naphtha. This preliminary treatment with H_2SO_4 is advantageous, for by controlling the quantity of acid a preliminary polymerization is accomplished which removes certain dark-colored and insoluble fractions. Further refining and separation may be attained by fractionation. Closer-boiling fractions yield paler and more uniform resins.

Control of the polymerization reaction is also very important for good color and high yield. This is accomplished by the following methods:

(1) Strength of acid
(2) Rate of addition of acid
(3) Agitation
(4) Temperature control
(5) Time of reaction

Higher concentration of acid gives higher melting points and darker-colored resins; 0.2 to 1.0 per cent of 66°Bé or 95 per cent H_2SO_4 is usually used. Lower temperatures give paler color and higher yield. The temperature is usually held between −20° and +20°C in commercial practice. The reaction can be controlled by checking the specific gravity of the solution as the catalyst is added. When there is no further increase in specific gravity sufficient catalyst has been added.

Excess of H_2SO_4 and any sulfonated coal-tar compounds are removed by diluting with cold water and allowing to settle. Any slight acidity is neutralized with caustic soda and the mixture is washed several times with water to remove any remaining salts. The volatile naphthas and oils are removed by steam distillation under reduced pressure, keeping the temperature as low as possible in order to preserve the color.

These resins are used in a variety of compositions for purposes other than protective coatings. A large part of the production goes into rubber, linoleum, floor tile, printing inks, adhesives, etc. Since they are produced from by-products, their color tends to be dark. Much work has been done to improve the color and with considerable success, although the price of the lighter-colored grades is much higher. Commercial grades range from pale amber to almost black.

The color system used in grading the various types is the same as used in grading coal tars and coal-tar solvents. This is a logical outgrowth of the fact that these resins have been developed by the coal-tar industry. The scale ranges numerically from 0 to 14 and is based on varying concentrations of $CoCl_2$, $FeCl_3$, and K_2CrO_4. The resins are tested by dissolving 2 grams in 25 ml of C.P. benzene and matching the solution with the nearest standard. A color of

½ approximates that of W.W. Rosin;
1 " " of WG to K Rosin;
2½ " " of E Rosin

There are several designations used for expressing the degree of hardness. For simplicity we can use Table 25 given below.

Table 25. Melting Points of Coumarone Resins.

Grade	Melting Point
High melting	150°-160°C
Hard or varnish grade	127°-140°C
Medium	110°-125°C
Soft or rubber grade	25°- 95°C

Coumarones are soluble in all coal-tar solvents and are moderately soluble in petroleum solvents. They are insoluble in alcohol. They are also readily incorporated in all vegetable oils with heat. Their similarity to the petroleum resins is shown by their low acid and saponification number, which is accompanied by excellent chemical and water resistance. These resins have found uses in the protective coating industry in a large variety of formulations, particularly where a neutral, chemically resistant vehicle or varnish is desired. Some of the more important uses are in wall sealers, concrete paint, aluminum paint, insulating varnish, fume-resistant paints, container coating, and floor coatings. They have been particularly successful in the formulation of ready mixed aluminum paints since they do not tarnish the aluminum pigment on storage.

Almost any of the vegetable oils works well with coumarone-indene resins. Although the resins show some unsaturation, there is no apparent reaction when they are cooked with any of the oils. Since they are very soluble, the most effective means of incorporation is to add them to oils which have been previously bodied or to blend them cold in the form of resin solutions. They show their similarity to the petroleum resins in that they are no aid in gas proofing China wood oil. Short wood oil varnishes offer no problem, but with the longer varnishes care must be taken to cook the oil to sufficiently high temperatures to eliminate gas checking.

The incorporation of driers offers some problem in view of the low acidity of these resins. Oxides of lead and manganese are not readily taken up by cooking. Cobalt acetate is cooked in without difficulty, or the soluble naphthenates can be used successfully.

A typical coumarone vehicle is:

100 lbs.	Cumar V 1½
25 G.	China wood oil
5 G.	Bodied linseed Z_2
41 G.	Mineral Spirits
10 G.	Xylol

50% NVM; Body E; Color—13 Gardner

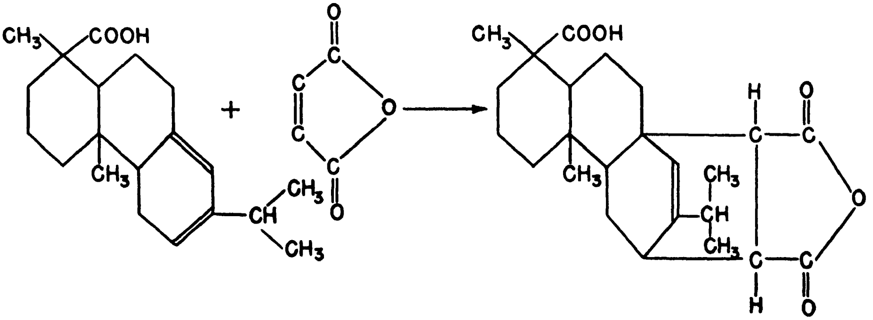
Heat 65 lbs. resin and the CWO to 580°F. Check with bodied linseed and 35 lbs. resin. Melt out and cool to 450°F. Reduce with solvent.

Commercial resins are available from the following producers:

Producer	Trade Names
Barrett & Co.	"Cumar"
Neville Co.	"Nevillac," "Nevindene," "R" Resin, "G" Resin "Nuba," "Paradene"
Pennsylvania Chemical Co.	"Piccoumaron" "Piccovar"

Maleic Resins

This very useful group of resins is made possible by the diene synthesis. This maleic rosin adduct shown by the structural formula below suggests the similarity of this resin to those terpene resins produced with maleic anhydride.



Maleic anhydride up to about 35 per cent of the rosin may be used in the process. The reaction proceeds readily without the aid of catalyst at 150°C, and since the adduct itself has a very high acid value, esterification with glycerin or other polyhydric alcohol is necessary to produce a resin sufficiently neutral for general use in protective coatings. (See also Chapter 7.)

The properties of these resins may be listed as:

(1) Excellent color and color retention.
(2) High melting point.
(3) High acidity.
(4) Poor solubility in solvents and oils.

Vehicles produced from these resins are excellent for white and pale tints. They are also useful in baking finishes. Their high melting point results in high viscosity in varnishes and resin solutions. One might consider their poor solubility as a disadvantage, but this property is utilized many times in obtaining good solvent release in a finish. They cannot be used with reactive pigments on account of their high acidity.

The lower melting point grades are used in nitrocellulose lacquers to improve adhesion and gloss.

In cooking varnishes with these resins some care needs to be observed in using the higher melting point grades that are usually choosen for this purpose. It is somewhat difficult to properly incorporate the less soluble types into the bodied oils. Best results are obtained by heating the resin with 5 to 10 gallons of the oil to 580°F and holding until a cold bead on glass is clear and brilliant. The remainder of the oil is then added in one or two portions, depending upon the amount, heating the batch to 580°F to clear each portion. Clear varnish with a high gloss is obtained in this manner.

These resins are of no assistance in gas-proofing China wood oil. Long China wood oil varnishes require high temperature treatment to render them safe from gas checking.

The following varnish is very suitable as a vehicle for industrial baking whites:

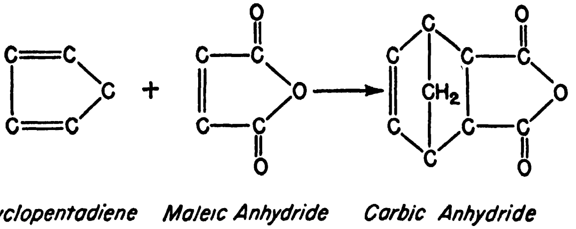
200 pounds	"Amberol" 801
10 gallons	China wood oil
20 "	Bodied linseed oil Z_2
68 "	Mineral spirits

Heat resin and China wood oil to 580°F in about 30 minutes. Check with 15 gallons bodied linseed oil. Hold at 500°F for 15 minutes. Check with the remaining five gallons of bodied linseed oil. Cool and reduce. 50% NVM. Viscosity, H. Color, 10 (Gardner).

Maleic resins are commercially available from the following producers.

Producer	Trade Name
Resinous Products and Chemical Co.	"Amberol"
Reichhold Chemical Co.	"Beckacite"
Hercules Powder Co.	"Lewisol" and "Pentalyn"
U. S. Industrial Chemical Co.	"Arochem"
Krumbhaar Chemicals, Inc.	"Krumbhaar"
France Campbell & Darling	"F.C.D. Resin"
Alkydol Laboratories	"Synaryl S"

There is one other resin produced from maleic anhydride which deserves brief mention. This is the Carbic or C9 resin. It is produced by the diene synthesis and differs from the maleic rosin ester resins by using cyclopentadiene in place of rosin. The reaction may be illustrated as follows.

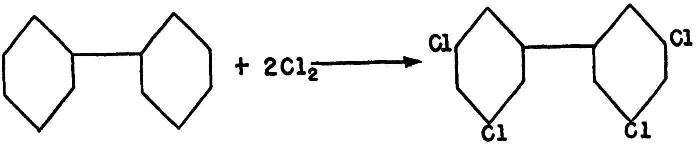


This anhydride is esterified with a polyhydric alcohol to a suitable acid value. This resin is very reactive and has shown its value as an accelerator for the slow-bodying oils used during the war. A 25 per cent addition to unbodied linseed oil will reduce the bodying time to about ⅙ of that of untreated oil. The color and color retention of these resins are excellent.

Other variations of this anhydride have been produced, probably by hydrogenation to eliminate the unsaturation, yielding non-drying resins that are useful softeners and plasticizing agents. These products are made by the Bakelite Corporation.

Chlorinated Resins

The Aroclors are manufactured by passing chlorine into diphenyl or mixtures of similar higher boiling homologs, sometimes known as polyphenyls. Metallic iron, iodine and antimony chloride can be used as catalysts.



Chlorine content up to 70 per cent of the finished product is possible. This represents substitution of chlorine in all open positions on the molecule. Resins made from pure diphenyl are limited in melting point to about 65°C, but mixtures of the higher-boiling point homologs can be used to obtain melting points up to 300°C.

These resins are pale in color and very inert chemically. They are soluble in petroleums, coal tar and most organic solvents, and may be incorporated into most vegetable oils. Their high chlorine content results in considerable fire-resistant properties. Their high price limits their use to the role of modifying agent or plasticizer where their inert characteristics or fire resistance can be economically utilized. They were developed and produced by the Swann Chemical Company, which is now a part of the Monsanto Chemical Company and are offered in about 12 grades ranging from a mobile liquid to a crystalline powder with a melting point of 300°C.

The chlorinated paraffins are prepared by passing chlorine gas into a solution of paraffin in carbon tetrachloride. Varieties up to 70 per cent chlorine are available, but they have found only limited usage as plasticizers and chemically inert modifiers.

Chapter 13

Solvent-type Resins

RECENT DEVELOPMENTS IN NITROCELLULOSE LACQUERS

J. R. YEAGER
Hercules Powder Company, Wilmington, Delaware

In the decade following World War I the development of low-viscosity nitrocellulose and butyl solvents caused the use of nitrocellulose lacquers to expand tremendously. Then followed a period of steady, but slower, growth in the use of lacquers, during which the quality of the nitrocellulose was further improved by a more uniform control of viscosity and by better stability. But it was realized that some new stimulus was needed if lacquers were to continue to expand. Considerable thought had been given to higher solids. A survey made in different sections of the country confirmed the opinion that higher solids was the property most needed to expand the use of lacquer. This property was expected to increase in importance with greater demands for industrial production at increased efficiencies. Higher solids would decrease the number of coats required in a multiple-coat system; thus, it would reduce the amount of work, equipment, and floor space required, and at the same time it would use less solvent to lay down each pound of solids.

In the last three years, much work has been directed toward the development of these high-solids lacquers, first for metals and later for wood. The main factors studied in this investigation were:

(1) Viscosity of nitrocellulose
(2) Solvent system
(3) Ratio of nitrocellulose to resin
(4) Choice of resin
(5) Temperature of application

The effect of these variables may be summarized in a general way as follows: As lower-viscosity nitrocellulose is used, higher per cent solids is obtained for any given application viscosity. For most practical applications, small changes in the viscosity of the nitrocellulose do not affect the physical properties of the film. According to various durability tests made during the past ten years, 27 centipoises appears to be the break point below which tensile strength and durability in orthodox lacquers drop off rather markedly. However, as we shall attempt to show later, quality finishes can be made from nitrocellulose of lower viscosity by proper formulation.

Concerning the ratio of nitrocellulose to resin, the study showed that the general tendency is for higher proportions of resin relative to nitrocellulose to give softer films with resultant better cold-check resistance, but with excessive dirt pickup and poor water resistance. A ratio of 2 parts resin to 1 part nitrocellulose appears to be the best combination for all properties.

The choice of resins will depend upon the properties desired in the lacquer film. The non-drying type of alkyd appears to be the most generally useful. The addition of hard resins, such as dammar or maleic-modified ester gums, increases the hardness but adversely affects cold-check, outdoor exposure, and resistance to humidity. Small additions of urea or melamine resins increase the hardness without any marked reduction in resistance to cold-check and without affecting outdoor exposure adversely. Oxidizing resins give satisfactory hardness and cold-check resistance. However, oxidizing resins, when used alone or as the major constituent in a blend of resins consisting of non-oxidizing and oxidizing alkyd resins, have a tendency to lift on second-coat application. This lifting tendency can be minimized by using at least 2 parts non-oxidizing to 1 part oxidizing alkyd resin. The addition of a small amount of solvent-type plasticizer, such as dibutyl or dioctyl phthalate, gives a marked improvement in cold-check resistance and a moderate improvement in resistance to humidity and outdoor exposure.

The solvent mixture should be chosen so as to give the best spraying and dissolving properties. A certain solvent combination may cost more per gallon but less per pound of solids deposited. Since in most cases the solvent is merely a carrier and is eventually lost, it is good economy to use the best system based on solids deposited.

And now to summarize all these variables. From 1100 clear formulations for metal, approximately 300 of the best were pigmented in black, blue, white, and maroon. After two years and nine months, the different colors were withstanding the exposure tests in the order given above. The outstanding formulations were of the following types:

	Parts by Weight			
RS Nitrocellulose (½ sec.)	1	1	1	1
Non-oxidizing alkyd	2	1	3	2
Oxidizing alkyd	—	—	—	1
Melmac 245–8 (hard resin)	—	—	0.3	—
Plasticizer	—	0.3	—	—

Using twelve outstanding formulations, the four low-viscosity RS Nitrocelluloses (½ second, ¼ second, 30–35 centipoises, and 18–25 centipoises) were compared by using them in each formulation, with both black and white pigments. These lacquers on metal panels have now been exposed for two years and nine months in both Wilmington and Florida, and the tests are being continued. There were 189 panels exposed in this particular viscosity-comparison group; of these, 135 are still in good condition. By viscosity types, the failures have been:

RS Nitrocellulose (½ sec.)	5 panels
RS Nitrocellulose (¼ sec.)	13 "
RS Nitrocellulose (30–35 cps.)	18 "
RS Nitrocellulose (18–25 cps.)	18 "

As may be seen, there are more failures for the lower viscosities. However, the following examples of formulation using all four viscosities, some showing no failures, indicate that with the proper selection of resins and other factors, high-quality lacquer can be made with nitrocellulose of viscosity lower than ½ second.

		Parts By Weight		
Nitrocellulose	1	1	1	1
"Rezyl" 99–5	2			3
"Aroplaz" 905		1	3	
Dibutyl Phthalate		0.3		
"Melmac" 245–8			0.3	0.3
Failures	0	0	1 30–35 cps. Florida-Black 1 18–25 cps. Wilmington-Black	1 30–35 cps. Florida-Black

With results from the metal lacquer program providing a background, wood lacquers were next considered. A survey of the furniture industry indicated a desire for a solids content of 30 per cent or higher with good print and sanding properties. Opinions varied considerably regarding cold-check resistance. The experimental laboratory work undertaken followed the same general approach as was used in the metal lacquer program.

In tests on nitrocellulose of various viscosities, other factors being kept constant, those of the lower viscosities gave higher solids content but less cold-check resistance. However, with the proper selection of resins and plasticizers, good-quality furniture lacquers were produced with the lower-viscosity type of nitrocelluloses. For example, one test formulation containing 30 to 35-centipoise material gave 30 per cent solids and 22 cold-check cycles. Higher ratios of resins to nitrocellulose gave higher solids content, but generally less print resistance. However, the results indicate that where high resin ratios are used, a forced-dry operation may be used to improve the print resistance. As was expected, plasticizers improved the cold-check resistance but decreased the hardness and sandability.

An example of a starting formulation is as follows:

	Parts by Weight
RS Nitrocellulose (30–35 cps.)	1
Glyptal 2477	0.6
Lewisol 33	0.4
Dioctyl phthalate	0.5
Total solids	30%
Cold-check cycles	22
Print, 2 psi, 3 hrs.	none
Sward hardness (1 hr. air-dry)	40
Alcohol softening after 1 hr.	very slight
Water spot	none

These high-solids lacquers may be applied hot or cold. Tests indicate that the quality of the finished product is the same with each method. There have been indications that hot-spray films have less orange peel. Hot-spray makes it possible to apply higher solids with the previously mentioned advantages.

Often, the question arises regarding possible degradation of lacquer by the heating process. The following figures show that when a 25 per cent solution of RS Nitrocellulose of 5 to 6 seconds viscosity was heated for 24 hours at 70°C, very little change took place in viscosity or physical characteristics. Since lower-viscosity nitrocellulose is affected less by heat than are the higher-viscosity types, nitrocellulose of 5 to 6 second viscosity was used to give a magnified example of the extreme effect to be expected.

	Before Heating*	After Heating*
Viscosity	70,500 cps.	61,900 cps.
M.I.T. flex, double folds	290 ± 20	330 ± 40
Tensile strength (psi)	13,800 ± 700	11,900 ± 700
Elongation (%)	36 ± 1	30 ± 5

* Heating was at 70°C for 24 hours.

Brush Lacquers

During the last years of the recent war there appeared to be considerable interest in brushing lacquers. Many companies were making them in small quantities, often upon special request, while others produced rather large quantities. A survey indicated that the faults of brushing lacquers were odor, brushability, lifting, and self-softening. An investigation showed that by careful selection of solvents, the proper balance could be obtained to overcome the above objections. Drying times of approximately 100 minutes gave best brushability and were still fast enough for common usage. An example of a good starting solvent formula is shown:

	Parts by Weight
"Cellosolve" acetate	35
Ethyl alcohol	10
Isopropyl alcohol	10
Turpentine or "Amsco" F	45
	100

Brushing lacquers have application possibilities in both homes and industry.

During recent years much thought has been given to reducing the flammability of nitrocellulose films. While most of the interest has been directed toward cloth coatings or artificial leather, it was felt that some work should be done to evaluate the burning rate of lacquer films on rigid surfaces. Therefore, tests were made according to U. S. Navy Specification 52-D11 (Par. F-31) July 2, 1945. Clear and pigmented lacquers, with and without fire retardant, were applied to wood and metal panels 31 inches long by 7 inches wide. The panels were placed in a horizontal duct 6 by 8 inches and exposed to two Meeker burners under a forced draft. Films of approximately 4 mils thickness were tested, and in no case did the flame propagate the full length of the panels.

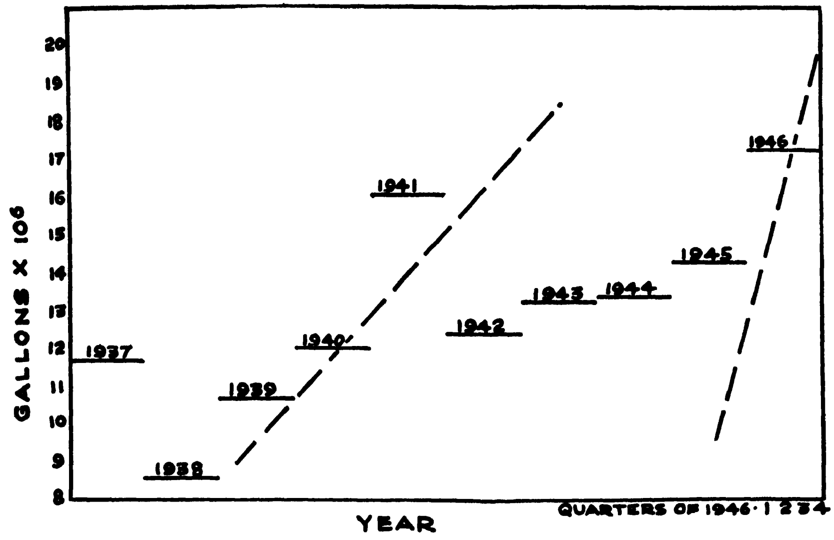


FIGURE 72. Lacquer sales; average per quarter; clear, pigmented, bases and thinner. (*Bureau of Census*)

Preliminary tests using films of 10 and 20 mils in thickness indicated that 10-mil films will not propagate but that 20-mil films may propagate. While this work is not yet complete, it is felt that these tests give useful information, particularly since the lacquers have been compared to other finishes such as shellac, varnish, and paint.

Bureau of Census figures show that lacquer sales are growing tremendously. Figure 72 shows that in the period starting with the first quarter of 1946, lacquer sales increased most rapidly, but reached the greatest volume (19 million gallons) in the third quarter. This was a much faster growth than was shown in the period from 1939 to 1941, when the greatest average quarterly sales amounted to 16 million gallons. This growth applied to practically all lacquer-consuming industries. For example, results of a recent survey of the furniture industry indicate that by 1950 wood furniture finished in lacquer will exceed one-half billion dollars at manufacturers' prices. This survey also indicates that 76 per cent of wood furniture is finished in lacquer.

All indications point to a future for lacquers even brighter than the extremely successful past.

Acknowledgment:

The author wishes to acknowledge the development work done on this subject by Messrs. Wm. Koch, J. J. Coughlan, and R. F. Wint and their associates at the Hercules Experiment Station.

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ETHYL CELLULOSE AND "PARLON"

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In the group of raw materials classed as solvent-type resins, sometimes referred to as film-formers, are both ethyl cellulose and "Parlon" (chlorinated rubber) as well as many other materials, some of which are covered in later sections in this chapter. While both ethyl cellulose and "Parlon" find uses other than in the protective coating field, this discussion will be limited to their use in protective coatings.

Ethyl Cellulose

Ethyl cellulose was first manufactured commercially in this country in 1936 by Hercules Powder Company and total production in the country increased from a few thousand pounds per month in 1936 to over a million pounds per month in 1947. It is made by reacting alkali cellulose with ethyl chloride under heat and pressure. The commercial product has a substitution of approximately 2.15 to 2.60 ethoxyl groups per glucose unit, or 43 to 50 per cent ethoxyl content. Hercules ethyl cellulose is available in the various ethoxyl types and viscosity grades shown in Table 26.

Table 26.

Ethoxyl Types (X refers to types now produced) ‡				Viscosity Grades	
G* 44.5–45.5% Ethoxyl	K* 45.5–46.8% Ethoxyl	N** 46.8–48.5% Ethoxyl	T** 48.5–50% Ethoxyl	(Viscosity on all types run at 5% concn. & 25°C) Designation	Limits
—	—	X	—	7 cps.	6.5–7.4 cps.
—	—	X	X	10 "	8.5–10 "
—	X	X	X	14 "	12–14 "
X	X	X	X	22 "	18–22 "
X	X	X	X	50 "	40–50 "
X	X	X	X	100 "	80–100 "
X	X	X	X	200 "	160–200 "
—	—	X	—	to order	above 200 "

‡ Blanks in the table indicate no demand at present for the particular type and grade. However, this does not mean that these types cannot be produced.

* Viscosity was determined in 70:30 toluene: ethanol by weight on sample dried 30 min. at 100°C.

** Viscosity was determined in 80:20 toluene: ethanol by weight on sample dried 30 min. at 100°C.

Some of the more important physical properties of the ethyl cellulose are its good solubility and compatibility, low specific gravity, flexibility and tensile strength. The complete list of physical properties of the N type ethyl cellulose are listed in Table 27.

Viscosity affects the physical properties. The tensile strength, elongation, flexibility and softening point increase with an increase in viscosity. Results obtained on films cast from a solution of 80:20 toluene: ethanol dried 16 hours at 70°C, conditioned 48 hours at 70°F and 65 per cent relative humidity, are shown in Table 28.

Just as viscosity affects the properties of ethyl cellulose so does the variation in the ethoxyl content alter certain properties. The moisture absorption and hardness decrease as the ethoxyl content increases, while the softening point decreases as the ethoxyl content increases up to approximately 48.3 per cent and then again begins to increase.

Ethyl cellulose is manufactured in viscosities that are quite similar to the standard viscosity types of nitrocellulose. This is helpful in the formulation of lacquers containing both ethyl cellulose and nitrocellulose, which is commercially important at the present time. For example, the N-7 type ethyl cellulose is similar to RS ¼ sec. nitrocellulose, N-14 to RS ½ sec., N-50 to RS 5–6 sec. and N-200 to RS 15–20 sec. In this connection it is well to point out that due to the difference in density one pound of nitrocellulose can be replaced with approximately 0.7 pound of ethyl cellulose to obtain the same coverage.

Table 27. Physical Properties of N Type Ethyl Cellulose.

Bulking value (lb./gal.) in granular form	2.6–2.8
Bulking value (gal./lb.) in solution	0.1035
Color (Hazen) in solution	2–5
Discoloration (by light) compared to cellulose acetate	as good
Discoloration (by light) compared to nitrocellulose	much better
Electrical Properties:	
Dielectric constant at 25°C & 52% R.H. (100 megacycles)	3.03
at 25°C & 52% R.H. (1 kilocycle)	3.44
at 25°C (60 cycles)	2.60
at 100°C (60 cycles)	2.90
Dielectric strength (volts/mil/10-mil film) ASTM step by step	1500
Power factor at 25°C (1 kilocycle)	0.025
at 25°C (60 cycles)	0.030
Specific surface resistivity (ohms x 10^{-10}) 70 hrs at 30°C and 78.7% R.H.	2000
Elongation (% on 3-mil film)	7–30
Flexibility (Schopper double folds, 3-mil film)	17–250
Hardness index, Sward (% of glass)	71
Light transmission, practically complete	3100–4000 A
Light transmission, better than 50% complete	2800–3100 A
Melting point (°C)	200–210
Modulus of elasticity (psi)	189 x 10^5
Moisture absorption, by film in 24 hrs at 80% R.H.	2
by granulated powder in 24 hrs at 80% R.H.	3.4
Moisture vapor permeability (g/sq cm/cm/hr on 3-mil film)	6.4 x 10^{-4}
Penetration softening point (°C on 10-mil film)	150–175
Odor	none
Refractive index	1.47
Specific gravity	1.14
Specific volume (cu in/lb in solution)	23.9
Taste	none
Tensile strength (psi in 3-mil film, dry)	7,900–11,000
Tensile strength, wet (% of dry strength)	80–85%

Table 28. Effects of Viscosity on Physical Properties.

Grade	Viscosity** Cps. in 5% Sol.	Viscosity** Intrinsic $(IV)_w$***	Film* Thickness (in)	Tensile Strength (psi)	% Elongation at Rupture	Flexibility by Schopper Double Folds	Penetration Softening Point (°C)
N-7	7.4	0.55	0.0031	7,960	7	17	151
N-10	9.3	0.66	0.0030	7,670	11	23	151
N-14	13.0	0.77	0.0030	8,100	14	42	156
N-22	19.7	0.91	0.0030	8,250	16	65	156
N-50	42.5	1.22	0.0030	8,390	14	90	161
N-100	93.5	1.67	0.0030	9,100	25	128	167
N-200	199.0	1.97	0.0030	9,240	27	248	171
N-300	319.7	2.22	0.0030	9,380	24	191	170
N-800	785.3	2.62	0.0030	9,660	23	157	173
N1200	1196.5	2.99	0.0030	10,800	25	199	172

* Films were cast from solution in 80:20 toluene: ethanol, dried 16 hrs. at 70°C, conditioned 48 hrs. at 70°F, and 65% R.H., and tested.

** Solvent was 80:20 toluene: ethanol.

*** $(IV)_w = 8/c\left(\sqrt[8]{\text{Rel. Visc.} - 1}\right)$ where c = 0.5% concentration by weight in a solvent composed of 80:20 toluene: ethanol.

In the formulation of ethyl cellulose coatings the ethyl cellulose is generally modified with resins and plasticizers, and in some cases, waxes, tars, etc., are added. In lacquer-type coatings organic solvents are used, and in practically all applications for ethyl cellulose it is important to add a stabilizer.

Stabilizers. Unmodified ethyl cellulose films are sensitive to continuous exposure to ultraviolet light and high temperatures. To overcome this sensitivity to heat and light the incorporation of a stabilizer is recommended. Many stabilizers are effective, including secondary amines such as diphenylamine and phenyl-beta-naphthylamine. Since the amines have a tendency to cause discoloration, menthylphenol—a tailor-made stabilizer for ethyl cellulose—is recommended as the best-all-around stabilizer for ethyl cellulose. Approximately 1 per cent of octylphenol based on the total vehicle solids of the coating gives satisfactory results. Certain plasticizers and resins exhibit some stabilizing effect on ethyl cellulose; in general the resins and plasticizers containing the phenyl groups are in this class. Resins such as the pure phenolics and plasticizers such as diphenyl phthalate, tricresyl phosphate, triphenyl phosphate and phenyl salicylate and "Pentaphen" are useful.

Solvents. Ethyl cellulose is soluble in a wide range of solvents. Almost all ketones, esters, aromatic hydrocarbons and chlorinated hydrocarbons are solvents for ethyl cellulose and can be greatly improved in solvent power by admixing with relatively small quantities of the lower aliphatic alcohols such as ethanol or butanol. In general the best solvent is a combination of coal-tar hydrocarbon and alcohol. For the N type or high ethoxyl content ethyl cellulose, a mixture of 80 per cent of coal-tar hydrocarbon such as toluene and 20 per cent of ethyl alcohol gives the best solubility. For lower ethoxyl contents such as the G or K type a solvent combination of 70 per cent of coal-tar hydrocarbon and 30 per cent of alcohol is indicated. It is possible to select lots of ethyl cellulose in the N type ethoxyl range which will give complete solubility in either alcohol or toluene. Economy type solvents containing fairly large percentages of mineral thinner are useful in ethyl cellulose coatings.

Table 29 shows the tolerance of ethyl cellulose for petroleum thinners; also the effect of ethoxyl content on the tolerance.

Of considerable interest is the effect of solvent composition on the film properties. In general, polar solvents such as alcohol and acetone result in the formation of films with poor physical properties, while non-polar solvents such as coal-tar hydrocarbon give films with good physical properties.

Resins. In ethyl cellulose coatings resins are useful in imparting hardness, gloss, adhesion, water resistance and dimensional stability. In general ethyl cellulose is compatible with the resin acids and the glycerol, glycol and diethylene glycol esters of resin acids, with varnish-type pure phenolics, with rosin-modified phenolics and with many natural resins. Ethyl cellulose is incompatible with all pure alkyds based on glycerol phthalate and short oil modifications of such alkyds.

Table 29. Petroleum Thinner Tolerance of Ethyl Cellulose.

Solvent	D-Type	Solubility N-Type	T-Type
Toluene: Ethanol: V.M. & P. Naphtha Ratio			
7: 3:90	I	Sw	Sw, J
14: 6:80	W	Sw, J	J, pS
21: 9:70	SW	J, pS	S
28: 12:60	Sw	S	S
35: 15:50	Sw, J	S	S
42: 18:40	S	S	S
49: 21:30	S	S	S
56: 24:20	S	S	S
63: 27:10	S	S	S

Legend: S—soluble, free of granulation and gel
pS—almost soluble, but contains gel and granulation
J—gelled
Sw—swollen, but granules not merged into cohesive gel
W—particles become translucent but not swollen
I—insoluble

Plasticizers. Plasticizers impart softness or flexibility to ethyl cellulose films. Practically all plasticizers are compatible with all the ethoxyl types of ethyl cellulose. Vegetable and mineral oils exhibit poor compatibility with the low ethoxyl types and fair compatibility with the high ethoxyl types of ethyl cellulose. It is of interest to note that ethyl cellulose films plasticized with non-solvent-type plasticizers such as mineral oils give the toughest films.

Waxes, Tars, etc. Ethyl cellulose is compatible with a number of waxes and coal tars. The addition of ethyl cellulose to wax and coal tar gives an increase in melting point and adds toughness and hardness.

In the protective-coating industry ethyl cellulose is generally referred to as a specialty material. However, many of the specialty applications offer very large potential markets. In lacquers the largest use is in coatings for electrical cables for automobile ignition systems. For this application the low ethoxyl types are recommended because of their better resistance to gasoline; the lacquers are generally quite highly plasticized with plasticizers of the sebacic acid ester type to give flexibility and toughness over a wide range of temperature. Another large volume outlet for ethyl cellulose coatings is for linoleum finishes. In this application ethyl cellulose is used as the total film-forming ingredient or in combination with nitrocellulose. In some floor coatings ethyl cellulose is used in combination with shellac. Ethyl cellulose is also used in wood finishes giving good cold-check resistance to both sealers and top coats. Specialty coatings on leather, cloth and paper are also important. Some ethyl cellulose coatings in the food-packaging industry are used both for their appearance and for functional properties, such as grease resistance, heat-sealing, and water resistance.

Ethyl cellulose is also used in combination with varnishes, as a small percentage of ethyl cellulose reduces the drying time and improves the film properties. For this application the varnish must be specially prepared so that the ethyl cellulose will be compatible with the varnish.

Other coating applications for ethyl cellulose, such as the hot-melt type, are in wide use. Hot-melt coatings for paper which are based on formulas of approximately 25 per cent ethyl cellulose, 50 per cent resin and 25 per cent mixture of plasticizers and waxes are used in the food-packaging industry. Considerable progress has been made on the development of satisfactory equipment for applying ethyl cellulose hot-melt coatings to paper, and this field offers an attractive market for ethyl cellulose coatings.

The plastic peel type coating, which is also a hot melt, is beginning to find increased use in peace-time applications. It was quite generally used during the war for the protection of metal parts shipped to all points of the globe. For this use Hercules Formula #25 which was approved by the Ordnance Department will serve as an example:

Ethyl cellulose N-50	25
Baker's #15 castor oil	10
Zerice 45	62
Paraffin wax	3
Menthylphenol	1

The formula is prepared by heating all the ingredients with the exception of the ethyl cellulose to a temperature of 375°F and then adding the ethyl cellulose as rapidly as possible with good agitation, maintaining the temperature at approximately 375°F until the ethyl cellulose dissolves. Ethyl cellulose is also used in miscellaneous applications related to the protective-coating industry such as inks, adhesives, pigment grinding, etc.

In view of the fundamental properties of ethyl cellulose it is reasonable to conclude that ethyl cellulose will find an increasingly large outlet in the protective-coating industry.

"Parlon"*

"Parlon" (chlorinated rubber) was first manufactured in this country in 1935. Practically all the sales of "Parlon" are to the protective coating or related industries. "Parlon" enjoyed a normal and quite rapid growth

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* Reg. U. S. Patent Office by Hercules Powder Company.

from the time manufacture was started in this country until the early months of the war, at which time rubber became a critical war material and production of chlorinated rubber was substantially decreased. During the war considerable effort was expended in an attempt to find a substitute for chlorinated natural rubber. Many substitute materials were developed and sold, including chlorinated balata, chlorinated polystyrene, chlorinated guayule rubber, chlorinated neoprene and chlorinated polyisoprene.

Of all these, only chlorinated polyisoprene offered real possibilities as a substitute for regular "Parlon," and this material was manufactured and sold under the trade name "Parlon X." From the close of the war until the latter part of 1946 regular "Parlon" remained under strict government allocation, and this restriction encouraged the development of the substitute, "Parlon X." At present, however, Parlon is readily available. Since "Parlon" and "Parlon X" have properties that are almost identical, this discussion will refer only to "Parlon," with the understanding that what is said about it will also apply to "Parlon X." The main difference between the two products is the fact that "Parlon X" is somewhat darker in color and does not appear to be quite as compatible or stable as regular "Parlon." Tests have indicated that "Parlon X" is also slightly softer.

"Parlon" is manufactured by passing chlorine gas through a solution of rubber dissolved in a solvent such as carbon tetrachloride. The double bonds in the rubber molecule are saturated with chlorine and part of the hydrogen in the rubber molecule is replaced with chlorine, so that a total chlorine content of approximately 67 per cent is obtained. "Parlon" is manufactured in only one chlorine content range and in viscosity types of 5, 10, 20, 125 and 1000 centipoises. The properties are shown in Table 30.

The important properties which have resulted in the use of "Parlon" in the protective-coating industry are its good solubility, its compatibility with resins and plasticizers, its extreme resistance to acids and alkalies, its hardness, and its ability to speed up the drying of compatible oil-modified alkyd resins.

In the formulation of coatings, the "Parlon" is modified with solvents, plasticizers, resins and pigments. The solvents normally used are either coal-tar hydrocarbons or high aromatic content petroleum derivatives. "Parlon" is also soluble in chlorinated hydrocarbons, esters and most of the ketones. However, the ester and ketone solvents are not recommended because of a tendency to cause gelation on long storage.

"Parlon" is compatible with practically all the common plasticizers with the exception of bodied castor oil and mineral oil. The plasticizers normally used are chlorinated paraffin, chlorinated diphenyls and drying and semi-drying oils. While "Parlon" is compatible with a large number of resins, the useful resins for most applications are restricted because of the hardness of "Parlon" to those which are quite soft, such as the long oil-modified alkyd resins, the soft phenolic resins, and the soft coumarone-indene resins. The hard resins are used with "Parlon" only in specialty wood finishes, in heat-sealing paper lacquers and similar applications.

Approximately 0.5 per cent of epichlorohydrin as a stabilizer for "Parlon" coatings is useful in increasing the storage life of "Parlon" finishes.

Table 30. Properties of "Parlon."

General Properties:		
Form	White granular powder	
Color (film)	Water white	
Odor	None	
Clarity (film)	Good	
Taste	None	
Moisture content	Less than 0.5%	
Physical Properties (Solid material):		
Specific gravity	1.64	
Specific volume (in^3 per lb)	16.9	
Bulking value (gal per lb)	0.0735	
Index of refraction (principal)	1.554	
Electrical Properties (Unplasticized clear films):		
Specific surface resistivity (ohms x 10^{10})	2000	
Dielectric strength (ASTM method) volts per mil	2300	
Dielectric constant 25°C, 1000 cycles	3.1	
Power factor 25°C, 1000 cycles	0.0015 to 0.0030	
Power factor after immersion in water for 140 hours, 1000 cycles	0.0027	
Mechanical Properties (Unplasticized clear films):		
	20 cps.	1000 cps.
Tensile strength (psi) (wet film)	4100	4360
(dry film)	4270	4850
Elongation (wet film)	3.8%	3.4%
(dry film)	3.6%	3.3%
Modulus of elasticity (psi)	1.4 x 10^5	
Sward hardness index (% of glass)	90%	
The flexibility of "Parlon" increases with increase in viscosity.		
Thermal Properties (Unplasticized clear films):		
Burning rate	non-flammable	
Effect of heat (dry)	Stable at 125°C	
Melting or softening point	Decomposes 135–150°C	

The incorporation of epichlorohydrin is especially important in clear finishes.

"Parlon" finishes can be applied by any of the normal methods. For spray application the 20-centipoise and lower-viscosity types are recommended. The 125-centipoise type has a tendency to cause spider-webbing if applied as a spray.

One of the largest industrial uses for "Parlon" base paints is for alkaline surfaces, such as concrete, stucco, plaster and asbestos cement boards. "Parlon" base paints are being accepted as the standard material for painting concrete floors and especially for basement floors below grade. The reasons for its acceptance for this use are quite evident. "Parlon" can be formulated into scuff-resistant coatings that are not affected by the moisture and alkali present in new concrete and in concrete below grade by formulating with plasticizers of the chlorinated paraffin or chlorinated diphenyl type and soft resins such as the long oil-modified alkyds. "Parlon" base paints are also widely used for painting swimming pools. For this application outdoor durability as well as water and alkali resistance are important.

Another large use for "Parlon" is in the fortification of alkyd resin enamels where the addition of "Parlon" decreases the drying time, improves the hardness and increases the water and chemical resistance. Finishes of this type generally contain from 15 to 35 per cent of "Parlon" of the low viscosity type. Such coatings are used in finishing trucks, buses, refrigerator equipment, air-conditioning equipment and similar applications.

The first and still a very important use for "Parlon" base paints is for resistance to corrosive conditions. Maintenance paints based on "Parlon" are standard in many chemical and sewage-disposal plants and similar applications. In formulating the chemical-resistant paints the 20-centipoise type of "Parlon" is generally used, modified with plasticizers such as chlorinated paraffin or chlorinated diphenyl and a soft resin.

"Parlon" is also used in inks where chemical resistance is important, such as in the printing of soap wrappers and soap boxes. It is used in special adhesives, one of the most important being in the adhering of rubber to metal. "Parlon" has also been used successfully as a fortifying agent for oleoresinous varnishes to reduce the drying time. About the only change necessary in the preparation of the original varnish is to substitute a solvent such as a high aromatic content petroleum in place of the mineral spirits normally used in varnishes. The use of "Parlon" in the protective-coating industry is growing rapidly, and its properties will make it even more widely accepted in the future.

VINYL RESINS, POLYSTYRENE AND STYRENE RESINS, ACRYLATE AND METHACRYLATE RESINS, ALLYL RESINS, PLIOLITE, AND SILICONE RESINS

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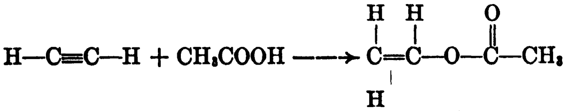
Vinyl Resins

The term "vinyl resin" is usually employed to define a class of synthetic resins that are derived from a vinyl ester, such as vinyl acetate, vinyl chloride, vinylidene chloride, etc. by polymerization of the monomeric compounds under conditions which are controlled to yield products of the desired characteristics. In contrast to the preparation of phenolic, urea and alkyd resins, which are formed by a condensation process, the vinyls are formed by polymerization. As a result, each polyvinyl resin molecule consists of a linear chain in which the monomers have reacted with one another to form high molecular weight polymers. This reaction to form the polymeric resin may be brought about by (a) irradiation with ultraviolet light or (b) the use of catalysts such as a peroxide, ozone or lead tetraethyl.

The characteristics of the vinyl resins are very closely associated with their molecular weights and with the relative quantities of the various polymer bands of which the resins are composed. Certain properties of polyvinyl resins vary with the average molecular weight, while others seem to be almost completely independent of it. For example, tensile and impact strength, abrasion resistance and solution viscosity increase with the molecular weight of the polymer, whereas water absorption, refractive index, hardness, and electrical properties are practically independent of molecular size. The solubility of the resins in organic solvents varies inversely with the molecular weight.

There are produced today essentially six types of vinyl resins which have wide application in the plastics and coatings fields: (1) polyvinyl acetate, (2) polyvinyl alcohol, (3) polyvinyl chloride, (4) copolymers of vinyl chloride and vinyl acetate, (5) polyvinyl butyral and, (6) polyvinylidene chloride and copolymers with vinyl chloride, vinyl cyanide, etc. These types will be discussed in turn in regard to (a) methods of preparation, (b) description and general properties, (c) uses and applications.

Polyvinyl Acetate. Vinyl acetate was first described in a German patent issued to Klatte in 1912. The method described is essentially the one now used and consists of the reaction of acetylene with acetic acid in the presence of mercury salts as catalyst according to the reaction:



$$\mathrm{H{-}C{\equiv}C{-}H + CH_3COOH \longrightarrow \underset{H}{\overset{H}{C}}{=}\overset{H}{C}{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3}$$

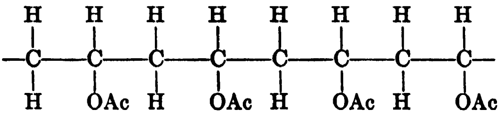
Acetylene *Acetic acid* *Vinyl acetate*

The product thus obtained is of very high purity (99.5 per cent) and has a boiling point of 72 to 73°C, a freezing point of -7°C and a specific gravity of 0.934.

Preparation. The polymerization of vinyl acetate to form polyvinyl acetate is carried out by heating the monomer, usually in a solvent such as benzene or toluene, at a temperature of about 72°C in the presence of a peroxide catalyst, for example, benzoyl peroxide. Aluminum kettles, steam-jacketed, are usually employed and are fitted with a reflux condenser system for the return to the kettle of vapors of the reaction mixture. After boiling for about five hours, the temperature rises to about 76°C, at which time the mixture is run into a still and the solvent and unchanged vinyl acetate are removed by distillation at about 150°C. The polymer is then removed from the kettle and formed by extrusion into rods which can be sliced or flaked. The resin has a tendency to form a solid cake; consequently it is usually sold in small packages to facilitate easier handling by the trade. At the present time, polyvinyl acetate is available in pellet form, and in such a condition as to prevent the caking process.

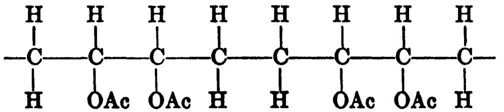
Polyvinyl acetate may be produced in a variety of molecular weights depending upon the conditions that persist in the manufacturing process. In general, the higher the temperature of polymerization, the lower the molecular weight of the resin. If polymerization is carried out in solution, the polymer tends to be smaller as the concentration of the vinyl acetate is decreased. Smaller amounts of catalyst tend to promote the formation of larger polymers. In addition to the above effects, the size of the polymer is affected by the nature of the solvent used in the polymerization process. Toluene gives the lowest and benzene the highest molecular weight, with solvents such as acetone, alcohol, and ethyl acetate giving intermediate polymer sizes.

The structure of the polyvinyl acetate molecule may be exemplified by the following formulas:



$$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OAc}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OAc}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OAc}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OAc}{C}}-$$

or,



$$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OAc}{C}}-\overset{H}{\underset{OAc}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OAc}{C}}-\overset{H}{\underset{OAc}{C}}-\overset{H}{\underset{H}{C}}-$$

The first of these two structures indicates the linear chain with the so-called "head to tail" linkage, and the second the "head to head" arrangement. There is also the possibility of a random arrangement where both of these linkages occur. However, it has been shown that such randomness does not occur in vinyl polymers. The molecular weights of the commercially available polymers range from about 5,000 to about 20,000.

Properties. The properties of polyvinyl acetate are summarized in Table 31.

Table 31. Properties of Polyvinyl Acetates for Four Types.

	Type 1	Type 2	Type 3	Type 4
Viscosity*	4–6	15–20	80–115	650–1000
Color	Colorless	Colorless	Colorless	Colorless
Density (20°C, g/cc)	1.190	1.190	1.190	1.190
Specific volume (cu in lb)	23.2	23.2	23.2	23.2
Melting range (°C)	95–105	120–130	180–200	Decomposes
Heat sealing temp. (°C)	70–80	90–95	95–100	120–125
Burning rate	Slow	Slow	Slow	Slow

* Centipoises of a molar solution in benzene at 20°C, measured with a Hoeppler Viscosimeter.

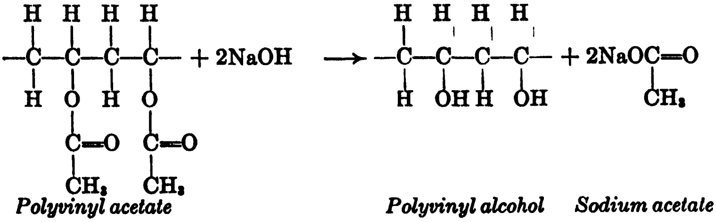
Polyvinyl acetate is readily soluble in the lower-boiling alcohols, esters, aldehydes, ketones, aliphatic acids, aromatic hydrocarbons, and a few chlorinated hydrocarbons. The resins are insoluble in petroleum hydrocarbons, animal and vegetable oils and fats and polyhydric alcohols. They will not dissolve in water although there is a tendency, on prolonged immersion, to swell and soften.

Among the materials with which polyvinyl acetate is completely or partially compatible are certain types of nitrocellulose and phenolformaldehyde resins, chlorinated rubber, terpene resins, rosin, and small amounts of coumarone-indene resins. There is also a limited compatibility with such natural resins as damar, kauri, copal, etc.

Polyvinyl acetate is compatible with most of the common ester-type plasticizers such as dibutyl phthalate, dicarbitol phthalate, dicellosolve phthalate, tributyl phosphate, tricresyl phosphate, "Santicizers" M-8, M-17, and B-16, "Flexol" 3GO and "Flexol" 3GH.

Applications. In either solution or emulsion form, polyvinyl acetate has found applications in a variety of fields, some of which are: Adhesives for leather, paper, cork, textiles, wood, ceramics, plastics, and in certain cases metals. It may also be employed as a heat-sealing or wet-bond adhesive. In the coatings field, polyvinyl acetate has found some uses either as a solution or emulsion as coatings for paper to improve the strength and oil resistance where desired. When applied to metals, excellent durability and corrosion resistance characteristics are observed.

Polyvinyl Alcohol. Polyvinyl acetate can be readily hydrolyzed to yield polyvinyl alcohol, a reaction which was first reported by Herman and Haehnel in 1927. The reaction may be either acid- or alkali-catalyzed to give a satisfactory product and is indicated by the following process:



$$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{\substack{O\\|\\C=O\\|\\CH_3}}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{\substack{O\\|\\C=O\\|\\CH_3}}{C}}- + 2NaOH \longrightarrow -\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}- + 2NaO\underset{CH_3}{C}=O$$

If the above hydrolysis reaction is about half completed, the resulting resin is soluble in mixtures of alcohol and water; if hydrolysis exceeds 80 per cent of completion, the product is soluble in water alone.

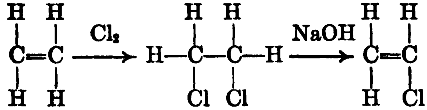
Properties. Polyvinyl alcohol is a white to creamy white powder, odorless and tasteless; it can be heated indefinitely in air at 140°C with no decomposition. At 160°C prolonged heating causes a slight darkening in color. Decomposition begins at 170°C when heated in air.

Polyvinyl alcohols are readily soluble or dispersible in water and the aqueous solutions are stable over an indefinite period. Films prepared from water solutions of polyvinyl alcohol are colorless, odorless, tasteless, transparent, exceedingly tough and unaffected by all oils, greases, fats, hydrocarbons and most organic solvents such as alcohols, esters, ethers, halogenated hydrocarbons, carbon disulfide, oxygen, nitrogen, air, etc.

Viscosity types of polyvinyl alcohol range from 5 to 55 centipoises (viscosity of a 4% aqueous solution at 20°C as determined on the Hoeppler viscosimeter).

Applications. The principal uses of polyvinyl alcohol are found in the paper and textile industries, where aqueous solutions are employed as surface coatings for special purposes, sizings to replace starch, etc. and for adhesives. The resin also finds application in extruded and molded forms and in film where extreme resistance to oils and organic solvents is essential.

Polyvinyl Chloride. The monomer, vinyl chloride, may be produced from cracked petroleum gases according to the following reaction:



$$\mathrm{H_2C{=}CH_2} \xrightarrow{\mathrm{Cl_2}} \mathrm{H{-}CHCl{-}CHCl{-}H} \xrightarrow{\mathrm{NaOH}} \mathrm{H_2C{=}CHCl}$$

Ethylene *Symmetrical dichloroethane* *Vinyl chloride*

Vinyl chloride is usually polymerized to polyvinyl chloride resins in the liquid phase with peroxide catalysts. Temperatures of 35 to 120°C have been recommended for the process. Polymerization may also be accomplished in solution or in emulsion. Because of the high volatility of vinyl chloride, the polymerization must be carried out under pressure in an autoclave.

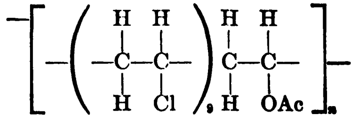
The mechanism of the polymerization and the structure of the polymer are quite similar to that discussed for polyvinyl acetate. However, polyvinyl chloride appears to be unique among vinyl polymers in that the polymer is insoluble in the monomer. This gives rise to the suggestion that there is a high degree of branching in the polymer structure.

Properties. The resin in the unplasticized state is a brittle solid, very resistant to acids and alkalies and most organic compounds. Polyvinyl chloride may be plasticized with some difficulty with tricresyl or dioctyl phthalate or the high-boiling aromatic ethers and ketones.

Applications. Since polyvinyl chloride as such is difficultly soluble and does not respond easily to plasticization, its uses have been limited to applications where extreme resistance to acids, alkalies and organic materials are required for molded or extruded parts. Transparent polyvinyl chloride film has found wide application. Further and more complete information on applications are discussed in connection with the copolymers of vinyl chloride and other vinyl compounds, such as vinyl acetate.

Vinyl Chloride—Vinyl Acetate Copolymers. In order to enhance the working properties of polyvinyl chloride, copolymerization with other vinyl derivatives is resorted to. The most important of the vinyl copolymers are those prepared from a mixture of vinyl chloride and vinyl acetate. Marvel* has pointed out that the copolymer formed does not necessarily have the same composition as the mixture from which it is formed. Since vinyl chloride polymerizes more rapidly than the acetate derivative, the copolymer first formed is richer in vinyl chloride. As the polymerization proceeds, the copolymer formed more nearly approaches the composition of the original mixture of the monomers.

The commercial resins are usually high in vinyl chloride content (somewhat over 80 per cent) and such copolymers are homogeneous resins. The polymer at 85 per cent vinyl chloride would contain about nine vinyl chloride segments for each vinyl acetate group and the co-polymer might be represented by the formula,



$$-\left[-\left(-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}}-\right)_9\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{OAc}}{\text{C}}}-\right]_n-$$

The presence of the vinyl acetate segment in the molecule has a very intense effect on the properties of the polymer, particularly in increasing the solubility over that of polyvinyl chloride alone. This is largely due to the fact that the polymers containing vinyl acetate have a much lower molecular weight. Commercial vinyl chloride—acetate copolymers have molecular weights of approximately 12 to 25,000. The structure of the copolymers is linear, with possible complex chain-branching mechanisms. The branches in the chains, if sufficiently long, might be compared to cross-links between the polymer chains, which probably accounts for the limited solubility of the vinyl chloride—acetate copolymers.

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* Marvel and Horning: "Gilman's Organic Chemistry," Vol. I, p. 701.

Properties. The properties of some typical copolymers, together with those of pure polyvinyl chloride, are shown in Table 32.

Table 32. Physical Properties of Typical Compositions of Vinyl Chloride and Chloride-Acetate Polymers.

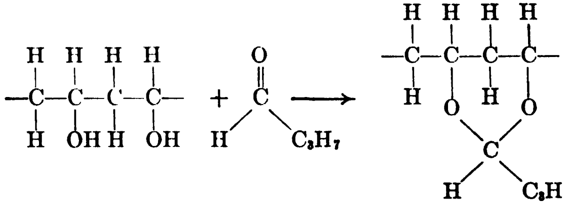
	Rigid Vinyl Chloride-Acetate	Plasticized Chloride-Acetate	Plasticized Vinyl Chloride
Molding qualities	excellent	good	good
Compression molding (°F)	280–325	250–340	290–350
Injection molding (°F)	280–300	250–340	300–350
Specific gravity	1.34–1.37	1.2–1.6	1.2–1.6
Tensile strength (psi)	8,000–10,000	1,000–9,000	1,000–9,000
% Elongation	——	to 500%	to 500%
Softening temperature (°F)	140	——	——
Volume resistivity	10 ohm-cm	——	10 ohm-cm
Dielectric strength	650	300	600
Dielectric constant			
60 cycles	3.26	9.0	6.5
million cycles	3.08	4.2	——
Power factor			
60 cycles	0.008	0.08	0.08
million cycles	0.017	0.10	——
Water absorption			
24 hours	0.05–.15	——	0.05–0.6
Effect of age	none	may harden by vaporization of plasticizer	
Sunlight	darkens slightly	darkens	darkens
Resistance to,			
weak acids	excellent	good	good
strong acids	excellent	very good	very good
weak alkalies	excellent	very good	very good
strong alkalies	very good	very good	very good
alcohols	excellent	very good	very good
ketones	dissolves	dissolves	dissolves
esters	dissolves	dissolves	dissolves
aromatic hydrocarbons	swells	swells	swells
mineral oils	excellent	excellent	excellent
vegetable oils	excellent	excellent	excellent

The copolymers of vinyl chloride and vinyl acetate may be plasticized to give resins of practically any degree of flexibility by using almost any of the common ester type plasticizers. The resins may be used for moldings, extrusions, or coatings either from solution, emulsions, or as calender stock. For coatings from solutions of the resins, the common solvent is methyl ethyl ketone with which solutions up to 10 to 12 per cent at convenient viscosities may be prepared. For calendering operations, the resins are compounded with plasticizer, pigment and inerts in a manner very similar to the process for rubber.

Applications. In view of special properties of the resins, vinyl chloride-vinyl acetate copolymers have a wide variety of uses. Some of these are listed below:

(1) Cable coatings
(2) Filter cloth
(3) Textile yarns
(4) Battery separators
(5) Sheeting for abrasion-resistant covers for equipment
(6) Shoe soles
(7) Transparent and pigmented sheeting for shower curtains, hand bags, clothes bags, etc.
(8) Belts, suspenders, etc.
(9) Coated fabrics for rain wear, table covers, etc.
(10) Miscellaneous coatings uses requiring special chemical resistance characteristics.

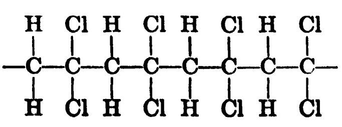
Polyvinyl Acetals. Reaction products between aldehydes and polyvinyl alcohol are broadly called polyvinyl acetals. The individual resin is called polyvinyl formal, polyvinyl acetal, or polyvinyl butyral, accordingly as the aldehyde is formaldehyde, acetaldehyde or butyraldehyde, respectively. The mechanism of the reaction is as follows for polyvinyl butyral:



Polyvinyl alcohol *Butyraldehyde* *Polyvinyl butyral*

Of the three acetal polymers mentioned, polyvinyl butyral is perhaps the most important from a commercial production standpoint. Its most important uses were developed during the war and involve for the most part applications as a rubber substitute for waterproofing and gas proofing fabrics for a variety of uses. Originally, polyvinyl butyral was developed for the lamination of safety glass. By compounding with certain thermosetting resins, polyvinyl butyral compositions are prepared which "cure" or vulcanize in much the same manner as rubber, thus lending themselves to many rubber applications.

Polyvinylidene Chloride. Polyvinylidene chloride is formed by the polymerization of unsymmetrical dichloroethylene, vinylidene chloride, which was reported as early as 1838. However, only in recent years was it found possible to polymerize the monomer. In 1930, it was found that the polymer was a "head-to-tail" structure with the unusual tendency toward crystallinity. The structure is as follows:



$$-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{Cl}{C}}-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{Cl}{C}}-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{Cl}{C}}-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{Cl}{C}}-$$

After much work on the polymerization of vinylidene chloride and copolymerization with other monomers, particularly vinyl chloride and vinyl cyanide, a number of commercially valuable resins have appeared on the market. Pure polyvinylidene chloride is a very hard, insoluble and resistant resin and is suitable only for moldings and extrusions. When copolymerized with small quantities of vinyl chloride, the plasticized resin has found wide use in the manufacture of resistant tubing and piping and in transparent film for packaging processes where the protection against moisture is paramount. When copolymerized with larger quantities of vinyl chloride (the greatest proportion of the resin being the vinyl derivative) resins for coating operations are obtained. The vinylidene chloride-vinyl cyanide copolymers are found to be quite soluble in ketone solvents and compare somewhat in characteristics and applications to the copolymers of vinyl chloride and vinyl acetate.

The outstanding advantage of the vinylidene chloride polymers is the extreme moisture and chemical resistance. The outstanding disadvantage is its poor light stability as compared to other vinyl resins. As emulsions and lattices, the vinylidene chloride polymers are finding more and more uses in the coatings field for paper and textiles and as laminating adhesives. Perhaps the most important and interesting use for the vinylidene chloride resins is in the fabrication of textile fibers for furniture, commercial "rattan" and for institutional drapery material when extreme resistance to staining, wear and fire is essential.

In Table 33 are given trade names of some of the vinyl resins which are on the market.

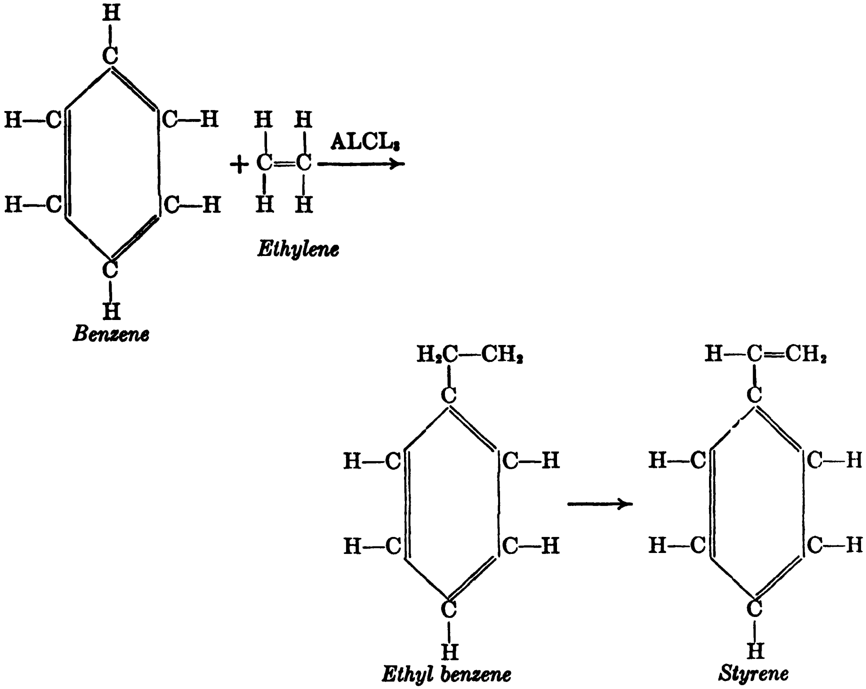
Table 33. Commercial Trade Names of Some Vinyl Resins.

Chemical Name	Trade Name
Polyvinyl chloride	"Koroseal"
	"Geon"
	"Vinylite Q"
Polyvinyl acetate	"Gelva"
	"P. V. Acetate"
	"Vinylite A"
Polyvinyl chloride-acetate copolymers	"Tygon"
	"Vinylite"
	"Vinylseal"
	"Vinyon"
Polyvinyl alcohol	"PVA"
	"Solvar"
Polyvinyl butyral	"Butacite"
	"Butvar"
	"Flexseal"
	"Saflex"
	"Vinal"
	"Vinylite X"
Polyvinyl formal	"Formex"
	"Formvar"
Polyvinylidene chloride polymer	"Saran"
	"Velon"

Polystyrene and Styrene Resins

Although polystyrene was one of the first vinyl polymers to be produced, and was recognized as early as 1839 by Simon, commercial development has been accomplished only during the last 10 or 15 years. As is well known, styrene and its copolymers with other materials such as butadiene, form the basis for the synthetic rubber industry, and styrene as a raw material for synthetic resins has become of extreme importance in this country and abroad.

Synthetic styrene (monomer) is produced by the dehydrogenation of ethylbenzene according to the following process:



The dehydrogenation of ethyl benzene to styrene is accomplished at high temperatures in the presence of iron and steam. Styrene also occurs in coal-tar distillates but its separation is not very satisfactory. For most uses in the production of polystyrene it is essential to have styrene monomer of very high purity, at least 98 per cent.

Polymerized styrene, or polystyrene, is a very hard, colorless, glass-like, thermoplastic resin which is readily prepared from the monomer by the action of peroxide catalysts under the influence of mild heat conditions. The polymerization may be carried out either *en masse*, in solution in aromatic solvents, or in an aqueous suspension or emulsion. By the proper control of the polymerization conditions, molecular weights of almost any value can be obtained. For example, there are commercially available polystyrenes possessing molecular weights as low as 500 (liquid polymers) and as high as 500,000.

The structure of polystyrene is typically a chain-like arrangement with a possible complex highly branched configuration. It is believed that polystyrene is a head-to-tail polymer.

Properties and Uses. Polystyrene is used almost entirely as a plastic material and is obtained in the form of powder or granules for plastic molding operations. Because of its lack of flexibility and certain unsatisfactory solubility characteristics, polystyrene as such has not found very wide usage in the coatings industry to date. For molding operations, the polymer is used without plasticization, a slight variation in flexibility being attained by a control of the degree of polymerization of the resin.

Polystyrene has a low density for plastic materials—1.05. Its surface hardness is somewhat less than that of glass and, being very clear, has a light transmission factor of about 90 per cent. The melting point of the polymer varies somewhat with the molecular weight, from room temperature and lower for the very low polymers to as high as 200°C for the extremely high molecular weight materials. Its excellent electrical properties give polystyrene wide application in the electrical insulation fields. Its water resistance is exceptionally high, being superior to that of almost all other plastics. Polystyrene is quite readily soluble in aromatic hydrocarbons and chlorinated hydrocarbons, and the solutions can be extended to a degree with aliphatic solvents. Strong acids and alkalies and oxidizing acids have almost no effect on polystyrene at ordinary temperatures.

Polystyrene lends itself very readily to compression molding operations, and its low cost makes it a very important resin in this field for a wide variety of products which might be regarded in the class of "gadgets."

In addition to *styrene* polymers, styrene derivatives such as the chlorostyrenes and alpha methyl styrene have reached a point of importance in the plastics field. In the coatings field, a series of low molecular weight styrenes and alpha methyl styrenes have found some application as "softening" and "gloss-promoting" agents.

Styrene Copolymers and Resins. Perhaps the most important copolymer based on styrene is the type of synthetic rubber known as "Buna S" or "GR-S," which is a copolymer of styrene and butadiene. This consists of a polymerized mixture of 60 to 75 parts of butadiene and 25 to 40 parts of styrene, the copolymer being formed by an emulsion polymerization process. The copolymer has a cross-linked structure which lends itself to "curing" or vulcanization similar to rubber. Needless to say, during the past five years this copolymer has played an inestimable part in all our lives.

Other types of styrene copolymers with butadiene have been discovered which to date have had only slight commercial value but which give promise of wide usage in the future.

Styrene Resins for Coatings. Because of its interesting characteristics, low cost and potential availability, styrene presents considerable interest as a raw material for resins used in protective coatings. Some work has been done in this country and abroad toward this end, with a variety of results.

Perhaps the most complete published presentation of the results obtained with styrene in the coatings field is given by a recent article by Hewitt and Armitage,* two English investigators. The work reported deals with the reaction between styrene monomer and vegetable drying oils such as dehydrated castor, China wood and linseed. Resins produced by such reactions were found to be of some interest because of their good drying characteristics, good water resistance, pale color, low acid value, good color retention and good electrical properties. It was observed that as grinding media for paints, the resins presented some difficulties because of only moderate wetting properties. The resins were excellent, however, from the standpoint of the stability of the pigment dispersions.

The most important conclusions reached from the work done on styrene resins involving the reaction between drying oils and styrene is that the work done to date indicates a very interesting series of new reactions with possible commercial value. Much more work will have to be done before such resins have reached a point of development paralleling that of the other well known synthetic resins.

Acrylate and Methacrylate Resins

Resins derived from acrylic acid and its esters have been known for some time, but have been of commercial importance only since 1931. The commercial development has been due largely to the work of Dr. Otto Rohm, who obtained the first patent covering acrylate resins in 1912. He was issued a later patent in 1915 which concerned the use of acrylate resins in lacquers. Since 1931, there has occurred a tremendous expansion in the production of these resins, and their wide use under the trade-names "Plexiglas" and "Lucite" has been greatly enhanced by the last war.

Acrylate and methacrylate resins are prepared by "vinyl" type polymerization of the lower esters of acrylic and methacrylic acid. The reactions are catalyzed by the conditions typical for "vinyl" polymeriza-

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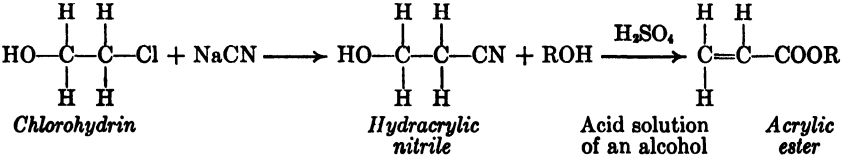
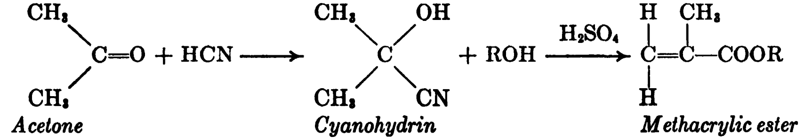
* D. H Hewitt and F. Armitage, Oil and Colour Chemist's Association, June 1946, p. 109–128.

tion, *e.g.*, ultraviolet light, heat, peroxide and acid catalysts. Following are the typical reactions showing the preparation of the monomers:



$$HO-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-Cl + NaCN \longrightarrow HO-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-CN + ROH \xrightarrow{H_2SO_4} \underset{H}{\overset{H}{C}}=\overset{H}{C}-COOR$$



The polymerization of the monomers results in a chain configuration typical of "vinyl" polymers. The monomers may be polymerized singly or may be copolymerized with each other or with other unsaturated compounds, such as vinyl chloride, styrene, etc. Polymerization in aqueous suspension, in organic solvents or *en masse* may be employed.

Properties of Acrylate and Methacrylate Resins. The resins of this type are for the most part thermoplastic and vary in properties from soft, sticky semi-liquids to tough, hard solids. They are characterized by colorless transparency and possess excellent resistance to aging, sunlight, oxygen and ozone. The acrylate resins are softer and more extensible than the corresponding methacrylates. Thus, methyl acrylate is a soft, tacky solid, whereas methyl methacrylate is the hardest of the common acrylic plastics. In general, lengthening the alcohol chain in the ester group causes softening of the polymer and lowers the heat-distortion temperature. For example, polyethylacrylate and polybutylacrylate are much softer than polymethylacrylate. The solubility of the polymers is a definite function of the number of carbon atoms in the alcohol chain. For example, methyl methacrylate is insoluble in petroleum hydrocarbons, whereas esters in which the alcohol group contains four or more carbon atoms, are in general soluble in paraffinic solvents. As is the case with most polymeric materials, the properties of the acrylates and methacrylates are dependent upon the molecular weight of the polymer.

Because of the wide variations possible in the properties of the polymers by a control of the temperature of polymerization, the catalyst concentration, polymerization solvent and copolymerization, it is possible to produce resins of almost any degree of flexibility, thus eliminating the necessity of plasticizers.

The following table (Table 34) gives some of the more important properties of methacrylate ester polymers.

Table 34. Properties of Methacrylate Ester Polymers.

	Methyl	Ethyl	N. Propyl	N. Butyl	Iso Butyl
Density	1.19	1.11	1.06	1.05	1.02
Hardness (Pfund at 25°C)	200	141	100	1	210
Thermal yield point (°C)	125	65	38	30	70
Tensile strength (psi)	9,000	5,000	4,000	1,000	3,400
Impact strength (kg-cm/cm^2)	10.5	7.1	6.5	11.5	1.6
Refractive index	1.490	1.485	1.484	1.483	1.477
Extensibility, 5-mil film (% at break)	4	7	5	230	2
Toughness	98	174	76	1,000	23

The acrylate resins are soluble in aromatic hydrocarbons, chlorinated hydrocarbons and esters. The viscosity varies greatly in different solvents, the least viscous solutions being obtained in the solutions of the resins in aromatic hydrocarbons. The viscosity of such solutions can be further decreased by dilution with alcohols.

Uses and Applications of Acrylate and Methacrylate Resins: These resins are widely used as plastic molding materials for a variety of applications including sheets, rods, etc. The polymer principally used for such purposes is polymethyl methacrylate. The plastic may be readily machined, sawed and otherwise mechanically worked and it can be given a very high polish.

In surface coatings, clear or pigmented lacquers may be prepared and are found to be useful where a very resistant protective coating is desired. Usually, such coatings are baked to yield the best characteristics.

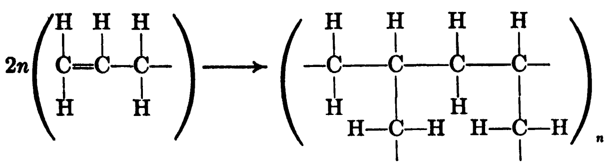
The coatings are resistant to water, acids, alkalies and have been used on paper, textiles, leather, wood, metal, glass, rubber, and plastics.

In solution or in aqueous suspensions, the acrylics have found wide use as adhesives and laminating formulations.

Allyl Resins

The allyl resins are characterized by the fact that, although they are formed by a polymerization process typical of thermoplastic polymers, their properties resemble more closely those of the thermosetting resins like the phenol-formaldehyde types. Consequently, the allyls will not flow appreciably at elevated temperatures and they are not resistant to solvents.

The allyl resins are formed by esterification reactions from allyl alcohol; which is prepared by the chlorination of propylene at elevated temperatures; this in turn is hydrolyzed to allyl alcohol. The alcohol may then be esterified by several methods to form the monomeric forms of the allyl resins. These monomers usually contain two or more allyl radicals in a molecular unit. The polymerization in the presence of a peroxide catalyst may be shown by the following:



This polymerization is similar to the formation of the thermoplastic vinyl resins, but the polymer differs from a typical vinyl in that there exist at least two unsaturated groupings in a molecular chain, forming three-dimensional net-works rather than linear polymers. This accounts for the abrupt increase in molecular weight as the reaction proceeds, in contrast to the well-ordered fashion in which the vinyl polymerizations occur. This phenomenon is exemplified by the fact that gelation takes place when only a small portion of the monomer has polymerized as a result of the addition of the low polymers to one another.

Properties. The polymerized or partially polymerized resins of the allyl type are strong, hard, insoluble, infusible, colorless to slightly yellow, solid resins. In Table 35 are listed some of the more interesting physical properties of the pure, fully hardened polymers. The ranges indicated are due to variations in the molecular structures of the resin-forming monomers.

Table 35. Typical Properties of Allyl Polymers.

Density	1.30–1.35
Hardness (Rockwell)	M95–M117
Tensile strength (psi)	5,000–13,000
Compressive strength (psi)	22,000–27,000
Flexural strength (psi)	9,500–31,000

Although the completely polymerized material is practically insoluble in organic solvents, the partially polymerized mixture is soluble in a number of organic solvents and may be useful for coating applications in such form. One of the most outstanding properties of the allyl resins is the extreme resistance to abrasion.

Uses and Applications. In the partially polymerized state, the allyls are useful as laminating and bonding resins, and for impregnation applications, where the completion of the polymerization occurs "in place." When reinforced by suitable fibrous fillers such as textiles, paper or glass fibers, materials of very high tensile properties are obtained which have the added advantage of being very light in weight compared to other structural materials.

A considerable amount of work has been done, but very little reported as yet on the use of allyl resins in coating formulations. The resins, however, definitely have a future in this type of application to yield very resistant coatings for applications not now satisfied by the conventional baking enamels.

"Pliolite"

Prior to the war, "Pliolite," a resin based on natural rubber, was used for paints which required unusual resistance to the action of chemicals. Because of the unavailability of natural rubber, a synthetic thermoplastic copolymer developed by the Goodyear Research Laboratories has been found suitable for a variety of types of protective coatings. This synthetic resin is called "Pliolite" S-5 and its exact nature is not known to the author. Its high resistance to moisture, acids, alkalies and other corrosive chemicals in addition to other unusual properties make it of particular interest in fast-drying protective coatings.

Properties. The resin is characterized by the following properties: excellent color and clarity; absence of objectionable "paint" odors; non-toxic; readily soluble in aromatic hydrocarbons and tolerance for considerable quantities of petroleum solvents; low solvent retention; drying by evaporation alone; highly resistant to corrosive chemicals such as acids, alkalies, soaps, etc.; highly resistant to water, alcohol, vegetable, animal and mineral oils and greases; exceptional toughness and adhesion; good flexibility; good thermal stability; high abrasion resistance; and good aging characteristics.

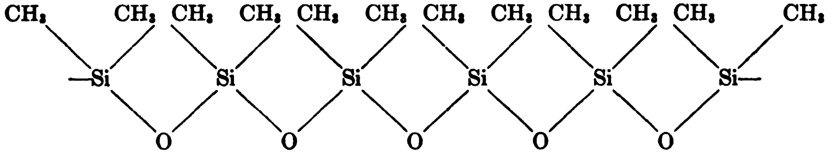
The hardness and flexibility of "Pliolite" S-5 coatings can be varied to meet specific requirements by the use of various plasticizers and modifying resins. For most applications only a small quantity of plasticizer is required. Typical plasticizers include, dibutyl phthalate, dioctyl phthalate, tricresyl phosphate, chlorinated paraffin, "Hercolyn," "Santicizer B-16," and also drying oils such as linseed, soya, tung and oiticica. Resin compatibility includes coumarone-indene oils and resins, "Piccolastic B-100," linseed-Cumar and linseed-Amberol varnishes. "Pliolite" S-5 has limited or no compatibility with alkyds, phenolics, maleic, acrylic or polyvinyl chloride resins. It is also incompatible with cellulose nitrate.

Applications in Paint Formulations. Suggested uses for "Pliolite" S-5 are for the following types of protective coatings: concrete floor enamels; architectural finishes; metal primers and finishes; oil- and grease-resistant coatings; baking primers and enamels; ship-bottom paints; and general corrosion-resistant coatings.

Protective coatings based on "Pliolite" S-5 can be prepared by using a solution of the resin powder or of the milled resin as the vehicle. Pigments are dispersed in the resin solutions by the conventional methods. Since the pigment dispersion is better accomplished by plastic milling than by wet grinding, the use of pigmented bases of the resins is preferable in order to obtain the best gloss in the finishes. For this reason, "Pliolite" S-5 bases, which consist of pigment dispersions in the milled resins, have been made available containing a variety of pigments. These bases can be cut in solvents by either (a) simple agitation, (b) simple agitation followed by a moderate grinding procedure, or (c) mixing in a paste or dough mixer.

Silicone Resins

The chemistry of silicone resins may be said to be based upon the fact that *silica* polymerizes. This is true of all oxygen-containing compounds of silicon. Thus, prosiloxane (H_2SiO) forms a liquid hexamer and a long series of solid polymers. It follows that an organo-siloxane of the composition R_2SiO will assume a polymeric form and that a great many different cyclic and linear arrangements of the R_2SiO units will be possible. An example of such a polymer is poly-dimethylsiloxane, the structure of which is shown as follows:



A compound of this type is called a "silicone" and is commonly prepared by a process of condensation. Thus, silicon tetrachloride ($SiCl_4$) may be partially methylated to form dimethyldichlorosilane [$(CH_3)_2SiCl_2$] which then hydrolyzes readily to form the unstable intermediate, dimethylsilanediol [$(CH_3)_2\ Si(OH)_2$], which in turn condenses intermolecularly and spontaneously to dimethyl silicone.

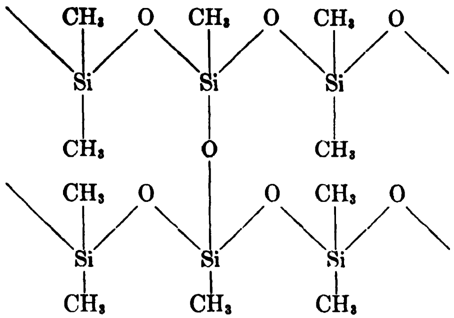
The rate of the condensation of the silicol to the silicone is influenced markedly by the nature and size of the organic group attached to the silicon atom. The dimethyl derivative, for example, condenses spontaneously upon formation, as indicated above, whereas the phenyl silicol, diphenylsilanediol may be isolated from the hydrolysis reaction as a white crystalline substance which is quite stable at room temperature. Upon heating to its melting point (139°C) this silicol condenses slowly to liberate water. Continued heating at 200°C or higher results in the formation of a clear, viscous liquid which on cooling is a brittle, resinous mass. At 400°C, or above, complete "curing" to an infusible resin occurs. Chlorination of the phenyl groups renders the resin non-flammable.

Dimethyl silicone, which polymerizes to a colorless oil, may be converted into solid resins by means of cross-linking two types of methyl siloxane chains. For example, methyltrichlorosilane is added to dimethyldichlorosilane and the mixture hydrolyzed:

$$(CH_3)_2SiCl_2 + 2H_2O \longrightarrow (CH_3)_2Si(OH)_2 + 2HCl$$

$$CH_3SiCl_3 + 3H_2O \longrightarrow CH_3Si(OH)_3 + 3HCl$$

The transitory silicols co-condense on subsequent heating to produce the cross-linked structure:



This polymer is an insoluble, infusible resin and its specific properties may be controlled by varying the proportions of the two silicols in the mixture. Furthermore, by varying the type of organic group and the proportions of the various types to control the degree of cross-linking, it is possible to produce an endless array of silicone polymers having a wide variety of properties.

Applications and Uses of Silicone Resins. Although the commercial importance of the silicone resins has to date been limited because of high cost and limited availability, this class of resins offers a very attractive future in many fields, including the protective-coating industry. The outstanding characteristics of the silicones which account for this interest are (a) excellent stability at high temperatures, (b) exceptional water resistance and resistance to all types of corrosive chemicals and, (c) excellent electrical properties. The silicones have already enjoyed wide application in the field of water-proofing and water-repelling coatings for textiles and paper for special purposes and as impregnating resins for materials used in the electrical insulation field. There are commercially available silicones at the present time in the form of oils, resin solutions, greases and plastic materials. In addition, a considerable amount of development is under way toward the utilization of the silicones for baking enamels, where extreme resistance to heat is a factor.

Chapter 14

Hydrocarbon Thinners

E. H. McArdle

As long as pigmented oils, varnishes and cellulose derivatives are too viscous to apply conveniently at ordinary temperatures, hydrocarbon thinners will be found useful to reduce viscosity. They are the cheapest of paint raw materials, and frequently are used in the largest volume; but the fact that the service they render is only a temporary one has led to a tendency on the part of formulators to take them for granted, and to treat them in the study of paints and paint films as more or less of a necessary evil. This is an unfortunate state of affairs, since the proper choice of thinner not only results in the most effective viscosity reduction, but also contributes largely to the perfection of the laid-down film. Thinners, therefore, should be studied from the point of view of their aid to paint application, rather than simply as fractions of petroleum or coal tar.

Volatile Lubricants

As the only non-polar ingredients of paint, hydrocarbons appear to behave as ordinary lubricants in their role of viscosity reducers. Like lube oils, they are considered to be "Newtonian" liquids, since there is no evidence that they themselves form molecular aggregates, or encrust the larger polar molecules of paint vehicle to form envelopes. (Polar solvents, *e.g.*, acetates, are known to associate with such highly polar vehicles as cellulose esters,[11] in the form of cigar-shaped envelopes surrounding the cellulose chain.) Thus, if hydrocarbon thinners are visualized merely as molecular lubricants, which effectively reduce the internal molecular friction by unpacking and further separating the individual vehicle molecules, an adequate picture of their behavior is obtained. This approach, as shown below, holds quantitatively when applied to hydrocarbon thinners with similar solvent properties.

A suitable hydrocarbon thinner should function somewhat as follows. It should have the power to dissolve the vehicle, *i.e.*, to unpack it and disperse it uniformly, and to maintain solution, or dispersion, during storage at the temperatures to be encountered. It should reduce viscosity as efficiently as possible, while fulfilling the necessary requirements as to solvency and volatility. It should not harm other paint materials, nor the surface being painted, *i.e.*, it must be "non-corrosive." Lastly, it must evaporate from the freshly laid-down film in such a fashion that a uniform coating, of maximum overall adhesion, is deposited upon the surface. Each of these four requirements may be predicted with fair accuracy with the aid of a number of well-defined control tests, now a part of the reference literature, *e.g.*, ASTM Methods (Sections D-1 and D-2), Government specifications, contributions from research laboratories, and recommendations of the Nationally Federated Paint and Varnish Production Clubs.

Measures of Solvency

The expressions "solvency," "solvent power," etc., refer to the ability of a thinner to unpack and disperse the molecules of a vehicle, and thus to reduce its viscosity. Familiar tests include kauri-butanol value[1,3,4,8,9] and its standard interpretation; aniline point and mixed aniline point;[4] dilution ratio tests with cellulose nitrate and with synthetic resins;[4] refractive index; specific dispersion; surface tension; and the proximate analysis of the thinner itself.[2,5,10] Substantially linear relationships between several of these tests are shown in Figs. 73 to 77.

The first mentioned and still the best known solvency test, kauri-butanol value, is the original dilution ratio method. It was developed in 1927 by S. R. Kiehel and cooperators of the Philadelphia Paint and

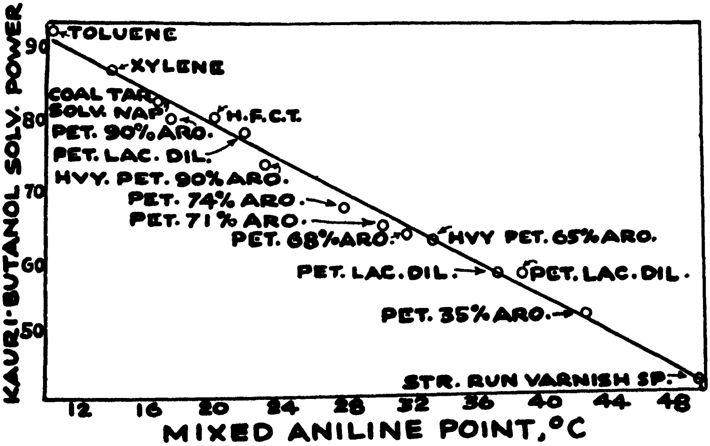


FIGURE 73. Commercial solvent naphthas. Straight line relationship between kauri-butanol value and mixed aniline point for high and medium solvency naphthas of various boiling ranges.

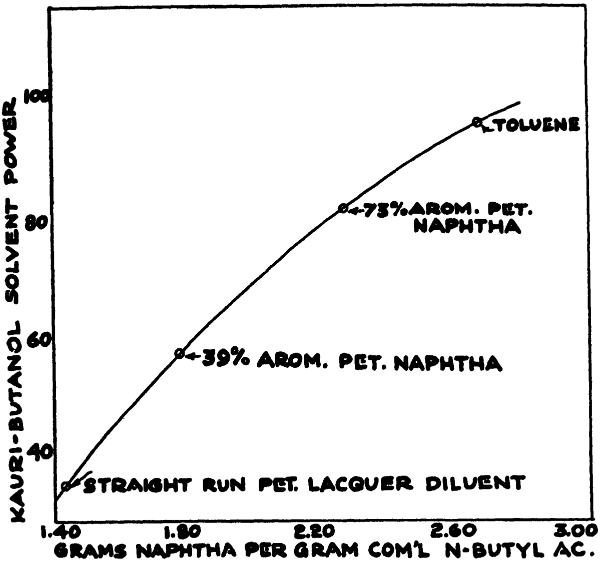


Figure 74. Commercial solvent naphthas. Relation between nitrocellulose dilution ratio and kauri-butanol value. Temperature = 77°F. All titrations at 10 per cent cotton final.

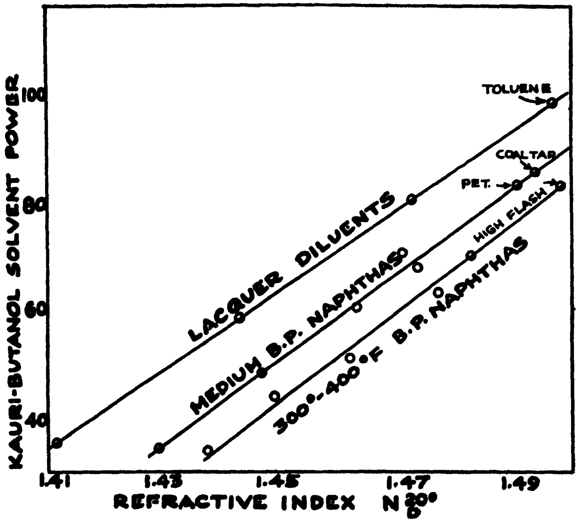


Figure 75. Commercial solvent naphthas. Straight line relationship between kauri-butanol value and refractive index. N. B. allowance must be made in lower two lines for differences in average boiling point.

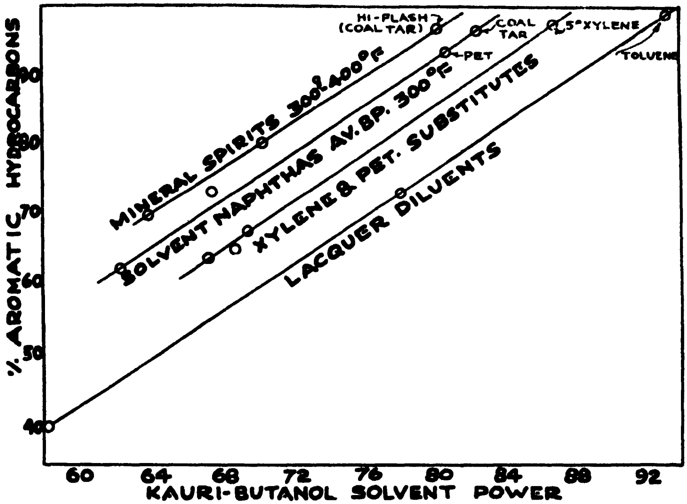


FIGURE 76. Commercial solvent naphthas. Straight line relation between kauri-butanol value and aromatic content in the high solvency range.

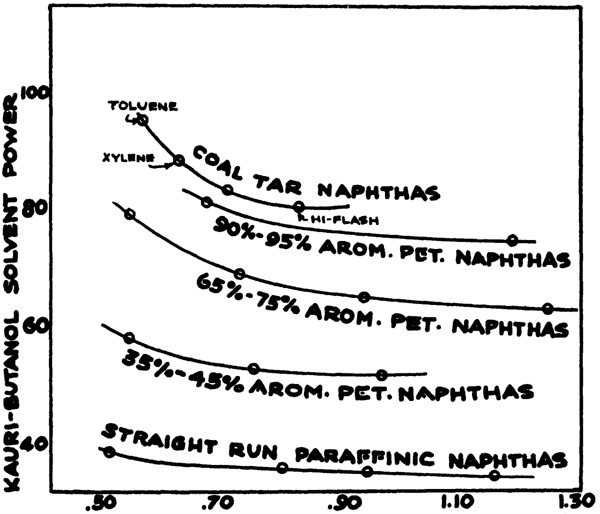


FIGURE 77. Commercial solvent naphthas. Relations between kauri-butanol value and absolute viscosity of products of varying solvencies and boiling ranges. No. 1 Ubbelohde tube at 77°F.

Varnish Production Club,[3] who at the time were being haunted by claims of superior solvency from a number of purveyors of all manner of thinners. Kiehel reasoned that if a resin, itself insoluble in hydrocarbons, were dissolved at standard strength in a polar solvent (butanol), and then titrated to the "kick-out" point with the hydrocarbon offering, the more hydrocarbon tolerated the higher would be its solvent power. The end point of the test—the sudden illegibility of typewriter type viewed through the pool of liquid—is sharp, and reproducibility was found to be within ½ per cent. Its success laid the foundation for an ensuing program of cooperative work on hydrocarbon thinners by the Mineral Spirits Committee of the Philadelphia Club, resulting in the now accepted standard KB interpretation (Primary Reference Mineral Spirits, 40; toluol, 100), as well as later in the "Philadelphia Club Method" of proximate analysis (whereby refractive index before and after removal of aromatic hydrocarbons provides a means of determining aromatics, naphthenes, and paraffins), and also in several recent observations as to the efficiency of a thinner in reducing viscosity.

Composition

Except for turpentine, of which only about 15 per cent is currently available as a paint thinner (the balance being consumed as a raw material for resins, camphor, isoprene and other terpene derivatives), and the cost of which has ranged from 33¢ per gallon in 1938 to $1.15 in 1945, commercial hydrocarbon thinners are derived from petroleum or coal-tar light oil.

Inasmuch as the same thinner may be used with baking whites or sulfur-sensitive colors, as well as with less demanding products such as japans and rubber cements, it must be refined during manufacture to a degree which substantially eliminates reactive sulfur compounds and unsaturated hydrocarbons. Hence, as derived from petroleum or coal tar, most commercial thinners are composed almost entirely of aromatic, naphthenic and paraffinic hydrocarbons. Roughly, on the KB scale, aromatics have "twice the solvent power" of naphthenes, which in turn have "double the solvency" of the correspondingly boiling paraffins. This rule-of-thumb relation assists in making blends, once the proximate composition of a thinner, or pair of thinners, is known in terms of these hydrocarbons; but it is not necessarily indicative of their efficiency as viscosity reducers.

Viscosity Reduction

Once a thinner has been found to be of suitable solvent power, its efficiency as a viscosity reducer should be taken into account. A general impression of long standing holds that the higher its solvent power the more efficiently a thinner will reduce vehicle viscosity. This probably arose from the fact that aromatic hydrocarbons are generally more effective on a volume basis than the (lower specific gravity) paraffins and naphthenes. A more recent approach,[7] wherein solution viscosity is considered as the result of increasing the viscosity of the thinner alone by adding vehicle solids to it, derives an equation for estimating comparative solution viscosities where substitute thinners of like solvent powers are concerned. Use of the equation facilitates the choice of the most efficient reducer.

Using rheological nomenclature, solution viscosity in centipoises (η) divided by the viscosity of the thinner alone (η_0) gives the well known "relative viscosity": (η_r), *i.e.*,

$$\eta_r = \frac{\eta}{\eta_0}.$$

It is apparent that relative viscosity is a property of the vehicle alone.

Then, if at the usual high concentrations of vehicle solids encountered in paints, the molecules of thinner are regarded simply as separators which reduce the internal friction between molecules of the vehicle, the more moles of thinner present, the lower the solution viscosity becomes. The relationship is a logarithmic one. Hence, for a single vehicle at a single concentration, expressed in pounds of vehicle solids per gallon of *solution*, the equation

$$\text{"Viscosity Factor"} = \eta_f = \text{constant} = \log \eta_r \times \text{moles of thinner per gallon}$$

should hold for any thinner as long as the "character of the dispersion" is the same for each thinner in question. This is found to be the case with a simple resin such as ester gum. "Viscosity factor" is a property of the vehicle, at the single concentration chosen.

When applied to varnishes and alkyds, a correction must be applied to the molality of the thinner present, according to the vehicle's oil length. The drying oil (whether combined or not) itself appears to act as additional lubricant for the "resin" present in the solution. Thus, if toluene and xylene are the thinners being compared, and toluene is taken as the basis of comparison, the "equivalent molality" of the xylene present is a larger value than its actual molality.[7]

In the case of lacquer solutions in polar solvents, dilution with hydrocarbon diluents proceeds according to the equation without correction, *i.e.*, the combination of cellulose derivative and polar solvent acts as the "resin."

Data required for using the equation are the viscosities and molecular weights of the thinners in question. The only vehicle datum needed is the drying oil length, if any. Handbooks list viscosities of pure hydrocarbons, *e.g.*, aromatics, but the necessary figures for commercial hydrocarbon thinners should be obtained from the supplier.

The equation may be utilized for a variety of concentrations, with the aid of the established expression

$$\frac{\log \eta}{C} = K$$

where concentration, C, is again expressed in pounds of vehicle solids per gallon of *solution*.

Tests for Purity

Paint technology now being well advanced, largely as a result of the research and publications of the Federation of Production Clubs, it is unusual to encounter a poorly refined thinner. Petroleum refiners and coal-tar products manufacturers are now thoroughly indoctrinated in the necessity of supplying stable, water-white, mildly-odored and non-corrosive products, and adequate fractionating and treating facilities are widely available. So anxious is the supplier industry to furnish thinners which are doctor-sweet, low in unsaturates, and non-corrosive to copper and mercury that separate terminal storage facilities as well as certain tank cars, tank wagons, steel barrels and drums are now maintained exclusively in hydrocarbon solvent service. It is thus necessary for the paint laboratory only occasionally to check purity, according to the above-mentioned tests, described in ASTM Sections D–1 and D–2.

Volatility

To the supplier of thinners, volatility refers to the ASTM distillation range, and this test should be run to control the uniformity of shipments. In evaporation from films of protective coatings, however, volatility as indicated by boiling range may be overshadowed by large differences in the latent heats of vaporization between similarly boiling thinners, *e.g.*, 83 calories per ml for benzene vs 55 for a comparably boiling straight-run paraffinic naphtha. (Fortunately, most paint vehicles are either low in molecular weight compared to the highly polymerized rubbers, or, as with cellulose derivatives, their chains are straight instead of snarled as in rubbers, and hence the factor of solvent retention is almost negligible. Evaporation from paint films thus parallels evaporation from a film of the thinner itself.)

Running a series of evaporation rate tests is a tedious operation, requiring maintenance of constant temperature throughout the several runs as well as carefully equalized air flow over the samples being compared. For this reason the test is generally shunned, and too much reliance placed upon boiling range alone. It is now possible, however, to estimate comparative evaporation rates with adequate precision from the 50 per cent ASTM distillation temperatures and the specific gravities of the thinners in question.[6]

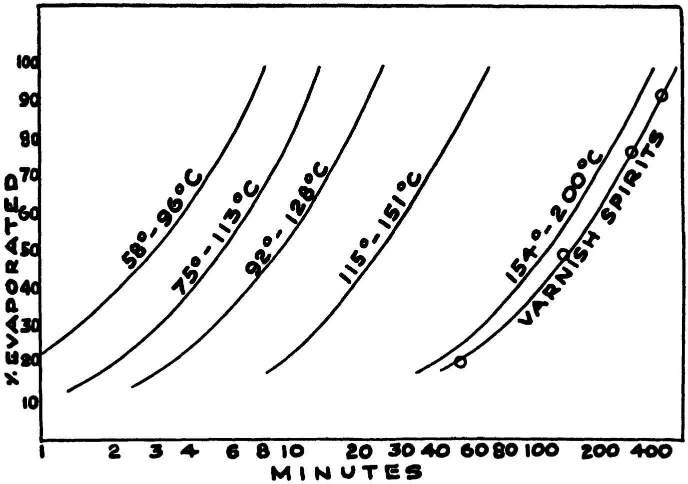


FIGURE 78. 40°C, wide straight-run naphthas.

Figure 78 shows a family of evaporation curves for straight-run petroleum thinners made from the usual sweet paraffinic base crudes, and with average spreads in boiling range. (The right hand curve should be neglected for the moment.)

If these data are now replotted as done in Figure 79, it becomes possible to construct on Figure 78 a curve for any straight-run paraffinic thinner of the usual boiling spread, simply by knowing its 50 per cent ASTM distillation temperature, and then reading from Figure 79 its 20, 50, 80 and 95 per cent evaporation times. For narrower-boiling paraffinic thinners, Figure 79 is also used, but for the infrequently encountered wide-cut products, *e.g.*, rubber solvents, some correction must be made.[6]

To utilize Figure 79 for naphthenic and aromatic thinners, a correction for their 50 per cent distillation temperatures is made according to the equation

$$T_P = T + 50\,(G - G_P),$$

where T is the 50 per cent point, in °C, of the naphthenic or aromatic thinner,
G its specific gravity,
G_P the specific gravity of a 40° C-wide paraffinic thinner with the same 50 per cent point, and
T_P the now corrected 50 per cent point to be used in reading from Figure 79.

That the equation holds adequately is illustrated in Figure 78 by the right-hand curve, where the calculated squares coincide well with the previously plotted data curve for the evaporation rate of a naphthenic mineral spirits.

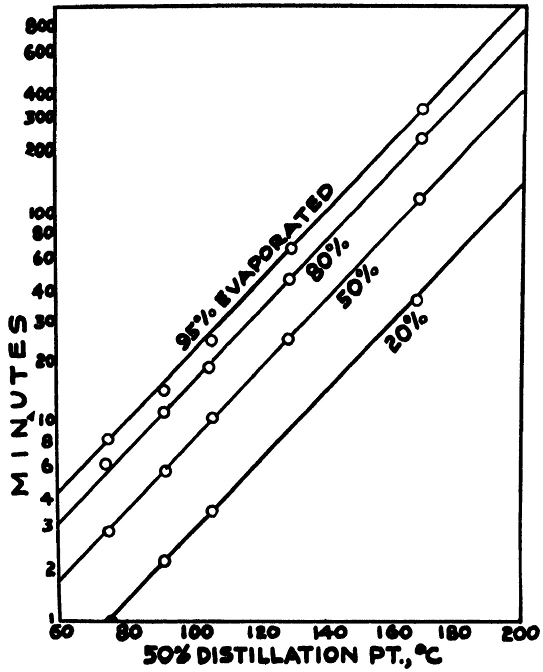


FIGURE 79. 40°C, wide straight-run naphthas.

Conclusion

As the lowest cost and chemically the simplest raw material in protective coatings, hydrocarbon thinners nevertheless contribute largely to successful paint performance, and a study of their properties and behavior should well repay the paint technologist.

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Chapter 15

Formulation of the "Volatiles" in Nitrocellulose Lacquers

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The volatile portion of nitrocellulose lacquers is ordinarily of a much more complex nature than that of varnishes and synthetic finishes, and usually contains as many as six ingredients. This difference is due essentially to two factors:

(1) Nitrocellulose is not soluble in the hydrocarbons used as the volatiles in the varnish-type materials, and while these hydrocarbons are used in lacquers in large proportions because of their low cost, they must be supplemented with esters and alcohols to provide the necessary solvency.

(2) In the case of the esters and alcohols above, there is usually an appreciable difference in price between the more desirable, slow evaporating materials, and the less desirable, fast evaporating ones. The ordinary lacquer is therefore usually formulated with members of both classes as a compromise, thus increasing the number of ingredients further.

The discussion below will present more detailed reasons for the use of the various ingredients of typical lacquer volatiles, and will attempt to develop the principles which determine the proportions in which they are employed. It does not aim to cover all the details of solvent formulation, however, since this is too big a subject to be covered in this chapter.

The volatiles of a typical lacquer consist of a mixture of butyl acetate, butyl alcohol, ethyl acetate, ethyl alcohol, toluene and naphtha. These six ingredients can be divided into three groups on the basis of their chemical nature and their functions in the lacquer, as per Diagram A below:

Diagram A

Solvents	Diluents	Latent Solvents
butyl acetate	toluene	butyl alcohol
ethyl acetate	naphtha	ethyl alcohol

The "solvent" and "latent solvent" portions can also be divided into two groups in accordance with their relative speeds of evaporation, as per Diagram B:

Diagram B

Slow-Evaporating	Rapid-Evaporating
butyl acetate	ethyl acetate
butyl alcohol	ethyl alcohol

SOLVENTS AND DILUENTS

To take up the division in the first diagram, the butyl and ethyl acetates in the first column are commonly known as "solvents," and their function is to supply the solvent power for the nitrocellulose. They are indispensable in the formula, since they are the only ingredients in it which are capable of dissolving the nitrocellulose, although it will be understood that the two particular esters used in this formula can be replaced by other esters or by members of several other groups of chemicals, such as ketones and nitroparaffins. The materials in this "solvent" group have always been at least moderately expensive, but fortunately most of them possess a great excess of solvent power and can therefore be mixed with fairly large proportions of cheap non-solvent hydrocarbons without losing their ability to dissolve the nitrocellulose. This permits the incorporation into the formula of the materials in the second column—the so-called "diluents"—toluene and naphtha.

Since these hydrocarbon materials are used essentially because of their low cost, they are naturally employed in the maximum proportion permissible; this proportion is determined by three characteristics of solvents and of lacquers. The first is known as the "diluent ratio," or "tolerance," of the solvent for the diluent. This term denotes the maximum proportion of any particular diluent which can be added to a solution of nitrocellulose in the solvent under consideration without gelling or precipitating the nitrocellulose. Thus, a solution of nitrocellulose in butyl acetate will tolerate about 2.7 cc of toluene for every cubic centimeter of the ester before showing any tendency to set to a gel, and a similar solution in ethyl acetate will tolerate 3.3 cc of toluene for every cubic centi-

Table 36. Tolerances (Dilution Ratios) of Nitrocellulose* Solutions in a Number of Solvents.

Solvent	Toluene Value	Naphtha Value
ethyl acetate	3.3	1.1
isopropyl acetate	3.0	1.1
normal butyl acetate	2.7	1.45
secondary butyl acetate	2.4	1.1
synthetic amyl acetate	2.0	1.2
acetone	4.5	0.65
methyl ethyl ketone	4.1	0.85
methyl isobutyl ketone	3.4	1.0
butyl lactate	5.1	2.0
butyl "Cellosolve"	2.6	2.0

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* The concentration of nitrocellulose at the end point is approximately 8%. The solvents and diluents used were of commercial quality.

meter of solvent. The toluene and aliphatic naphtha dilution ratios of some of the more important solvents are given in Table 36.

At first sight, this dilution ratio principle may appear to be a fit standard for determining the proportion of diluents to be used in a lacquer formula, since any mixture of solvents and diluents containing less diluent than the proportion permitted by the dilution ratio values is still capable of holding the nitrocellulose in solution. Actually, however, commercial lacquers and thinners of reasonable quality contain about 10 to 15 per cent more of solvents, and 10 to 15 per cent less of diluents, than is indicated by the dilution ratio values. This practice is dictated by considerations of viscosity and of film smoothness, since the solvent-diluent mixtures approaching the dilution-ratio end point too closely are very greatly inferior to moderately richer mixtures in regard to these important characteristics of lacquers. In general, the loss of solvent power by the nitrocellulose solvents, on the addition of diluents, is not as abrupt as might be deduced from the sharpness of the end point in the dilution-ratio test, and this power really falls off gradually long before the precipitation end point. As a result of this, solvent-diluent mixtures of very high diluent content produce nitrocellulose solutions of much higher viscosities than those of lesser diluent content, and the films deposited by their lacquers are not as smooth. The relations involved are somewhat similar to those used in handling work horses, where the load normally put on the animal never approaches the maximum load which would be necessary to stop him from moving altogether (the last corresponding to the precipitation end point in the case of solvent-diluent mixtures), as the long-term results of such a practice would be ridiculously uneconomical.

Viscosity

Let us examine the first of the two above unfavorable effects of extra-high proportions of diluents, namely, high solution viscosities. Nitrocellulose lacquers tend to be on the low side in regard to their content of film-forming solids, because of the high viscosity imparted to the lacquers by the nitrocellulose and the resulting need for high proportions of volatiles to reduce the solutions to workable viscosities. The lacquer formulator is therefore very conscious of the importance of viscosity in his lacquers, and is watchful for any factors that may raise it and thus reduce the solids content. The presence of excessive proportions of diluents is one of the most important of these factors, and some data regarding this are given in Figure 80. The curves show some typical relations between the proportions of diluents present in lacquers and the viscosities of the latter. All the lacquers in each curve were identical as regards the nature and

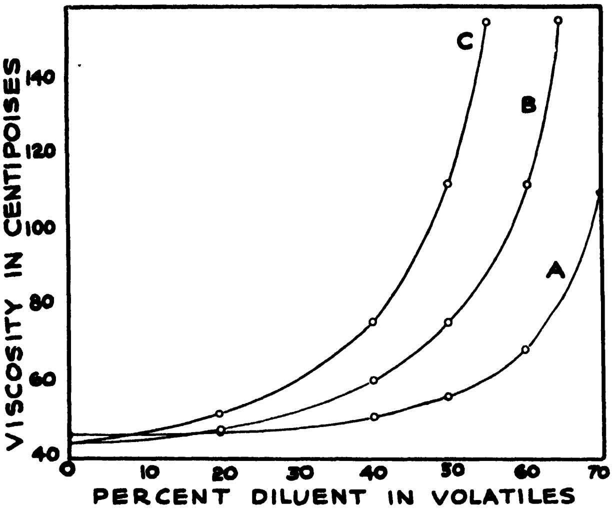

FIGURE 80. Effect of diluent proportions on the viscosity of lacquers. The volatiles of the lacquers in this graph all contained the same combination of nitrocellulose solvents, consisting of 40 per cent butyl acetate, 20 per cent butanol, 30 per cent ethyl acetate, and 10 per cent ethyl alcohol. The lacquers, however, differed in the relative proportions of diluents and solvents. The lacquers in the three curves also differed in respect to the nature of dissolved solids, and in the nature of the diluent used.

	Lacquers on Curve A	Lacquers on Curve B	Lacquers on Curve C
Nature of diluent used	toluene	toluene	toluene 50 naphtha 50
Film-forming ingredients (*in grms. per 100 cc of volatiles*)			
¼ second nitrocellulose (dry)			
alkyd resin A	—	15	15
ester gum	7	—	—
dibutyl phthalate	3	2	2

proportions of the dissolved matter in them, and all contained the same mixture of nitrocellulose solvents*—a mixture of 40 per cent butyl acetate, 20 per cent butanol, 30 per cent ethyl acetate and 10 per cent ethyl alcohol; they differed in respect to the relative proportions of this "solvent" mixture and that of the diluent. Examining Curve A in the figure, as

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* The "solvent" portion in these lacquers is made up of a mixture of esters and alcohols, rather than straight esters. The reason for this will become evident after the discussion of the functions of the alcohols in lacquers, later on, but it might be mentioned at this point that the relations shown in Figure 80, especially the bad effect of excessive proportions of diluents, holds just as fully, and even more so, if the solvent portion is made up of straight esters.

an example, it will be seen that the lacquers containing 20 and 40 per cent of toluene are of almost exactly the same viscosity as the one containing straight solvents and totally free from any diluents; the introduction of the first moderate proportions of diluents into the formula thus appears to have no bad effect on the viscosity of the lacquers. A further increase in the proportion of toluene to 50 per cent similarly has only a very moderate effect on the viscosity, but the next increase in the toluene content—up to 60 per cent—increases the viscosity much more; the introduction of still another 10 per cent of toluene—raising it to 70 per cent—increases it very greatly. As a matter of fact, the last 10 per cent of toluene increased the viscosity of the lacquer by 45 centipoises, an increase twice as large as that produced by the full earlier 60 per cent. These relations illustrate the fact that the loss in the dispersing power of the nitrocellulose solvents does not occur suddenly at the dilution-ratio end point, but begins to fall off substantially when the proportion of diluents approaches within 15 to 20 per cent of the end point composition.

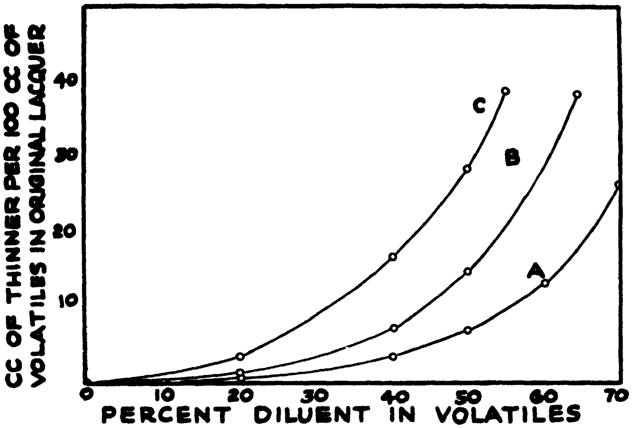

FIGURE 81. Effect of diluent proportions on the volumes of thinner required to reduce the lacquers shown in Figure 80 to spraying viscosity (45 centipoises). The composition of the thinners used for reducing any particular lacquer was the same as that used in the lacquer itself.

Figure 81 presents the relations in Figure 80 from another angle—that of the proportions of thinner necessary to dilute all the lacquers in Figure 80 to the same viscosity. It will be readily appreciated that this is a more practical way of considering viscosity data, since all the compositions in Figure 80 will in practice be thinned to the same application viscosity; the more practical interest is therefore not in the viscosity values themselves, but in the relative volumes of thinner necessary to adjust the various lacquers to the proper viscosity level. An examination of Curve A in Figure 81 will show, very similarly to the data in Figure 80 that lacquers containing 20 to 30 per cent of toluene are not appreciably different from the diluent-free lacquers as regards the volume of thinner required for viscosity adjustment while, on the other hand, the difference between the lacquer containing 60 per cent of toluene and the one of 70 per cent is very marked, the second one requiring the addition of 14 cc more thinner per 100 cc of lacquer than the first.* In the last case, the saving in costs resulting from the use of the higher proportions of diluent in the original lacquer is more than fully cancelled out by the cost of the extra volume of thinner necessary to adjust the lacquer to the proper viscosity.

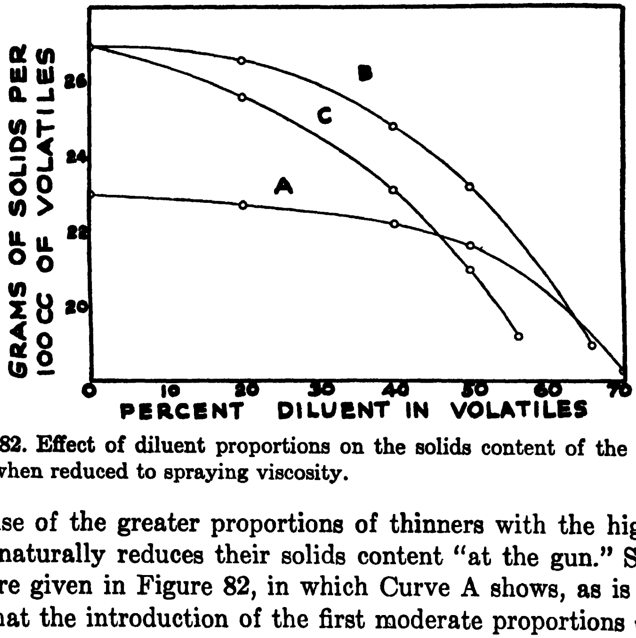

FIGURE 82. Effect of diluent proportions on the solids content of the lacquers in Figure 80 when reduced to spraying viscosity.

The use of the greater proportions of thinners with the high-diluent lacquers naturally reduces their solids content "at the gun." Some data on this are given in Figure 82, in which Curve A shows, as is to be expected, that the introduction of the first moderate proportions of diluent into the lacquer formula does not noticeably reduce the solids content of the lacquer "at the gun." The increase in the proportion of toluene from 50 to 60 per cent, on the other hand, results in a moderate decrease in solids, while a further increase in the toluene content to 70 per cent reduces the solids content from 20.4 to 18.2 per cent, corresponding to a full 10 per cent reduction. Since the solids content of nitrocellulose lacquers is low at best, this drop in solids is naturally a serious objection to the use of excessive proportions of diluents.

Altogether, it will be seen that from the point of view of viscosity and solids content, the proportion of diluents to be employed in lacquer

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* The thinners used were in all cases of the same composition as the "volatiles" in the lacquer to which they were added.

formulas should be substantially lower than that indicated by the dilution ratio values. The exact proportion to be used in any particular lacquer will depend principally on the importance of solids content in the material and on the differences between the prices of solvents and diluents at the time, although there are also some other factors. Thus, at the present time there is a great demand from the furniture industry for lacquers of higher and higher solids, and the lacquer formulator will therefore tend to go in the direction of low proportions of diluents in his furniture lacquers—as low as 50 per cent of toluene. On the other hand, in the case of toy lacquers, where film thickness and solids content are of much less importance, the proportion of diluent may be allowed to rise as high as 60 per cent. Similarly, the difference between the prices of solvents and diluents in 1945–1947 was temporarily more than five times as large as in 1939.* This caused the formulator to increase the proportions of diluents in his lacquers during that period. No "quality" formula, however, contains the diluents in proportions corresponding to the vertical portion of the viscosity curve, as the saving in cost produced by this formulation practice is more than counterbalanced by the cost of the additional thinner required and by the reduction in the solids content of the lacquers.

Toluene vs. Naphtha

The tolerances of all solvents for aliphatic naphtha are substantially lower than their corresponding toluene values (see Table 36). Thus, the tolerance of butyl acetate for naphtha is about 1.4, while the corresponding toluene value is 2.7; the differences are still greater in the case of ethyl acetate or the ketone solvents. As is to be expected, therefore, the turn in the viscosity curves from the horizontal to the vertical direction occurs at much lower diluent proportions in lacquers containing some naphtha than in those employing toluene as the diluent. Some results in this regard will be seen by comparing Curves B and C in Figure 80. Thus, the above turn starts in Curve C at a place corresponding to about 10 per cent less diluent than in Curve B, and this is related to the fact that the diluent used in the lacquers of Curve C consists of a mixture of 50–50 toluene and naphtha, rather than the straight toluene used in the lacquers of Curve B. Further data are given in Figure 83, where it will also be seen that xylene is somewhat worse than toluene in this respect. The lacquer industry employs both toluene and naphtha as diluents, and it will be appreciated from an examination of the data above that these materials are not interchangeable, and that the replacement of some toluene by an equal volume of naphtha produces an effect similar to that of a general increase in the proportion of diluents in the formula. The substitution of toluene by

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* This difference is much smaller now (Nov., 1948).

naphtha must therefore be accompanied by an increase in the proportion of solvents. As a crude generalization it can be stated that in most lacquers, 100 volumes of toluene can be replaced by a mixture of 80 to 85 volumes of aliphatic naphtha and 15 to 20 of nitrocellulose solvents, without any change in viscosity one way or the other. The choice between naphtha and toluene as a lacquer diluent will thus depend largely on the relative costs of the above naphtha-solvent mixture and that of toluene.

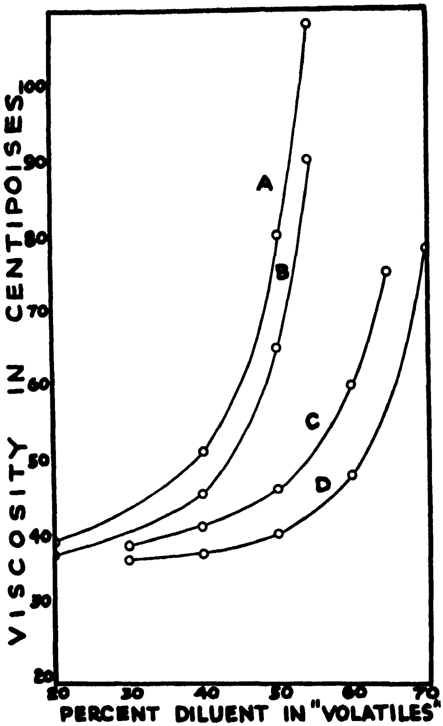

FIGURE 83. Viscosities of nitrocellulose solutions in solvent mixtures containing various diluents. All the solutions contained 12 *gm* of ½ second nitrocellulose per 100 *cc* of volatiles. The solvent portion of the volatiles was composed of a mixture of 40 per cent butyl acetate, 20 per cent ethyl acetate, 20 per cent butanol and 20 per cent ethyl alcohol. The diluents used were as follows:

Curve A = petroleum naphtha of boiling range 120–150°C
Curve B = petroleum naphtha of boiling range 90–130°C
Curve C = xylene
Curve D = toluene

Similarly to the differences in dilution ratio between toluene and aliphatic naphtha, there are considerable differences between the various solvents themselves in this respect. In the homologous series of the ordinary esters and ketones, the toluene dilution ratios fall off as one ascends in the series;* thus, the toluene dilution ratio of butyl acetate is lower than that of ethyl acetate. Similarly, the presence of iso and secondary groups also leads to lower dilution ratios, and isopropyl acetate and secondary butyl acetate have lower dilution ratios than the corresponding normal propyl and butyl esters (see Table 36). The viscosity characteristics of solutions of nitrocellulose in various solvents follow

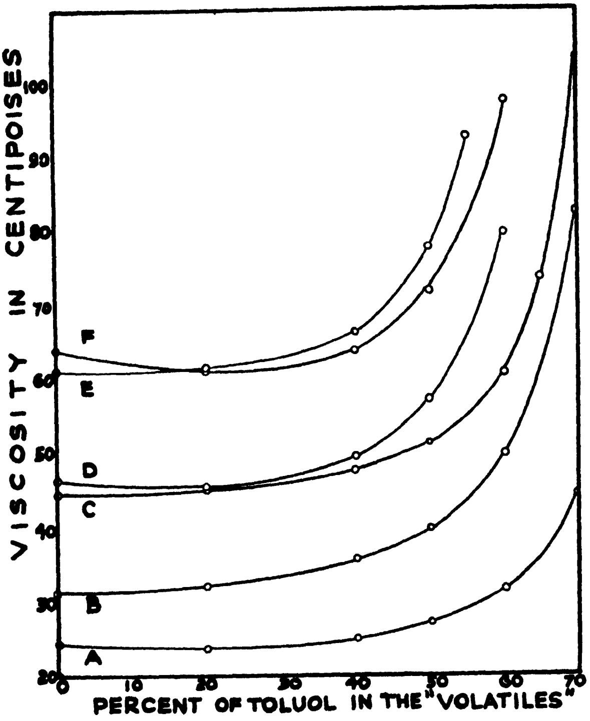

FIGURE 84. Viscosities of solutions of nitrocellulose in mixtures of various solvents and toluene. All the solutions contained exactly 12 *gm* of ½ second nitrocellulose per 100 *cc* of volatiles. The solvent-portion was made up of a mixture of 80 per cent ester and 20 per cent corresponding alcohol, rather than straight ester, for reasons discussed under "latent solvents."

Curve A = ethyl acetate
Curve B = isopropyl acetate
Curve C = butyl acetate
Curve D = secondary butyl acetate
Curve E = secondary amyl acetate
Curve F = synthetic amyl acetate

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* The relations are somewhat more complex in the case of naphtha dilution ratios.

these dilution ratio relations quite closely. It will be seen in Figure 84 that the turns in the viscosity curves occur at progressively lower proportions of toluene as one goes from ethyl to isopropyl, to butyl and to amyl acetates—quite in line with the progressive fall in the dilution ratio values in this homologous series. The relations between normal butyl and secondary butyl acetate are especially illustrative of the relation between viscosity and dilution ratio. These two esters produce nitrocellulose solutions of exactly the same viscosity in the absence of toluene or in their low-diluent mixtures, such as when containing no more than 40 per cent of toluene. Beyond that point, however, the two curves begin to diverge, and the one of secondary butyl acetate bends to the vertical at about 7 to 8 per cent less toluene than the one containing normal butyl acetate, apparently in consequence of the lower dilution ratio of the secondary ester, which causes it to reach the "semi-exhaustion" condition at a lower toluene content than is the case with the normal material.

Effect of Resins

The dilution ratio values in Table 36, as well as all similar values in lacquer literature, are for simple solutions of straight nitrocellulose, and they are not fully true for many of the more complex practical lacquers, which contain a large variety of resins in addition to the cellulose material. This is especially true for lacquers containing the very important alkyd resins. The latter reduce the dilution ratios of all ordinary solvents considerably* (see Table 37), and lacquers containing them must be formulated with higher proportions of solvents and lower proportions of diluents, than straight nitrocellulose solutions. These lower dilution ratios show up very strongly in the viscosity relationships as well, as will be seen by comparing Curves A and B in Figure 80, or by examining Figure 85. In both of these, the bends in the curves of the alkyd resin lacquers start at about 10 to 15 per cent less toluene than in the parallel ester gum lacquers, as is to be expected from the effect of the alkyd resins in lowering the dilution ratio values of solvents.

While the position of the bend in the viscosity curve undoubtedly bears some relation to the dilution ratio values, as shown in the discussion above, it should not be assumed that these relations are very simple or quantitative. A striking example of a disagreement along this line is one shown by alkyd resin lacquers containing some alcohols. As will be seen from a comparison of lines No. 2 and No. 5 in Table 37, the dilution-ratio-reducing effects of the alkyd resins are much weaker in the case of a mixture of butyl acetate and butanol than in solutions of straight

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* For details, see C. Bogin, H. L. Wampner, and K. R. Gosselink. "Effect of Alkyd Resins on the Tolerance of Nitrocellulose Solutions and on the Viscosities of Nitrocellulose Solutions." *Paint, Oil and Chemical Review,* Jan. 21 and Feb. 4 (1937).

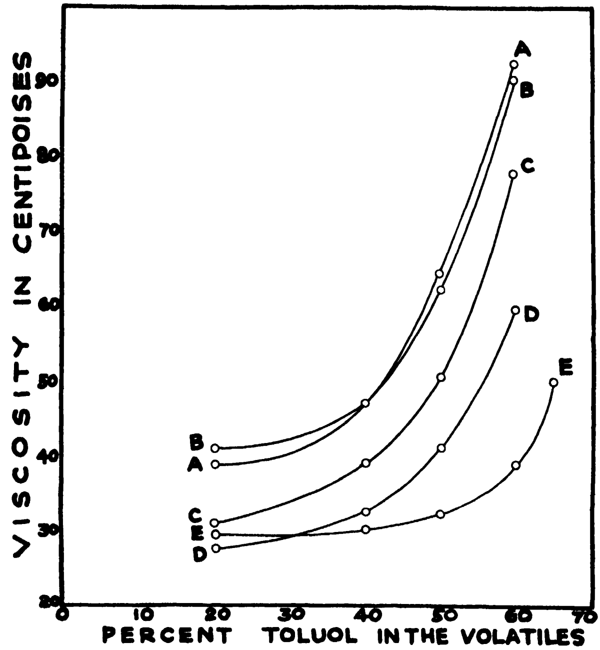

FIGURE 85. Relation between percentage of toluene and viscosity—in nitrocellulose lacquers containing some typical alkyd resins. All the lacquers contained the same mixture of nitrocellulose solvents, consisting of 40 per cent butyl acetate, 20 per cent butanol, 20 per cent ethyl acetate, and 20 per cent ethyl alcohol, but differed in the proportions of toluene. The lacquers contained 9 grams of ¼ second nitrocellulose and 18 grams of resin. The nitrocellulose solution E, given for comparison, contained 12 grams of nitrocellulose, the higher proportion being used in order to approach more closely the viscosities of the combined nitrocellulose-resin solutions.

A = Non-oxidizing; medium-short oil
B = Semi-oxidizing; short oil
C = Non-oxidizing; short oil
D = Oxidizing; medium oil
E = Nitrocellulose

Table 37. Effect of a Typical Alkyd Resin on the Tolerances (Dilution Ratios) of Solvents for Diluents.

	TOLERANCE FOR TOLUENE		TOLERANCE FOR 50–50 TOLUENE-NAPHTHA	
SOLVENTS	in presence of ester gum	in presence of a typical alkyd resin	in presence of ester gum	in presence of a typical alkyd resin
Ethyl acetate	3.3	2.7	2.0	1.5
Butyl acetate	2.7	2.1	2.1	1.4
Synthetic amyl acetate	2.0	1.3	1.5	0.9
Methyl isobutyl ketone	3.4	2.6	1.8	1.4
67–33% mixture of butyl acetate and butanol	2.7	2.5	2.1	1.4

NOTE: The values above are for compositions containing the average proportions of resins. They vary somewhat with variations in such proportions, and with the grades of alkyd resin used.

butyl acetate. When considering viscosity relations, however, this beneficial effect of the alcohol is apparently of no help, and the alkyd resins affect the position of the bend in the viscosity curve in the presence of the alcohol to the same degree as in its absence. Similarly, while the maleic acid resins do not affect the dilution ratio values of solvents, some of them act like the alkyd resins as regards the position of the bend in the viscosity curves, although their effect is not quite as great.

Altogether, as a result of the viscosity relations discussed above, lacquer formulas of ordinary quality employ about 60 per cent of toluene, rather than the 70 to 75 per cent indicated by dilution-ratio considerations; in lacquers containing alkyd resins, or in those containing appreciable proportions of naphtha, the proportion of diluent is still lower—as low as 50 and 45 per cent. In lacquers where the solids content is of extra-great importance, the proportion of diluents may be even lower than this.

It is of interest to note that the effect of diluents on viscosity, as expressed in the general nature of the curves in Figure 80, is not peculiar to nitrocellulose solutions, but holds also for solutions of other colloidal materials—whenever mixtures of solvents and non-solvents are employed. Thus, they are fully duplicated in solutions of cellulose acetate, ethyl cellulose, "Vinylite" resins, etc.; similar relations are also found in the case of solutions of many alkyd and urea-formaldehyde resins, whenever aliphatic naphtha is used as a diluent and aromatic hydrocarbons as the true solvents.

Flow

The application by spray of smooth finishes, fully free from orange peel and similar imperfections, is not easy at best, and the expense of the sanding and rubbing operations, used to smooth the surface, often represents a large portion of the total finishing costs. Nitrocellulose lacquers also tend to be somewhat worse than varnishes and synthetics in this respect, primarily because of the very much faster rate of evaporation of the volatiles used in them. The degree of smoothness obtained with any particular formula—its so-called "flow"—is therefore a very important point in considering its value. The main factor determining this flow characteristic is that of speed of evaporation of the volatiles. Thus, the rapidly evaporating ethyl acetate is very much worse in this respect than the slowly evaporating butyl acetate. However, the solvency characteristics of the formula also appear to play some part in this effect, and solvent-diluent mixtures approaching the precipitation end point are worse in this respect than richer mixtures, similarly to their differences in respect to viscosity. Such differences are difficult to demonstrate in a mathematical manner, as was done with the viscosity effects of the diluents, but the recital of a few observations will serve to illustrate the general relations. Thus, the replacement of 10 to 15 per cent of toluene in a lacquer by 10 to 15 per cent of secondary butyl acetate—a liquid of almost exactly the same rate of evaporation—produced a decided improvement in flow if the lacquer contained 60 to 65 per cent of toluene, but produced no such result in the case of formulas containing 30 to 40 per cent of toluene. This difference is readily explainable by the idea that in the first formula the solvency conditions were improved considerably by the replacement of the diluent by a solvent, while in the second, these solvency conditions were already so good as to make any further enrichment of the formula of no benefit. As a matter of fact, in the case of the 65 per cent toluene formula above, even the replacement of 15 per cent of the diluent by 15 per cent of the very much faster evaporating ethyl acetate gives some improvement in smoothness, probably because the improvement in "solvency" resulting from the change has more than compensated for the harmful effect of the increased rate of evaporation of the mixture. In a similar way, the replacement of as much as 30 per cent of benzene by the much slower evaporating toluene was found to improve the flow of a lacquer no more than a parallel replacement of only 5 per cent of ethyl acetate by 5 per cent of butyl acetate, probably because in the toluene replacement the solvency in the film was reduced during the drying process by the slower evaporation of the new diluent. Finally, an ethyl cellulose lacquer made with 65 per cent of toluene produced almost perfectly smooth films; but a parallel nitrocellulose lacquer was found to be very bad on "flow." This difference was probably due to the fact that toluene is a semi-solvent in the case of the ethyl cellulose, rather than a true diluent, and that the same high-toluene formula which is of very low solvency with nitrocellulose is still quite rich for ethyl cellulose solutions.

Many other demonstrations of the connection between solvency and flow could be given and, altogether, the proportion of diluents in a lacquer must be kept well under that indicated by the dilution ratio values for reasons of flow and film smoothness, as well as for those of viscosity and solids content.*

LATENT SOLVENTS

Referring back to Diagram A, the third group of liquids is made up of alcohols—butyl and ethyl. These substances are not solvents for nitro-

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* The examples above refer to tests made by flowing the lacquers on strips of smooth metal inclined at an angle of about 45°, rather than by spraying. While the same differences can be demonstrated in spray application as well, the results are not as sharp there, being influenced greatly by other factors connected with the spray method of application.

cellulose, and therefore do not belong in the first or "solvent" group. At the same time they cannot be put into the diluent class, if for no other reason than that some of them are high-priced materials and their function is therefore not that of reducing costs. They are usually classed as "latent solvents"; the term "latent" refers to the fact that, although not themselves capable of dissolving nitrocellulose, they contribute very greatly to tolerance and solvency when present together with true solvents, such as the esters, ketones, etc. Thus, a solution of nitrocellulose in 10 cc of butyl acetate and 5 cc of butanol will tolerate 40 to 41 cc of toluene—the same volume tolerated by 15 cc of straight butyl acetate, showing that the butanol has contributed as much solvency to the mixture as an equal volume of butyl acetate. Still more, it will be seen in Table 38 that with many solvents, such as nitropropane and methyl-isobutyl-ketone, the dilution ratio per cubic centimeter of mixture of true solvent and butanol is actually substantially higher than that of the true solvent by itself; thus the butanol has contributed even more than its share to the solvency of the mixture.

In general, there is some reason for believing that the ideal solvents for nitrocellulose are not the straight esters or ketones, but rather their mixtures with alcohols; as an extreme example of the superiority of such alcohol mixtures, there is the well known combination of ethyl ether and ethyl alcohol used in collodion compositions, where the ether is totally incapable of dissolving the nitrocellulose by itself, but acquires this power in the presence of the alcohol. The reason for this contribution of the alcohols to solvency may be related to the fact that the nitrocellulose used in lacquers is not a fully nitrated material, and still contains a fairly high proportion of free hydroxyl groups on some of the molecules in its micelles; this creates some need for hydroxyl groups in its solvents, on the old principle of "like dissolves like."

Table 38. Toluene Dilution Ratios of Solvents and of 67–33% Solvent-Alcohol Mixtures

Solvent	Alcohol	Dilution Ratio in cc of toluene per cc of the combined liquids in the other two columns
Ethyl acetate	none	3.3
Ethyl acetate	Ethyl alcohol	3.3
Butyl acetate	none	2.7
Butyl acetate	Ethyl alcohol	3.0
Butyl acetate	Butyl alcohol	2.7
1-Nitropropane	none	1.3
1-Nitropropane	Butyl alcohol	2.7
Methyl-isobutyl-ketone	none	3.4
Methyl-isobutyl-ketone	Butyl alcohol	3.7

Of course, the ratio of alcohol to true solvents must be kept within reasonable limits; and some results are shown in Figure 86, which gives the toluene dilution ratios of various mixtures of true esters and alcohols.

It will be seen that the proportion of butanol in its ester-alcohol mixture should not exceed 30 to 40 per cent for best results; in the case of ethyl alcohol, proportions as high as 60 per cent can be used without any appreciable loss of solvency.

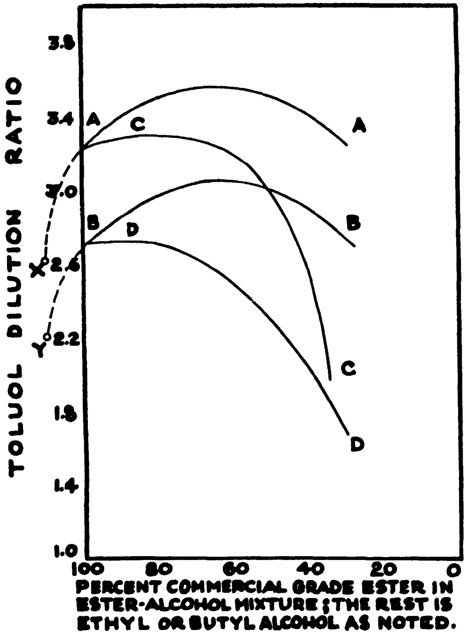

FIGURE 86. Toluene dilution ratios of mixtures of esters and alcohols. The esters used were of the standard commercial quality. The ethyl acetate was 85–88 per cent ester value, and the butyl acetate of 88–92 per cent. The outside points X and Y are for 100 per cent esters—*free from alcohols.*

Curve A = ethyl acetate-ethyl alcohol mixtures
Curve B = butyl acetate-ethyl alcohol "
Curve C = ethyl acetate-butanol "
Curve D = butyl acetate-butanol "

The above effect of the alcohols on the dilution ratios of solvents is well duplicated in their effects on the viscosity characteristics of nitrocellulose solutions. Pertinent results are given in Figure 87, which shows a number of toluene viscosity curves similar to those discussed earlier in the section on diluents. It will be seen in this figure that mixtures of butyl acetate and butanol containing moderate proportions of the alcohol, such as 80 to 20 and 67 to 33 mixtures (Curves B and C), are definitely superior to straight butyl acetate, as with them the toluene does not manifest any viscosity-raising effects until the 50 per cent point; but when straight butyl acetate is used as the solvent (Curve A), the viscosity

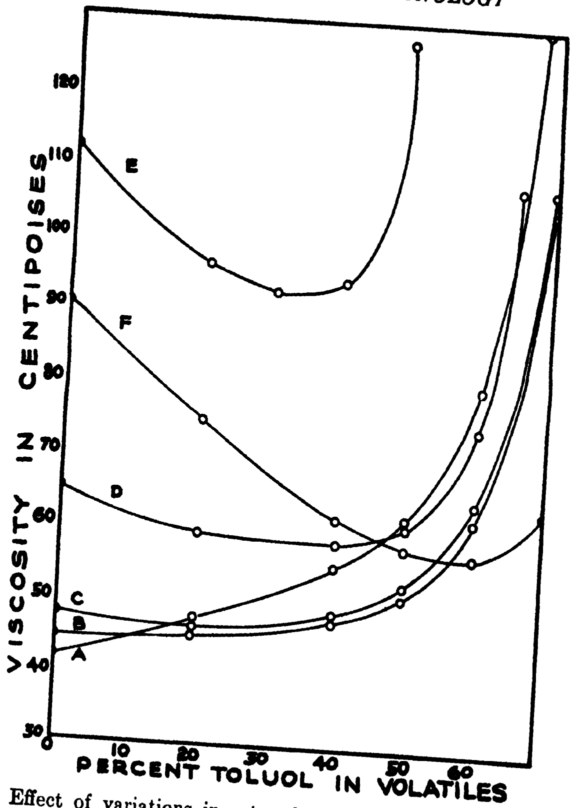

Figure 87. Effect of variations in ester-alcohol proportions on the viscosity of nitrocellulose solutions. All the solutions contained 12 *gm* of ½ second nitrocellulose per 100 *cc* of liquid.

A = butyl acetate—commercial 92% ester
B = 80% commercial butyl acetate—20% butyl alcohol
C = 67% commercial butyl acetate—33% butyl alcohol
D = 50% commercial butyl acetate—50% butyl alcohol
E = 25% commercial butyl acetate—75% butyl alcohol
F = Cellosolve

curve is inclined quite steeply right from the very beginning—with the introduction of the first few per cent of the diluent into the formula. As a result of this, when comparing practical mixtures, such as those containing about 60 per cent toluene, those containing some butanol are of appreciably lower viscosity than those based on straight butyl acetate.*

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* The results would undoubtedly have been still more in the favor of the alcohol if 100 per cent butyl acetate were used in these lacquers rather than the ordinary commercial butyl acetate; the last has an ester value of 92 per cent and thus already contains about 8 per cent of butanol.

At the same time, the presence of excessive proportions of alcohols is definitely objectionable, as seen from Curve D, where the solvent portion is made up of a mixture of equal proportions of butyl acetate and butanol; the viscosities there are appreciably higher than those of Curves B and C at all concentrations of toluene.

Actually the idea of latent solvency is probably of doubtful scientific foundation, and there is some evidence in favor of the belief that the contribution of alcohols to solvency is manifested mainly, and possibly altogether, only in the presence of hydrocarbons. Thus, in Figure 87 the mixture of 50–50 butyl acetate-butanol, free from toluene (Curve D), is as bad on viscosity as the 50–50 butyl acetate-toluene mixture in Curve A. Still more, a mixture of 25–75 butyl acetate-butanol (Curve E) produces solutions of very high viscosities; in its case the addition of toluene reduces the viscosity considerably, indicating that mixtures of alcohol and toluene are superior to alcohol by itself. Similarly, in the case of "Cellosolve," a solvent possessing both an ether and a hydroxyl group in the same molecule, as well as in the case of the similar hydroxyl-containing diacetone alcohol, the addition of toluene causes a very marked drop in viscosity (see Curve F). These facts suggest that from the strictly scientific point of view, the contribution of the alcohols to solvency is better expressed by the theory that their mixtures with hydrocarbons are superior diluents than either of the two separately, rather than that the alcohols contribute to the solvency of the true solvents—the esters, ketones, and nitroparaffins.

These ideas, however, are only of scientific interest. From the practical point of view, a diluent is really to be defined not as a precipitant or as a hydrocarbon, but essentially as a cost-reducing liquid, while a solvent is primarily the opposite of a diluent—a material which is used for its quality-contribution to the formula, in spite of its cost. Since the alcohols are definitely not in the diluent category as thus defined, their position is best understood and evaluated by considering them as latent solvents, *i.e.*, materials which, while not capable of dissolving nitrocellulose by themselves, contribute enough to solvency to justify their use at their solvent-like prices.

It is of some interest to note that butanol in normal pre-war years was sold at the same price per pound as butyl acetate; but since it has a lower specific gravity, and therefore weighs about 0.6 pound per gallon less than butyl acetate, its cost per gallon has always been moderately lower—about 8¢ per gallon less when butyl acetate is $1.00 per gallon, for example. It is of some importance to realize in this connection that although the lacquer manufacturer purchases his solvents on a pound basis, he sells them in the form of lacquers and thinners by the gallon, and he is therefore really interested only in the cost per gallon, and the cost per pound is only a matter of accounting.

The cost of ethyl alcohol has normally been very close to that of toluene, and therefore it could not be considered an expensive ingredient. However, ethyl alcohol is bad as regards the blushing of lacquers, and cannot be used in very large proportions as a diluent for this reason. It is thus used in lacquers for its contributions to solvency and viscosity, and in spite of its handicap of blush-producing tendencies.

Evaporation

Let us go back to Diagram B at the beginning of this chapter, which divides the "solvent" and "latent solvent" portions of the volatiles into two groups—the slowly evaporating and rapidly evaporating materials, often called the high-boiling and low-boiling solvents. This division is of considerable importance in lacquers for reasons of speed of drying, smoothness of finish, cost of the rubbing operations, danger of blushing, etc. In general, the proper speed of evaporation of the volatiles is much more important in lacquers than in varnishes and synthetics. With the latter, the speed of drying and hardening is dependent on the rate of evaporation of the volatiles only to a moderate degree, since the length of time required to oxidize the liquid oils in their films into solid substances is very much greater than that necessary to evaporate the volatiles. Varnish-type products can therefore employ grades of naphtha boiling as much as 30 or 40°C apart without any pronounced effects on the hardening speed of their films. In lacquers, on the other hand, the film-forming materials are essentially of a solid and non-reactive nature, and the speed of hardening of their films, as well as the length of time which these films remain sufficiently liquid and fluid to flow, is therefore almost entirely a question of the speed of evaporation of the volatiles used. The relative rate of evaporation of the various solvents and diluents available to the lacquer industry is, therefore, a prime consideration in their choice and utility (see Table 39).

Rapid drying and hardening is one of the principal advantages of lacquer over other finishes, and is an important reason for its use. This condition puts an upper limit on the boiling point of liquids suitable for use in lacquer volatiles, and butyl acetate is the highest-boiling solvent used by the industry in any appreciable quantities. The very slowly evaporating butyl lactate and butyl "Cellosolve" are used in a few specialties, such as silk-screen lacquers, lacquer inks, etc., and some use small percentages of amyl acetates here and there. Under the normal, prewar supply and price conditions, however, there was probably not a single commercial spray lacquer in which a substantial part of the solvent portion was composed of solvents or latent solvents boiling higher than butyl acetate.

Table 39. Relative Rates of Evaporation of Some of the Common Liquids Used in Nitrocellulose Lacquers.
(*The evaporation rate of butyl acetate is taken as a standard, with the value of 100*)

Name of Liquid	Relative Evaporation Rate
(1) *Low-boilers:*	
Ethyl acetate	525
Isopropyl acetate	435
Methyl-ethyl-ketone	465
(2) *Intermediate:*	
Ethyl alcohol	205
Isopropyl alcohol	205
Toluene	195
Secondary butyl acetate	180
(3) *High-boilers:*	
Methyl-isobutyl-ketone	145
Butyl acetate	100
1-Nitropropane	100
Butanol	45
Xylene	68
(4) *Super-high-boilers:*	
Butyl lactate	6
Butyl "Cellosolve"	10

Orange Peel

On the other hand, the presence in a spray lacquer of large proportions of extra-fast-evaporating solvents, such as ethyl acetate and methyl-ethyl-ketone, leads to blushing in humid weather, and to the various manifestations of poor "flow," such as orange peel, dry-spray, over-spray, etc. These defects in the smoothness of the films are very objectionable, partly because they spoil the decorative quality of the finish, and partly because their correction by sanding and rubbing is very expensive; the cost of the latter is often as great as that of the original lacquer itself.

The degree of this orange-peel type of defect depends greatly on the speed of evaporation of the volatiles, for the following reasons: the spray application deposits the lacquer on the surface in the form of small globules and clusters of such globules, and the sprayed material must be kept fluid for a sufficient time to allow these globules to flow together into a continuous, smooth film; lacquers containing large proportions of the rapidly evaporating solvents of the ethyl acetate class dry up too rapidly to allow this flowing-together process to complete itself. Furthermore, even in the case of a lacquer finish originally applied as a continuous film by flowing or knife-edge methods, rapid evaporation of the volatiles causes the formation of a rough, broken-up surface as a result of vortex-action currents in the wet film,* and it is more than probable

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* See: Bartell and Van Loo, *Ind. Eng. Chem.*, 925, 1051 (1925).

that this phenomenon also opposes the flowing-together of the globules in the sprayed films as well.

Excessively rapid evaporation of the volatiles is thus quite objectionable. If strictly technical considerations alone were to decide the composition of the volatiles, the ideal lacquer would probably be formulated with very small proportions, if any, of low-boiling materials, and the "solvent" and "latent solvent" portions in it would be composed almost entirely of materials of the class of butyl acetate and butanol. However, cost considerations cannot be disregarded too easily in commercial products, and the fact that the low boilers are usually appreciably cheaper than butyl acetate and butanol has been in their favor. Commercial lacquers, therefore, represent a compromise, and usually contain a mixture of both the slowly evaporating, flow-producing materials of the butyl acetate class, and the fast-evaporating, cost-reducing materials, such as ethyl and isopropyl acetates.

The proportions in which these two classes of materials are employed naturally depends on many factors. The principal two of these are (1) the prevailing differential between the prices of the two classes of solvents, and (2) the importance and need for "flow" in any particular lacquer in question. The degree of this "need" will differ widely in different lacquer-type products. Thus, the dopes used in making artificial leather do not ordinarily contain any butyl acetate at all, but employ the low-boiling ethyl acetate and ethyl alcohol as the only solvents. These dopes are applied by knife-edge devices, rather than being atomized by spray guns, and their volatiles therefore evaporate much more slowly. Furthermore, the smoothness of the finish is not as important with them as in the case of lacquers applied on metal or wood, since their final films are eventually embossed. In a similar way, lacquers applied by dipping or gasket devices do not require quite as slowly evaporating volatiles as spray lacquers, and can therefore use higher proportions of the rapidly evaporating solvents. In spray lacquers, too, the division of the solvent and latent solvent portions of the volatiles between the slowly and rapidly evaporating materials will depend on a number of factors. One is the standard of smoothness expected in the finish; there is naturally a difference in this respect between the finish on a piano and that on cheap toys, for example. The gloss of the finish is a similar factor of importance; a moderate degree of orange peel may be almost invisible on a flat finish, but it will stand out strongly on a glossy one. The atmospheric temperature at the time the lacquer is applied is similarly of considerable influence, since the evaporation rate of volatiles increases about 50 per cent by a rise in temperature of only 18°F, such as one between 73 and 91°F; a "volatiles" composition which is only just good enough under winter conditions of application may thus be well expected to give films of considerable orange peel under summer conditions.

The size and complexity of the article to be sprayed, the skill and cooperative spirit of the spray men and other such conditions also influence greatly the degree of orange peel which will be produced in spraying a lacquer, and thereby determine the need for slow evaporation in the volatiles and their division between the slowly and rapidly evaporating materials. Some of these factors are summarized in Table 40.

Table 40. Principal Factors Influencing the Smoothness of Sprayed Lacquer Films.

1. The speed of evaporation of the volatiles in the lacquer.
2. The solvency conditions of the lacquer, *i.e.*, the relative proportions of solvents and diluents present in the lacquer film throughout the drying period.
3. The viscosity of the lacquer at the spray gun.
4. The effectiveness of the atomization.
5. The temperature of the lacquer, of the spraying air, and of the atmosphere in which the lacquer film is dried; these influence the speed of evaporation of the volatiles in the spray cone and from the drying film, and they thereby affect the length of the "flowing" period.
6. The strength of the air currents in the spray hood and the length of time which the coated article remains in the forced draft there; these factors also act by influencing the speed of evaporation of the volatiles from the drying film.
7. The number of coats applied: two- and three-coat applications tend to give rougher films than single coat jobs.
8. The gloss of the finish: orange peel and similar defects show up more in a glossy finish than in a flat one.
9. Variations in the conditions and technique of spraying, as follows:
   a) Excessive distance between the spray nozzle and the surface increases the loss of volatiles in the spray cone, and is a strong factor toward decreased smoothness.
   b) The use of excessive proportions of atomizing air similarly tends to increase the evaporation of the volatiles in the spray operation, while the opposite use of insufficient spraying air produces bad results through poor atomization.
   c) Within practical limits, the greater the thickness of the liquid coat, the longer the drying time and the better the smoothness of the film. Excessive thickness, however, may lead to sagging.
   d) The use of the widest spray fan is naturally advisable to save time and to reduce the number of laps. The extra volume of atomizing air which is used to bring this about, however, increases the loss of the volatiles during the spray operation, and thus reduces the flowing period.
   e) Rapid speed of spraying is naturally desirable, but when carried to excess it tends to produce thin films, unless the supply of lacquer is increased correspondingly, and it naturally makes the control of the spraying more difficult.
10. The shape and size of the article being coated and proper illumination during the spray operation; these are very important insofar as they influence greatly some of the factors in 9 above.
11. The nature of the surface being coated—wood, under-coat, or polished metal; the nature of the resin used in the lacquer, the alkyds for example being worse than ester gum in respect to the smoothness of the finish.
12. The general skill and cooperative attitude of the spray man. These naturally control the factors in 9, and other similar factors, to a considerable extent.

In principle, an excess of slowly evaporating solvents can be just as harmful as an excess of low boilers, as it may cause the very objectionable and unsightly sagging of the finish when applied on vertical surfaces, as a result of the film being kept liquid and fluid too long. Such is often the case with varnishes and synthetics when applied in thick coats. In lacquers, however, sagging has always been of very rare occurrence, partly because even butyl acetate and butanol evaporate substantially faster than the volatiles used in the other finishes above, and partly because the large differential in price which existed between the butyl and ethyl solvents in the early years of the lacquer industry has created a tradition whereby the ordinary lacquer formulas usually err in containing insufficient proportions of the butyls rather than the reverse. Most of them, therefore, usually need some correction in the direction of improved flow, rather than being conducive to sagging.

Diluents

As will be noticed in Diagram B, the distinction between the slowly and rapidly evaporating ingredients of the volatiles is applied only to the solvents and latent solvents, but not to the diluents. In the latter group toluene, and some grades of aliphatic naphtha duplicating the evaporation rate of toluene, are practically the only materials used in any quantity, and both the faster and slower evaporating hydrocarbons are used only very sparsely. The reasons for this are as follows: the cost advantage, which is principally responsible for the use of the low-boiling materials in the solvent classes, is absent in the case of the diluents, since the rapidly evaporating hydrocarbons sell for about the same prices as those with higher boiling points. Benzene is also quite toxic and is objectionable for this reason as well. At the same time, the use of xylene in place of toluene is ordinarily inadvisable. It does not seem to improve the flow of lacquers appreciably, in spite of its slow evaporation, probably because its beneficial effect in retarding the evaporation of the volatile mixture is counteracted by its effect in keeping the solvency in the drying film at a lower level. An illustration of some similar relations is given in Figure 88, which shows the solvency conditions in a pair of toluene lacquers during the drying of their films. It will be seen there that in the case of the formula containing the high proportions of ethyl acetate (Curve A), the rapid escape of this fast-evaporating ester in the early stages of the drying of the film, and the resulting increase in the relative proportion of toluene, cause a substantial drop in the solvency during the first 60 per cent of the drying period. The replacement of toluene by the slower evaporating xylene would cause a similar solvency drop even in lacquers containing fairly high proportions of butyl solvents.

Viscosity

An examination of Figure 84 will show that the low-boiling solvents, such as ethyl acetate, form nitrocellulose solutions of lower viscosities than those produced by the slower evaporating materials, and the ad-

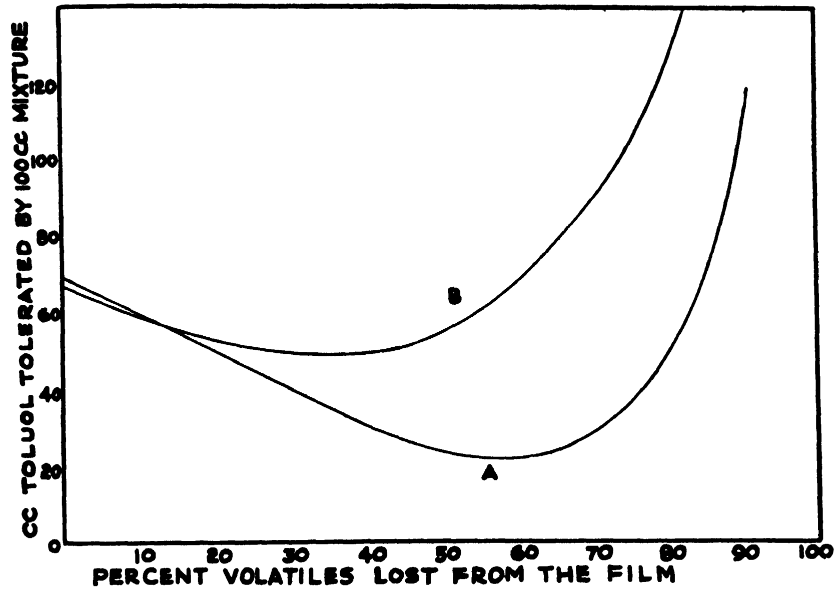

FIGURE 88. Solvency conditions in lacquer films during the drying process. Obtained by determining the toluene dilution ratio of two solvent mixtures at various stages in the evaporation process. The solvency falls off at first due to the loss of low boiling solvents, and the resulting relative increase in the proportion of toluene. Beyond the 60 per cent point, the process is reversed, since the difference between the evaporation rates of the toluene and butyl acetate produces an increase in the relative proportion of the latter.

Composition of the Mixture Used

	A	B
Ethyl Acetate	25%	—
Butyl Acetate	15%	27.5%
Ethyl Alcohol	—	12.5%
Toluene	60%	60.0%

vantage of superior "flow" produced by increasing the proportion of the high-boiling solvents is therefore partly offset by the disadvantage of the higher viscosities of the solutions. Some people in the lacquer industry are inclined to attach much importance to this disadvantage of the higher-boiling solvents, but actually the viscosity differences involved are comparatively minor. For one, it will be seen in Figure 84 that the differences in viscosity between the solutions in ethyl and butyl acetates are small in comparison with the effects of excessive proportions of diluents. Furthermore, it should be appreciated that the lacquer technologist is not ordinarily concerned with the replacement of large proportions of one of these solvents by the other, since even a poor solvent formula will contain 18 to

20 per cent of butyls (butyl acetate and butanol); on the other hand, one containing 35 to 40 per cent of butyls could be considered a very rich formula—in a different class altogether. The replacement of about 15 to 20 per cent of one of these solvents by the other thus represents a very radical change, and ordinarily the lacquer formulator is only concerned with a 7 to 10 per cent replacement; the effect of such minor variations in solvent composition on viscosity is very slight indeed.

It should further be realized that the difference in viscosity between the high and low boilers shows up mainly in the presence of excessive proportions of diluents, and is comparatively small in more reasonable formulas, containing the proper proportions of the latter. Some pertinent data are shown in Figure 89, which plots the increase in viscosity pro-

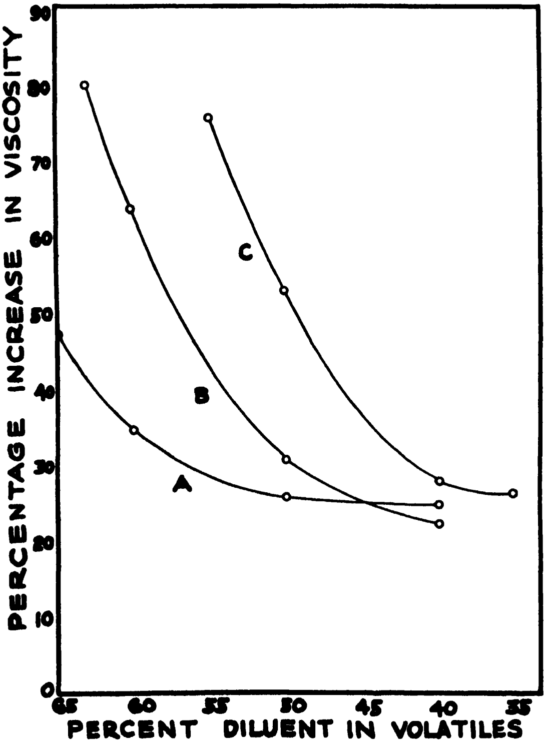

FIGURE 89. Percentage increase in viscosity produced by replacing 15 per cent of ethyl acetate-ethyl alcohol (50–50) by 15 per cent butyl acetate-butanol, and the relation of this increase to the per cent of diluents in the lacquer—for three series of lacquers differing in the nature of the resin and diluents.

A = ester gum lacquer; diluents: 50–50 toluene-naphtha
B = alkyd resin lacquer; diluents: toluene
C = alkyd resin lacquer; diluents: 50–50 toluene-naphtha

duced by replacing 15 per cent of ethyls by 15 per cent of butyls, as related to the diluent content of lacquers. It will be seen that although this replacement of low-boiling solvents by high boilers increases the viscosity only about 25 per cent in the case of mixtures containing moderate proportions of diluents (such as 50 per cent of toluene in an alkyd resin lacquer and 55 to 60 per cent in an ester gum lacquer), this increase in viscosity mounts to as high as 70 to 80 per cent if the lacquers contain excessive proportions of diluents. This relation gives an additional reason for keeping the proportion of diluents in lacquers within reasonable limits, as their presence in excessive proportions not only increases the viscosities of the lacquers by itself, but also makes it much more difficult to use the desirable proportions of the high-boiling, flow-producing solvents.

Blushing

A few words about blushing, mentioned very briefly at the beginning of this section on evaporation: Lacquers containing large proportions of rapidly evaporating volatiles tend to deposit whitened films when applied under conditions of high humidity. This phenomenon is caused by the fact that the very rapid evaporation of these volatiles in the spray cone and in the drying film causes them to cool below the dew point of the air around them, thereby precipitating minute quantities of water into the lacquer. During the drying of the film, the evaporation and escape of this deposited water is greatly hampered by the high humidity conditions, while that of the solvents and diluents continues at the normal pace. The proportion of water in the film therefore increases continuously to a point beyond its solubility in the lacquer. This excess of water emulsifies with the lacquer, thus producing a discontinuous film which scatters the rays of light and therefore appears white. Some people are under the impression that the nitrocellulose is actually precipitated in the blushing process. This is not really the case, as can be very readily demonstrated by mixing some water with any typical lacquer; it will be found that even very thorough agitation fails to precipitate the nitrocellulose, and that the mixture of water and lacquer produces only an emulsion. It might be stated, however, that to the practical man there is very little difference whether the blushing phenomenon is one of precipitation or emulsification, as the whitened, flattened (low gloss) appearance, and very low adhesion of the blushed film makes it very objectionable in either case.

THINNERS

The above discussion of the formulation of the volatile portion of lacquers refers to lacquers in condition ready to be sprayed. In actual practice, many lacquers are normally supplied in a very viscous condition and are mixed with about an equal volume of thinner before spraying; the volatiles in the final lacquer thus come from two sources—from the lacquer proper and from the thinner. On strictly technical grounds, there are no good reasons why the volatiles in any pair of lacquer and thinner should not be of the same composition. The competitive situation in the marketing of thinners, however, is much more severe than in the lacquer field, and this tends to reduce their quality somewhat as regards the proportions of the lower-cost diluents and the low-boiling solvents used in them. The lacquer formulator therefore tends to compensate for this by increasing the quality of the volatiles in his lacquers, and as a result of this there is often a substantial difference between the composition of the thinner and that of the volatiles in the lacquer with which it is used.

Typical Solvent Formulas

The following typical formulas for lacquer volatiles, diluted for spray, will serve to illustrate and summarize the principles developed in the discussion above. These formulas are for lacquers employing the simpler resins, such as ester gum or damar.

	High Quality	Medium Quality	Low Quality
Butyl acetate	27	18	12
Butyl alcohol	13	9	6
Ethyl acetate	—	7	10
Ethyl alcohol	5	6	10
Toluene	55	60	62

About one-half of the toluene in the above formulas can be replaced by a mixture consisting of approximately 80 to 85 per cent of aliphatic naphtha, 7.5 to 10 per cent of slowly evaporating, and 7.5 to 10 per cent of rapidly evaporating nitrocellulose solvents. Also, in lacquers containing many of the maleic acid grades of resins the percentage of diluents should be about 5 per cent less than that given in the formulas above, while in lacquers containing the true alkyd resins the proportion of diluents should be about 10 per cent less than the above.

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Chapter 16

The Application of Metallic Soaps as Driers, Fungicides, Suspending Agents and Flatting Agents

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In any consideration of the function of driers in oil films, questions invariably arise as to the phases of the subject which should be treated extensively. In this review the mechanisms operating to cause film drying are touched on briefly, the observable effects of driers on these mechanisms are discussed, and the chemical composition of driers is considered. The last-mentioned topic is included because of the profound effect which drier composition may have on the activity of the drier metal. Thus, though some phases of this review may seem redundant, it is thought impossible to omit discussion of these contributory effects without impairing the broad understanding of the function of driers.

In this chapter, driers in general are considered in the narrow sense of being the soaps of certain heavy metals whose activity is such as to make them useful in promoting the more rapid solidification of drying oils. By soaps is meant the salts formed by replacing the acid hydrogen of certain organic acids, usually moderately complex and monobasic, with heavy metals. Though the complex reaction products obtained when, for example, litharge and linseed oil are fused, promote the drying of oils, the devious directions which the reactions may take make reproducibility of results and general analysis of performance impossible.

Though the amount of driers used varies widely, depending on the composition of the vehicle, they are virtually always incorporated in air-drying finishes as well as in many baking finishes so long as molecules are present which, because of their structure, are susceptible to oxidation and polymerization.

I. THEORIES ON THE MECHANISM OF THE ACTION OF DRIERS

A. Driers as Modifiers of the "Drying" Process

The addition of driers to paints and varnishes tends to introduce complications. Drying oils, being natural products, are variable in composition, the resins often introduced are of extremely variable nature, the driers used are made of various raw materials, using different manufacturing methods, and the films, deposited in different ways, are dried in varying environments. Under these circumstances, it is almost impossible to do more than establish approximations of the directing effect of driers.

As noted, some of the mechanisms operating in drying oil films containing no driers have been established; and, since driers appear to modify rather than completely change these mechanisms, the same general outline is suitable for consideration of oils containing driers.

(1) *Oxidation.* The degree to which the oxidation of drying oils is modified by the presence of driers is substantial, and the modifications fall into the following phases:

(*a*) *Shortening of the Induction Period* (*I.P.*). The I.P. is the time before the drying oil combines with a measurable quantity of oxygen. The *pure* glycerides of unsaturated fatty acids are presumed to have zero induction periods as compared to the impure glycerides in natural drying oils in which the I.P. is attributed to natural antioxidants not removed during refining.[1]

Drying oils have shorter induction periods when they contain drier than when they do not. To account for this it has been proposed that driers may be considered as materials which chemically precipitate the natural antioxidants from true solution and/or as positive oxidation catalysts which counteract the natural antioxidants present.

(*b*) *Acceleration of Oxygen Combination.* When driers are absent, the film, at the end of the I.P., combines with oxygen at a rate characteristic of the oil. When driers are present, the rate of combination is accelerated. This has been explained in the following ways:

(i) Driers act as true oxidation catalysts, promoting the reaction but not entering into the reaction.

(ii) Driers enter into the oxidation reaction, acting as oxygen carriers because of their susceptibility to oxidation-reduction reactions. The effective drier metals are postulated[2] to be those of multiple valence. Further it is proposed that the lower valence state must be more stable than the higher valence state. High metal concentrations cause oil films to reach a maximum weight increase in a shorter time and begin losing weight in a shorter time than lower concentrations.[3] No evidence has been found to support the contention that driers concentrate in the surface of the drying film and thus serve as special oxygen carriers. Activation of films deposited on other dried films containing driers appears to occur[4] because of the high peroxide concentration in dried films during certain periods of their life.

(iii) Driers may combine with the double bonds of the drying oils to form new compounds more susceptible to aerial oxidation. Experimental evidence[5] indicates that this mechanism is unnecessary and probably does not occur.

(2) Polymerization. Since polymerized films are more desirable for many purposes than oxidized ones, it is desirable to promote polymerization as much as possible. Some of the observed occurrences where polymerization has been modified by driers follow:

(*a*) *Solidification of Film at Earlier Stage in Oxidation Process.* When driers are present, oil films solidify when less oxygen has combined than when driers are absent. Such a phenomenon may be caused because polymerization as well as oxidation is promoted by driers, so that the film reaches a given degree of thickening at a lesser degree of oxidation than when driers are absent.

(*b*) *Decrease in the Maximum Oxygen Combined.* Less oxygen finally combines with the oil when driers are present than when absent, and this has been thought to occur because polymerization of unsaturated systems is accelerated in the presence of driers so that fewer double bonds are available for oxidation.

(*c*) *Promotion of a Higher Degree of Polymerization.* It appears obvious from physical and chemical data that polymerization involving carbon-to-carbon bridging at the double bonds is promoted by driers. To explain this, polymerization has been postulated to be catalyzed by the formation of an addition compound with the drier at the double bond As evidence to support such a proposal, it is known that lead soaps, which are known to form various complexes with drying oils, are very active polymerization catalysts in spite of the fact that lead does not change valence readily. Other work,[6] in many instances, has shown that the function of positive polymerization catalysts involves the formation of a complex with the catalyst.

(3) Association. Metallic soaps (driers) are strongly polar compounds which show pronounced tendencies toward formation of complexes as well as exhibiting a dispersing action toward many colloidal aggregates. The chemical composition of the metallic soap used largely determines its dispersing activity. So, depending on the soaps used, various effects may be noted:

(*a*) *Solidification of Film at Earlier Stage in Oxidation Process.* Driers may be considered, because of their high polarity, as capable of actively orienting oil molecules into micelles so that gelation or solidification may occur more readily. Such orientation of oil molecules, normal to the surface during the final stages of drying have been shown to occur in the absence of driers,[7] so promotion of such action is feasible. The magnitude of this action, as compared to polymerization as a factor leading to solidification of the film at an earlier stage in the oxidation process, is unknown.

From these comments on the mechanism of the action of driers, it is apparent that the effect of driers in promoting more rapid drying of oils is marked. It is also apparent that a great deal more is known about the changes occurring in the films than is known about the reasons for the changes. This general situation obtains in many fields but is especially obvious in the case of driers.

Since "driers" by now includes a very broad range of metallic soaps, it seems apparent that one cannot safely continue to refer loosely to "driers," but must be more explicit when commenting on specific phenomena. The next section will consider in detail the factors involved in the efficiency of driers.

II. EFFICIENCY OF DRIERS

A. General Requirements

If driers are to be effective as promoters of oxidation, polymerization and possibly association of drying oils, the drier metal must be "available." What is known of this "availability" is discussed below.

(1) Potential Activity of the Metal. The general requirements for a metal to be efficient as a drier have been reviewed above. The metals which have shown the necessary activity, either when used alone or as one component of a combination, are listed below. Though drying metals of marginal activity have arisen from time to time, these are the only ones enjoying widespread application: *cobalt, lead, manganese, calcium, zinc,* and *iron.*

(2) Solubility of the Drier. For a metal of potential activity to be useful, it must be combined with other materials which, among other things, must render it soluble in the drying oils, resins, or materials to be dried.

Not only should the drier possess good initial solubility but, because it has a structure stable to oxidation and exhibiting few residual valence forces, it should maintain this solubility over long periods in vehicles of poor solvency.

Because the use of driers in paints and varnishes has matured over a span of some years, the soaps of a number of organic acids have been utilized for drying purposes. At the turn of the century a limited number of acids were available, so that the soaps of linseed and similar vegetable oils and rosin became widely used. It was not till about 1930 that naphthenic acid was used in this country, and it was still later that tall oil and octoic or 2-ethyl hexoic acid were introduced.

Since driers are used in such small proportions in paints and varnishes, the plasticizing effect of the low percentage of the saturated, chemically stable type of acid exemplified by naphthenic acid necessary to carry the metal is negligible. The chemically stable structure of the naphthenate molecule, however, makes possible a solubility over long periods in the concentrate or in the paint or varnish which is quite impossible to attain with linseed, rosin, or tall oil–based driers. This is true because these soaps oxidize to materials as insoluble in ordinary vehicles as a dried paint film would be.

Thus, for initial and continued solubility, naphthenic acid or an acid such as octoic possesses inherent advantages because of its stable, saturated structure. The naphthenic acid radical, further, because of its cyclic structure, has inherently fine solubility characteristics as compared to aliphatic acids such as octoic, stearic, lauric, etc. Thus, the widespread adoption of naphthenate soaps has been reasonable and desirable. A general correlation of structure and solubility of a more theoretical nature may be expressed as follows:[8]

(a) The siccative metal salts of polycarboxylic acids, in which both carboxyls are attached to the metal radical, are as a rule insoluble in petroleum naphtha and can be dissolved in drying oils only at high temperatures, whereby a double decomposition probably takes place resulting in the formation of the metal linoleates which in turn dissolve in the oil.

(b) In the salts of monocarboxylic acids the maximum oil and hydrocarbon solubility, together with maximum metal content, stability toward auto-oxidation, and moisture and pale color are shown by the aliphatic ether acids.

(c) The siccative metal salts of the aryl oxyacetic acids are much less soluble in oils than those of the alkylated aryl oxyacetic acids and the latter, in turn, are less soluble than those of the alkylated hydroaromatic oxyacetic acids.

(d) In the strictly aromatic carboxylic acid salts, the best properties as siccatives are shown by the salts of alkylated benzoyl-*o*-benzoic acids.

(e) The introduction of an ether group in a straight-chain fatty acid tends to give salts of lower viscosity in hydrocarbons or fatty oils.

(f) A branched chain in the molecule of an aromatic aliphatic or hydroaromatic acid gives siccative salts of lower viscosity than does a corresponding straight chain.

(g) Going from an aromatic acid to the corresponding hydroaromatic acid increases the oil and hydrocarbon solubility of its siccative metal salts.

(h) The presence of a free phenolic group in a siccative does not necessarily lessen its drying activity.

(i) The fatty aryl group in siccative salts of a monobasic acid is a greater oil-solubilizer than is a nonalkylated aryl group having the same number of carbon atoms.

(3) *Availability of the Drier Metal.* The compound containing the drier metal must be soluble in the unsaturated compounds it is desired to dry, and the drier metal must be available for promoting polymerization, oxidation, and association. Since electrovalent, covalent, or coordinate covalent bonds could conceivably serve to combine the metal, there have been numerous theories advanced as to the requirements for "availability."

Research in the author's laboratory and elsewhere[9] has demonstrated that some coordinated compounds possess neglible power as promoters of drying, in spite of excellent solubility. Indeed, since numerous compounds can coordinate with the ordinary metallic soaps used as driers, it is possible that loss of drying power may be associated with the formation of coordination compounds. However, in some cases, the *degree* of coordination has been shown to have a great effect on the effectiveness of the metal as a drier, so that coordination is not necessarily accompanied by inactivation.

B. Efficiency of Commercial Driers

Because commercial driers vary somewhat in composition, it is not possible to comment exhaustively on the factors leading to superior performance. However, the following characteristics are of outstanding importance. The success with which all these various factors are met in a commercial drier will determine the efficiency and general performance of the drier.

(1) *Purity.* The purity of all driers should be kept as high as possible.

(*a*) *Metallic.* Foreign metals are best kept to a minimum, for the soaps of many metals such as Na and Mg possess such poor solubility as to lead to sludging.

(*b*) *Organic.* To secure most efficient action, the acids used to carry the metal should be highly purified. Some of the impurities encountered, and their effect, follow:

(i) Naphthenates high in alkyl phenols, a naturally occurring impurity, have been shown to be much poorer driers than those made from purified acids.

(ii) Driers high in deeply colored, naturally occurring tars have been shown to cause undesirable film staining. This type of staining can lead to serious difficulty if much drier is used.

(iii) Linoleates made from off-grade linseed oil or acids containing large quantities of the phosphatides believed to cause the induction period of drying oils, produce soaps having poor efficiency.

(2) Composition. The literature abounds in work involving driers in which only the type name such as resinate, linoleate, or naphthenate, is mentioned. This means little, since different compounds, usually exhibiting drastically different solubility characteristics, are known. These compounds, mixtures of which usually comprise ordinary driers, appear to have the following composition:

(*a*) *Basic Soaps*. The formula for these soaps may be expressed as $M(OH)\overline{\overline{FA}}$, where M is a divalent metal and $\overline{\overline{FA}}$ is a monobasic acid radical.

Lead and zinc are the only two common drier metals which can form stable, soluble basic soaps, and the soaps of even these metals exhibit better solubility when a mixture of basic and neutral soaps is prepared. Perhaps compounds of the type $M_2OH\ \overline{\overline{FA}}_3$ then form.

(*b*) *Neutral Soaps*. The formula for these soaps may be expressed as $M\overline{\overline{FA}}_2$. Cobalt, manganese, iron, and calcium form neutral soaps of moderately good solubility when the proper acids are used.

(*c*) *Acid Soaps*. The formula for these soaps designated as acid soaps for want of a better name, may be expressed as $M\overline{\overline{FA}}_2 \cdot x\ H\overline{\overline{FA}}$, where $H\overline{\overline{FA}}$ is an acid, monobasic in this instance. Virtually all metallic soaps appear to form such compounds,[10] and whether acid soaps, dipole-dipole complexes or covalent compounds are formed is not certain, though it may well be the latter. Depending on the structure of the acid, complexes having varying degrees of stability are formed, as indicated by the heat evolution. Thus, ordinary naphthenic acid mixed with various commercial naphthenates in a 1–1 mol ratio evolves 2000 to 3000 calories per mol. It is possible, in view of the acidity of many vehicles and the affinity of neutral soaps for free acid, that acid soaps are active agents in many cases. Their improved solubility and stability and, in some cases, activity, as compared to some neutral types probably accounts for many of the variable results in the literature where vehicles of different acid values were used.[11]

(3) Stabilization. Even as acids form highly stable, highly soluble complexes with metallic soaps, so do other polar compounds. It is this reaction which lends credence to a proposal of covalent compound formation with acids rather than acid soap formation.

The use by the drier industry of trace amounts of compounds capable of forming addition complexes in solutions of driers has continued for years; alcohols, acids, amines, and compounds of similar high polarity are used, the exact type varying with the manufacturer.

The ideal stabilizer produces a drier solution having these qualities:

(*a*) *Excellent Solubility.* Ordinary drier, that is metallic soap, molecules exhibit strong tendencies to clump together or associate into relatively large colloidal units or micelles not visible to the eye, and these large aggregates, of course, disperse in vehicles very poorly, compared with single molecules or very small aggregates. Different metals show varying tendencies toward such association, the series of common metals, in diminishing order, being aluminum, calcium, manganese, cobalt, zinc, and lead.

By suitable stabilization, the formation of large micelles is prevented because the residual valence forces causing association are neutralized. Thus, not only do the smaller aggregates exhibit much more rapid initial dispersion, but they are frequently soluble in vehicles which will not tolerate large micelles. Further, since their residual valence forces are of insignificant magnitude, the tendency to associate after dispersion in the vehicle is not present, so that clarity and drying efficiency are kept at a maximum.

Some research has been directed toward the improvement of solubility and viscosity by the use of smaller soap molecules prepared, for example, from high acid value naphthenic acid. This work is fundamentally less interesting and rewarding than that directed toward neutralization of residual valence forces, since the tendency toward association, with all of its attendant solubility troubles, persists. Thus, though the micelles from high acid value acids may be slightly smaller, and the fluidity of a solution containing a fixed metal concentration lower because of the lower solids content, the inherent solubility is not comparable with that of stabilized material. This difference in solubility, of course, will be apparent to a degree dependent on the association proclivities of the metal, being most marked with aluminum and least with lead. Further, the difference in solubility becomes more apparent as the drier is introduced into vehicles of diminishing solvency; it is most marked with the unthinned oils and least marked when considerable solvent is present.

(*b*) *High Efficiency.* A satisfactory stabilizer exhibits no antioxidation action so that no interference with normal drying action occurs. However, because the soap molecules exist in single or small units rather than large micelles, an increase in effectiveness over a non-peptized soap occurs.

(*c*) *Low Viscosity at Room Temperature.* A satisfactory stabilizer is characterized by the small amount required, of the order of 1 per cent of stabilizer in a soap solution containing 50 to 60 per cent solids, to eliminate almost completely the colloidal association which gives ordinary metallic soap solutions their high viscosity.

(*d*) *Low Viscosity at Low Temperatures.* Further, association of soap molecules at low temperature is almost entirely inhibited by the ideal stabilizer, so that a soap solution having a flat viscosity curve is obtained rather than the customary steeply rising one.

C. Drying Efficiency of Various Metals

The drying efficiency of various metals depends on a number of factors other than the ones discussed above. Some of the more important are those mentioned below.

(*1*) ***Effect of Environment.*** (*a*) *Temperature.* A rise in the temperature of drying oil films containing driers accelerates the drying rate. This effect is brought about by the increased reaction velocity.

(*i*) *Increased Reaction Velocity.* Since drying results from reactions which are predominantly chemical, an increase of temperature greatly increases the reaction velocity whether or not driers are present. Though the reaction velocity does not necessarily double for each 10°C rise, the increase is not too far from this in many cases. Introduction of driers such as cobalt, manganese, and lead does not change the temperature-rate coefficient drastically. However, iron soaps are unique in greatly accelerating the reaction velocity as the temperature rises.

(*b*) *Humidity.* Very high humidity in most instances seems to cause a decrease in the drying rate of films either with or without drier, no unusual retardation being found in the case of films containing driers. It appears that a high absolute humidity is more significant than a high relative humidity.

(*c*) *Light.* Light, both in the visible and ultraviolet portions of the spectrum, exhibits a pronounced accelerating effect on the drying of oil films. However, there seems to be no evidence that this effect is of a different order of magnitude in the presence of driers as compared to drier-free films.

(*d*) *Film Thickness.* Since diffusion of oxygen into and through the film is an important factor in the drying of oil films, the film thickness can be very important. When such a metal as cobalt is used alone in substantial percentage, a completely solidified, very thin surface layer, apparently poorly permeable to oxygen, rapidly forms. Thus, if the oil film is thick, this skin can greatly prolong complete film solidification.

However, if a properly balanced drier is used, no surface skin forms, diffusion of oxygen is not retarded and films can be somewhat thicker.

Thus, tolerable film thickness can be said to be a function of the drier or driers used as well as composition of the vehicle.

(2) *Formation of Addition Compounds.* It has long been the practice to use a combination of two or more metallic soaps for promoting the drying of oils and resins. In most instances, a moderately active drier such as lead is mixed with a potent drier such as cobalt to form a well balanced combination capable of promoting rapid, uniform film solidification. In even more startling instances the soaps of metals such as zinc and calcium, which seem to be inactive when used alone, have been used with cobalt or manganese soaps to produce a highly effective combination.

Various mechanisms have been proposed to account for the effectiveness of combinations, but at this time it appears reasonable to hypothesize the formation of addition compounds, possibly through covalent linkage. Some of the phenomena supporting such a proposal follow:

(*a*) *Calcium-lead soap mixtures,* as compared with a pure lead soap, exhibit greatly decreased reactivity and thus decreased hazing when used with vehicles containing saturated fatty acids or alkyl hydrogen phthalates. Further, the stabilizing effect of calcium is only moderate until a molar ratio of calcium to lead of 1:2 is reached, at which point a very great increase in stabilizing effect occurs.

Cobalt-lead or manganese-lead soap mixtures, though not as stable as calcium-lead mixtures, nevertheless show greatly improved stability as compared with the lead soap used alone.

(*b*) *Cobalt-zinc or cobalt-calcium soap mixtures* promote the drying of oils almost as markedly as cobalt-lead soap mixtures.

(3) *Effect of Drier Concentration.* Any drier added to oils, as well as differing in formulation along the lines discussed, may exhibit somewhat different ratios of higher valence to lower valence metal, depending on such factors as the dehydration temperature of the drier during manufacture. This initial degree of oxidation has been shown to be of little importance, since the maximum amount of oxygen which can be combined with the minute amount of drier used is a negligible portion of the total required.

A gradual color change of drying-oil films containing drier metals having colored cations from that typical of the lower valence ion to that of the original lower valence ions is often proposed. Rather, a dynamic oxidation-reduction system is conceived to exist, the average life of a higher valence metal ion increasing as the percentage of oxidizable molecules decreases, the ratio of higher valence metal ions to lower valence metal ions increasing.

(*a*) *Concentration–Drying Time Curves.* A large number of data have been accumulated to demonstrate the change in drying time of various drying oils with various driers. Considerable litigation has arisen over the exact shape of the drying curve, investigators in many cases interpreting their data far more universally than conditions would seem to warrant.

In general, concentration–drying time curves are close to parabolic,[12,8] though very low and very high metal concentrations usually produce deviations. There have been reported many cases where the drying time reached a minimum and then, as the concentration of drier was increased still further, the time increased. It is believed this phenomenon may be attributed, at least in part, to interference with the normal polymeric association of the oil molecules because of the dispersing effect of high concentrations of metallic soaps.

The concentration–drying time curves of single metals or combination metals do not have the same slope, so that it does not follow that the most efficient drier or driers to secure a given drying time may be the best choice in order to secure a drying time greater or less than the original.

(*b*) *Polymerization-Oxidation Reactions.* The course of the drying reaction, until drying has occurred—the solid film representing an aggregate effect of oxidation, polymerization, and association—seems to change little as the amount of drier varies, the time necessary to reach a given physical state being the major variable. However, there seems to be a continuation of the polymerization reaction after solidification has occurred, excessive quantities of driers promoting this unduly.[8]

(*c*) *Metals Used.* Though the anion with which the metal is combined, the temperature of drying, and a multitude of other factors confuse attempts at concise conclusions concerning the performance of various metals, certain features of the action of various metals are so dominant as to make possible the formation of well known generalities. The important metals are discussed below.

(*i*) *Lead.* The salient features of lead driers may be listed as follows: "Drying" is more by polymerization than oxidation and is promoted through the depth of the film, though it is very slow. The low activity generally requires the use of substantial quantities of lead. Lead soaps, in combination with such powerful driers as cobalt, minimize film wrinkling. These soaps, because of their physical nature, contribute toughness, flexibility, and weathering resistance to films in which they are incorporated. These soaps cause very little yellowing of the films in which they are incorporated.

(*ii*) *Cobalt.* Cobalt is one of the most essential of drier metals because of its potency, and flexibility of application. "Drying" is largely by oxidation, a marked tendency being exhibited toward oxidation of only the outer layer of the oil film. Such surface oxidation results in wrinkling. Because of its potency, from a few thousandths to a few tenths of a per cent of cobalt is used.

(*iii*) *Manganese.* Manganese is intermediate in activity between cobalt and lead. It is an active oxidation promoter, though not nearly so active as cobalt, and it promotes polymerization as well. Thus, drying is rapid, but it tends to be through the depth of the film. Because of the activity of manganese only a few tenths of a per cent are used. Films whose drying was accelerated through the use of manganese tend to be hard and brittle. The pronounced staining effect of the manganic ion in the final, dried film usually limits the use of manganese.

(*iv*) *Iron.* Though the ferrous ion is light in color, the ferric is very dark, so iron soaps are applicable only in very dark finishes. Iron promotes oxidation and polymerization only feebly at room temperature, though it actively accelerates polymerization at elevated temperatures to form tough, flexible oil films.

(*v*) *Zinc.* Though zinc does not function as a drier when used alone, it has a number of uses when used in combination with other metals. It is used with cobalt to form an active combination free of tendency toward wrinkling. Zinc, when used with other metals, generally delays the initial setting time of the oil film though the drying time is not much changed and the final film hardness is usually increased. Since it is not highly active, substantial quantities are generally used. Zinc-active metal combinations prove very useful in vehicles which react with lead driers to form insoluble precipitates.

(*vi*) *Calcium.* Calcium does not function as a drier when used alone, but it is being applied ever more widely in combination with other metals. It may be used with such an active drier metal as cobalt to form a well balanced combination devoid of wrinkling troubles. Calcium may be used with typical lead-active metal combinations to form a three-component combination exhibiting substantially lessened tendency to form insoluble precipitates with vehicles which react with lead driers.

III. Effect of Vehicle

Vehicles for film forming have become extremely complex in recent years, so that detailed comments on the effect of the vehicle on the drier problem are not possible. The type and degree of unsaturation of the vehicle affects the response of the vehicle to driers in many ways, which in turn can affect such important film qualities as water resistance. Again, impurities present in some vehicles not present in others can undergo reactions which cause serious hazing difficulties with driers.

A. Structure

(1) Driers vs. Water Resistance. As the polarity of a drying-oil film rises, either because of the formation of oxygenated molecules during drying or because of the addition to the oil of increasing quantities of polar molecules such as metallic soaps, the sorption of water by the films rises and the imbibition pressure rises. High imbibition pressures, of course, lead to a swelling of the film.

It appears impossible to predict accurately the degree of effect of drier additions on water resistance, though in every case the resistance decreases as the drier concentration increases.

In one investigation of oil films containing drier[13] it was found that oils which dried largely by polymerization because of conjugated bonds (tung oil and dehydrated castor oil) showed a decreasing susceptibility to water in the order of Co, Mn, Pb. Linseed oil, drying largely by oxidation, exhibited the inverted order Pb, Mn, Co.

Since many components go into varnish and paint formulations, it is not feasible to predict the change in water resistance when various amounts and kinds of driers are added. Therefore, empirical determinations are necessary. However, it appears clear that the structure of the vehicle molecules determines the degree to which various drier additions will reduce water resistance.

(2) Degree of Unsaturation vs. Drier Response. There appears to be no definite correlation between change in unsaturation, as indicated by a changing iodine value, and change in drying time when driers are present. Increase, as well as decrease, in drying rate with increasing unsaturation has been observed,[14] depending on the drier metal used.

(3) Peroxide Content vs. Drier Response. There appears to be no unanimity of opinion as to the magnitude of the effect of peroxides in the vehicle on the drying efficiency of metallic soaps.[14,15] It is generally agreed that peroxides in the vehicle make possible an increase in efficiency, as indicated by a reduced over-all drying time.

B. Impurities

Because of the diversity of compositions found among the vehicles used by the paint industry, the types and concentrations of impurities are variable. Two illustrative types are discussed below.

(1) Saturated Fatty Acids. Many of the oils used in preparing film-forming compositions contain saturated fatty acids. Some of these acid molecules are free or are freed through radical interchange in processing, though the great majority are combined in esters. Since the lead salts of most of the saturated acids have very poor solubility in ordinary paint

vehicles, reaction of soluble driers with the saturated acids occurs, followed by precipitation of the corresponding soaps.

(2) *Alkyl Hydrogen Phthalates.* In most alkyds small quantities of phthalic acid or alkyl hydrogen phthalates are present because of incomplete esterification and inadequate removal of such materials after esterification had been taken as far as possible.

Because of the variation in concentration and structure of the alkyl radical usually combined with the phthalic acid, the tendency to form insoluble lead salts, as well as the rapidity and degree of such formation when it does occur, is variable in alkyd resins. However, such insoluble precipitates impose severe problems both from the standpoint of maintaining adequate drying power and depositing satisfactory films.

METALLIC SOAPS AS FUNGICIDES

Besides the use of metallic soaps as driers, several other applications have become important enough to warrant discussion. The first of these uses depends on the fungicidal activity of certain metal cations.

The fungicidal potency of the copper, mercury and zinc cations has been known for many years, inorganic salts of varying degrees of solubility having been used for the treatment of cellulosic products for many decades. Objections to such salts usually arose through their property of rapid leaching, however.

With the development of improved metallic soaps for use as driers, more attention was paid to metallic soaps as fungicides, but it was not until the introduction of naphthenates that such application became feasible. This was true because no other soaps were adequately soluble in inexpensive petroleum solvents and at the same time saturated in character so that oxidation of the soap molecule, together with increase in susceptibility to leaching and hardening, did not occur.

High quality copper, zinc, and mercury naphthenates became standard articles of commerce before the recent war, though the amounts used were small. With the war there arose an unprecedented demand for highly effective, inexpensive fungicides having negligible toxicity toward humans, high resistance to leaching, negligible destructive action toward textiles, and ease of application. It was found that copper and zinc naphthenate met these requirements admirably, and many millions of pounds of these materials were used with great success.

At present copper naphthenate is being used as a fungicide more widely than other metallic soaps. As a replacement for creosote in the pressure treatment of heavy timbers and poles, 0.25 per cent of copper (as copper naphthenate) dissolved in a high-boiling solvent is being used. Other treaters are using a mixture containing 50 per cent of creosote and

50 per cent of a high-boiling solvent in which copper naphthenate is dissolved to produce a copper concentration of 0.50 per cent.

Besides the use of naphthenates for technically controlled industrial treatment, there is a large farm and home market developing. For the preservation of rope, cloth, paper products, and wood by non-pressure or non-vacuum treatment, solutions containing 1.0 to 2.0 per cent of copper as copper naphthenate are widely used. For boats, farm buildings, garden stakes, ropes, fish nets and all of the scores of objects used in such places, or in such a fashion that fungus growth is possible, a brushing, dipping, or spraying makes possible highly effective preservation.

If a dark cover coat is used, or if two coats of a white or pastel paint are applied over ordinary copper naphthenate from which the solvent has evaporated, bleed-through will not be important. If, however, a single coat of white is applied over copper naphthenate on a resinous wood having poorly permeable areas, then bleed-through can occur. To eliminate this trouble, some linseed oil and drier can be compounded with the copper naphthenate so as to produce a non-bleeding film.

Zinc naphthenate may successfully be used where dark colored solutions or films are undesirable, though the low toxicity of zinc generally requires the use of solutions containing 2.0 to 4.0 per cent of zinc, or twice as much as copper. This higher solids concentration retards penetration into slightly porous cellulosic materials such as hard wood, and is liable to impart a stiffness to fabrics.

Mercury naphthenate is very useful where light-colored fungicides are required, and it is so potent that solutions containing only 0.1 to 0.2 per cent of mercury may be used in most cases. However, the toxicity of mercury toward humans has caused considerable consumer resistance so that neither mercury nor aryl mercury naphthenate has been widely used.

Mercury compounds have been used in most cases in paints or varnishes to impart fungicidal resistance to these products, since the high fungicidal activity makes them less useful for such purposes because of the plasticizing effect of the rather large quantities of naphthenates needed.

Summarizing, it can be said that the farm, home, and marine market, in which the paint industry is most likely to be interested, is better served by the active metallic naphthenates than by any other fungicide because of a combination of attributes. In the South the need for fungicides is accepted and the sales growth of naphthenate solutions can be anticipated to be most rapid there. In the northern states where fungicidal problems develop more slowly, and thus have not received proper attention, it is anticipated sales growth will be slower but, nevertheless, sure.

METALLIC SOAPS AS SUSPENDING AGENTS

In the formulation of paints and enamels, there is often need to minimize the flow or sag of the material as applied, as well as the heavy sedimentation and dry caking of pigment in the can. For these purposes the aluminum, calcium, zinc and magnesium soaps of such saturated fatty acids as stearic, palmitic and lauric have long been used.

Aluminum soaps are probably more widely used than any of the others because their thickening power is greater. However, to offset the advantage of the great thickening action of certain aluminum soaps are certain disadvantages.

Aluminum soaps, though they are often sold as the mono, di, and triacid soaps, are always basic soaps with more or less organic acid bound to them. The mode of manufacture of the soap can change substantially the crystal structure of the soap, the amount of fatty acid bound to the basic soaps, and to some degree the way it is bound. Since these same factors control the rate of gelation of the soap, and the type of gel formed, it appears impossible to buy aluminum soaps on the basis of some easily determined characteristic such as the aluminum content.

In general the thickening power of aluminum soaps of comparable degrees of basicity and made in the same way increase as the chain length of the fatty acid decreases, though the chain cannot be too short since solubility in hydrocarbons is necessary. Thus, laurates are more soluble than palmitates which, in turn, are more soluble than stearates. However, since many industrial laurates and palmitates are made from broad mixtures of acids such as coconut fatty acids or coconut fatty acid fractions, the chemical name is often not too informative of the type purchased.

In common with many metallic soaps, the viscosity of aluminum soap solutions is greatly reduced by such polar agents as water, fatty acids and amines. Further, aluminum soaps, as well as some of the soaps mentioned above, are hygroscopic when exposed to the air so that sufficient water can be adsorbed to greatly reduce the viscosity. Further, any water in solvents added, water loosely sorbed on pigments, or held in flushed pigment pastes or fatty acids due to excessively high vehicle acid values may lead to substantial viscosity reduction.

Since ordinary calcium, zinc, and magnesium stearates, palmitates, or laurates do not show the same hypersensitivity to water, there appears to be a trend toward their use as thickeners in spite of their lower efficiency.

For the thickening of oil paints, hydrated pulps are sometimes used, calcium linoleate pulp being most widely used. In such instances a substantial quantity of water is present, 65 per cent being a common amount. Though some of the water is free, being held in the mass of soap particles by capillary attraction, a large percentage is bound to the precipitated soap molecules by residual valence forces. Such hydrated pulps are useful in pigmented goods in order to minimize settling though too much cannot be used because of undesirable side reactions caused by the water.

METALLIC SOAPS AS FLATTING AGENTS

Flatting agents are merely minute particles of irregular shape which when ground into a vehicle cause incident light to be reflected from a deposited film in a diffuse rather than specular fashion. A good flatting agent has a refractive index close to that of the vehicle so that its presence in the body of the film is not obvious, it is friable enough that it may be readily ground to an appropriate particle size in the vehicle. It is highly insoluble in the vehicle so that maximum flatting per unit of weight is secured, and it is not so soft as to appreciably soften the dried vehicle film.

The stearates of calcium, aluminum, zinc and magnesium are the soaps most generally used as flatting agents. Whereas partial solubility is necessary for soaps to function as successful suspension agents, the opposite is true here so that soaps having poor suspension properties are often good flatting agents. Thus, zinc stearate is widely used; calcium stearate and aluminum stearates of higher aluminum content are also useful.

Metallic soaps suffer the disadvantage of causing vehicle thickening when too high a concentration is used so that the solids content of the vehicle must generally be kept low in order to secure proper flow. This low solids content causes thin films whose weathering qualities are not too good.

The gelling temperature of the soap should be as high as possible since slow, pebble mill grinding must be used if a soap which gels at low temperature is used. Thus, zinc, calcium and magnesium stearates may generally be ground on roll or stone mills.

The calcium, magnesium and zinc soaps of tung and oiticica oil have been produced commercially since they have been demonstrated to be excellent flatting agents. Production difficulties, because of the high degree of unsaturation of tung oil and its proneness to oxidation and polymerization, have to some degree inhibited developments in this field. Production techniques have demanded inert atmospheres in some cases, production in an inert vehicle in others and similar specialized handling so that development has been slow.

It can be said at this time that flatting agents of improved performance are still required in spite of improvements in metallic soaps, introduction of silica aerogels, and the production of flatting type resins in small amounts.

In conclusion, it is fitting to admit the paucity of knowledge as regards the performance of metallic soaps in all of the field mentioned. However, research in many instances is being conducted on an expanding scale and it is confidently expected that substantial progress will result.

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Chapter 17

The Testing of Raw Materials

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The protective-coating industry of today is a great and modern one: its factories, large and small, are scattered across the country from coast to coast. Many of them are new and modern buildings. The output of this industry may well amount to a billion dollars this year. The uniformity of its products, day in and day out, year in and year out, has contributed in no small measure to its growth and prominence. Without uniform raw materials this uniformity of finished product would be difficult if not impossible to obtain. This leads to the subject of the testing of raw materials.

What do we mean by "testing"? Webster defines a test as "a critical examination," or "subjection to conditions that show the real character of a person or a thing in a certain particular," or "a procedure or reaction used to distinguish any particular substance or constituent."

In our sense, then, testing is a procedure or series of procedures, which may be chemical or physical in nature, or both, by which we determine

(1) Whether or not a material conforms to a certain standard
(2) Whether or not a substance is what it is purported to be
(3) The identity of a substance.

Reasons for Testing Raw Materials

(1) We test raw materials to determine conformity to established standards. Years ago when laboratories existed primarily in schools and colleges and rarely in manufacturing plants, manufacturing procedures were largely by rule of thumb, and rather wide variations could be expected in the products of these plants.

Today laboratories for research and control are considered a necessary part of a plant whose products are of a chemical nature. It is very rarely that raw materials do not conform to established standards, particularly when they originate in plants of well established, reputable concerns.

(2) We may test a raw material to determine its suitability for a particular or special purpose. For example, ½-second nitrocellulose may be supplied over a range of viscosities, while for a particular use a nitrocellulose having a viscosity at the high end of the standard range may be preferable. The viscosities of several lots are then checked to determine which one best suits the particular purpose. Also, raw materials of different manufacturers may vary from one another in certain respects. Ester gums, for example, may have different melting points and/or acid numbers; these are tested for these characteristics so that their suitability for certain products or uses can be determined.

(3) In times of shortage we may test a raw material of unknown or questionable origin to determine its usefulness in or adaptability to certain products.

(4) Testing is the only way an unknown product can be identified. For instance, a dozen drums of oil may have been left in the shortage yard by an employee no longer connected with the firm. Weathering has obliterated all identifying markings. This 600 gallons of oil is useful only if it can be identified. The proper tests will establish this identity and the value may then be recovered in the form of saleable products.

(5) A new raw material of unknown composition and characteristics may have these properties identified by tests, so that its value and usefulness to the formulators, whose job it is to find a use for new products, may be established.

(6) Occasionally trouble will suddenly develop in the manufacture of some product. Raw material tests may locate the source or cause of the trouble and thus make the solution of the problem obvious.

Completeness of Testing

How thorough-going should the tests be? A specific answer is difficult. Certainly they should be complete enough to satisfy the requirements of the case. Unnecessarily involved testing will become burdensome and serve no useful purpose, but may, at least temporarily, serve to give the analyst added experience.

Due to the wide variety of raw materials used in the protective-coating industry, the tests required will be discussed in groups, as they apply to various classes or kinds of products.

The first point to be considered is the matter of sampling. Unless the sample brought to the laboratory for test is truly representative of the lot, package or shipment, trouble may be expected sooner or later. Of course, reputable manufacturers do not pack their wares as does the itinerant fruit peddler with the best apples on the top of the basket and the small, unripe, wormy ones on the bottom. Rather it is a question of what has happened to the shipment after it left the manufacturer and has been in transit and storage.

For example, a sample of solvent taken from the top of a tank car in cold weather may be clear and dry, that is, free of water. A similar sample taken from the bottom of the same car may be cloudy, may contain suspended particles of iron rust, and may be half water and half solvent. A half-and-half mixture of the two samples is not representative of the entire contents of the car, and the amount of water present in the car may not be greater than permitted in the specifications. Considerable care and judgment must be used in sampling in order to insure reliable samples. Proper sampling of oils is also of utmost importance. A rather complete description of the proper precautions to be observed in the sampling of oils has been given by G. S. Jamieson in his book on "Vegetable Fats and Oils" (2nd edition), pages 372–4.

Likewise lump resin in a barrel or case will classify itself to some extent, with fine particles and dust settling down. A sample of the dust or of one lump is not representative of the contents of the package.

The testing of solvents will be the first discussed and the tests will be those required to determine conformity to specifications.

Solvents

General tests applicable to solvents as a whole are: general appearance, specific gravity, color, distillation range, non-volatile matter, odor, water, acidity.

General Appearance. The solvent sample and comparison standard should be compared in Nessler tubes having flat, colorless bottoms; to avoid sidelight the sides of the tubes should be covered with opaque paper. The height of the sample in each tube should be approximately equal, and about 10 inches of solvent should be used for comparison. In good light, the sample should be examined end-wise in the tube against a white paper background. The examination should be made not only for color but also clarity and freedom from suspended matter.

Specific Gravity. The specific gravity of solvent samples may be determined by any convenient method which gives an accuracy at least to the third decimal point. A constant temperature of 20°C should be used.

Distillation Range. In order that the results of the distillation range determination shall be reliable, it is necessary that both the equipment used and the technique applied in running this determination follow the prescribed specifications in all details. The equipment should be set up in a draft-free place, to avoid variable results. The equipment consists of a standard 100-milliliter Engler distilling flask with a side arm, a brass condenser tube running through a large-volume water bath, a graduated 100-

milliliter flask, used as a receiver, an electric heater with a temperature control rheostat, and the necessary draft shields and supports.

With the apparatus clean and dry, the graduated receiving cylinder is filled to the 100-milliliter mark with the sample to be tested, which is then transferred to the distilling flask in such a way that none of the sample gets into the side tube. The distilling flask is then connected to the condenser and placed over the electric heater. The specified distilling thermometer is placed in the flask neck with a cork stopper and so positioned that the bulb of the thermometer is circled within the neck of the flask and at such a height that the lowest point of the capillary tube of the thermometer is in line with the lower edge of the side tube of the distilling flask. The receiver is placed under the discharge spout of the condenser in such position that the first drop to fall from the condenser can be readily observed.

Heating is started at such a rate that the first drop of condensate shall fall from end of the condenser in not less than five nor more than 10 minutes from the time of application of heat. The temperature existing when the first drop of condensate falls from the condenser shall be recorded as the initial boiling point. The receiver shall then be moved so that the tip of the condenser discharge tube shall touch the edge of the receiver and further distillate shall flow down the walls of the receiver rather than drop into it. Distillation shall be continued at such a rate that not less than four nor more than five milliliters of condensate shall be collected per minute of distillation time.

The results of the distillation may be reported in either of two ways, namely, as the volume collected for each 10°C rise in temperature of the distilling thermometer, or as the temperature for each 5°C increment in distillate collected.

No change in the adjustment of the heat input to the distilling flask shall be made during the distillation except that the heat input may be raised or lowered in order that the last 5 millimeters of distillate shall be collected within the required period, which is 3 to 5 minutes. The end joint of the distillation shall be that temperature at which the bottom of the distilling flask first becomes completely dry.

The total volume of distillate collected in the receiving graduate shall be recorded as the "Recovery." The cooled liquid residue in the distilling flask shall be recorded as "Residue" and shall be measured in a small graduate. The difference between the sum of the recovery and the residue and the original 100 millimeters shall be recorded as the "Distillation Loss."

For routine examinations of most solvents, the results obtained by the method described are satisfactory, however, in cases of dispute and referee tests, it may be necessary to make corrections both for barometric pressure and for the variation in the thermometer, due to the fact that the emergent stem above the cork is at some temperature which was not the calibration temperature of the thermometer. Only in exceptional cases will these corrections be necessary.

Non-volatile Matter. The non-volatile matter in a sample shall be calculated from the increase in weight of a tared dish, when 100 milliliters of solvent is evaporated to near-dryness on a water bath and dried to constant weight in an oven at a temperature of 100 to 110°C. It should be reported in grams per 100 milliliters. Obviously, as most of the organic solids used in the protective-coating industry are inflammable, care should be taken not only in this test, but also in the others, to avoid fires or explosions by the contact of open flames or sparks with the volatile vapors in air.

Odors. The initial and residual odor of solvent samples should be compared with standards by dipping pieces of heavy filter paper to the same depth, into the respective samples and comparing the odors initially, through the drying period, and after the sample has had opportunity to dry more or less completely at room temperature. This test is an important one, as occasional objectionable contamination may escape other means of detection.

Water. Five milliliters of the sample shall be shaken with 5-milliliter portions of 60 degree API Gasoline in a stoppered 100-millilter glass cylinder until the total volume of gasoline added shall equal the volume required in the specification. The presence of excessive amounts of water is indicated by turbidity in the mixture; if turbidity appears, the reference standard should be likewise tested, and the results of the two tests compared.

Inasmuch as temperature affects the results to some extent, a standard temperature of 20°C should be used.

Acidity. The acidity of a sample of solvent is determined by titrating a 50-milliliter sample in an Erlenmeyer flask with 0.1 normal potassium hydroxide in 99 per cent methyl alcohol, using phenolphthalein as the indicator. The acidity is reported as milligrams of potassium hydroxide per gram of sample, and the weight of sample can be calculated from the specific gravity. In the case of esters, such as butyl or ethyl acetate, the acidity may be reported as per cent by weight of the acid involved.

Alkalinity. In solvents which may be alkaline rather than acid in nature the alkalinity rather than acidity is calculated, following the procedure for acidity but using instead 0.1 normal sulfuric acid and methyl orange as the indicator.

Special Procedures for Particular or Specific Solvents. While the aforementioned tests cover solvents as a whole, certain specific solvents require additional tests in order to assure conformance to standards. Among these are the group of lacquer solvents known as esters.

Ester Value. A one or two-gram sample is weighed after sealing it in a tared glass ampoule. The sample may then be readily handled without fear of loss. The ampoule is broken with a glass stirring rod in an Erlenmeyer flask in the presence of approximately 1½ times the theoretical 0.5 normal aqueous caustic potash which might be required for saponification in an Erlenmeyer flask. If the sample is not soluble in water, enough ethyl or methyl alcohol, free of saponifiable matter and acid, is added to effect solution, or a 0.5 normal potassium hydroxide solution in methyl alcohol instead of in water. The stirring rod and the inside of the flask are then washed down and a reflux condenser connected to the top of the flask. Heat on a steam bath for a period of 1 to 4 hours, or until saponification is complete, checking the contents of the flask during the saponification period.

When saponification is complete, rinse the condenser down into the flask with a small quantity of distilled water and titrate with 0.5 normal hydrochloric acid, using phenolphthalein as indicator.

Two blanks, using the same potassium hydroxide solution and the same amount of alcohol, if alcohol is used, should be run. These blanks should check to the first decimal place. The amount of potash required to saponify the sample can be determined from the difference in the titration of the blank and the sample and the amount of ester then calculated from this figure. Allowance should be made for the acidity or alkalinity of the sample in calculating the ester content.

In place of using an Erlenmeyer flask and reflux condenser, a round-bottomed pressure flask may be used, or a spring-top citrate of magnesia bottle. Other details of this test are the same as when using the Erlenmeyer flask. In the case of esters which saponify readily, the sample need not be heated, but if shaken at regular intervals and allowed to saponify overnight, satisfactory results will be obtained.

When the pressure flask method is used, it is desirable to surround the flask with a protective screen while it is on the steam bath, in case the flask should break while under pressure. It is also necessary to cool the flask at least to room temperature before opening, to avoid the possible loss of sample, due to the pressure in the flask while at a high temperature.

A Copper Corrosion Test. This test is made by exposing a recently polished strip of copper in a sample of solvent on a water bath for a period of 30 minutes. The flask containing the sample should be connected to a reflux condenser with a cork stopper to avoid loss of solvent. At the expiration of 30 minutes from the time the flask was placed in the water bath, the copper strip is removed and examined for discoloration or corrosion.

Flash Point. The flash point test as applied to volatile solvents in the paint industry is ordinarily run in the Tag closed cap tester. Both the tester itself and the method of running the test have been carefully standardized and are the subject of detailed specifications.

The test consists of applying a small flame at regular intervals to a measured quantity of solvent in a small covered cup, while the temperature of the sample is gradually being increased at a rate prescribed in the specifications. The flash point is that temperature at which a definite flash of flame appears across the top of the sample, when a small flame is admitted into the closed cup. This test, like the test for distillation range, must be run in strict accordance with the details of the specification if reliable results are to be obtained. The apparatus must be clean and dry at the time of starting the test. The temperature of the water in the tester must be at or below the specified temperature. The rate of heating and the speed with which the test flame is admitted to the sample are important, as variation in either of these will affect the flash point. Once a sample has been subjected to the flash point test, it should be discarded and, if the test is repeated, a fresh sample should be taken. A careful operator, following the details of the specification, can make check runs which will agree to within 1°F. It is desirable but not essential that this test be run in a darkened room; it must be run in a location free of draft.

For routine determinations, no corrections are necessary, but in the case of referee determinations or disputes, a correction should be made for barometric pressure, adding 1.6°F for each 25 millimeters which the barometer reading shall be below 760 millimeters, or subtracting 1.6°F from the flash point for each 25 millimeters of barometer reading above 760 millimeters.

Drying Oils

The second group of tests will be those applied to drying oils. The tests usually recommended for these oils are: specific gravity, acid number, saponification number, iodine number, ash, drying time, color (and odor), foots.

Specific Gravity. Due to the difficulty of reading the graduated stem of a hydrometer under the oil level and the slowness of response of a hydrometer or the plummet of a Westphal balance, particularly in the case of bodied oils, it is preferable to use a specific gravity bottle or pycnometer in determining specific gravity. The determination is made at a temperature of 15.56°. The bottle should be carefully filled, being sure that there are no air bubbles. Remove any surplus and weigh. The weight of the oil divided by the weight of a similar volume of water gives the specific gravity.

Acid Number. Five to 10 grams of oil is heated with 50 ml of neutral 95 per cent ethyl alcohol over a steam bath for 30 minutes. Titrate with 0.2 normal alkali and calculate the acid number (mg KOH per gram of oil). Acid number is a measure of the acidity or free acid present in the oil. In view of the complicated mixture of fatty acids present, it is not possible to report this value in per cent without lengthy, involved analysis of these free acids.

Saponification Number. The saponification number of an oil is a measure of the total fatty acids of an oil, both free and combined. It is numerically equal to the combined acid and ester numbers or values.

About 2 grams of oil weighed in a 300-ml Erlenmeyer flask are saponified with 25 ml of 0.5 normal alcoholic KOH, over a steam bath. The use of a condenser loop in the flask neck is recommended. After one hour on the steam bath, remove the flask, cool and titrate with 0.5 normal H_2SO_4, using phenolphthalein as indicator. Two blanks of the alkali should be run at the same time and should check each other within 0.1 ml of 0.5 normal H_2SO_4. Calculate the saponification number from the difference between the titrations of the blanks and the sample.

Iodine Number. The iodine number of an oil is a measure of the degree of carbon-to-carbon unsaturation existing in the oil. Inasmuch as the drying characteristics of an oil vary with the degree of unsaturation, or iodine number, and most oils have iodine numbers within fairly definite ranges, this characteristic is of value in determining the quality of an oil.

Weight accurately by difference 0.10–0.15 gram of oil into a 500-ml Erlenmeyer flask with a broad, funnel-shaped neck. Add 10 ml of chloroform and dissolve the oil by swirling. Add 25 ml Wijs solution, put in place the glass stopper, which should be tight-fitting, and pour a few ml of 10 per cent KI solution around the stopper to absorb any iodine which may escape. Let stand 1 hour in the dark at 21–23°C with occasional shaking. Then add 10 ml of 15 per cent KI solution and 100 ml of water and titrate with 0.1 normal sodium thiosulfate solution, using freshly prepared starch solution as indicator. Two blanks should be run at the same time. From the difference between the blank titration and that of the oil sample and the iodine value of the thiosulfate solution, calculate the iodine number of the oil. It is reported as grams of iodine per 100 grams of oil.

The method given is the Wijs method, which is the most commonly used. The Hanus method, using bromine instead of iodine, has been used to some extent, but is not as popular as formerly. A newer bromometric method has been developed by Kaufman and it has certain advantages over the others in some cases.

Ash. Ash is determined by igniting a 10- to 20-gram sample in a crucible with a Bunsen flame and allowing it to burn quietly until nearly consumed. Then ignite in a muffle furnace or over a flame at no more than a dull red heat until all the carbon is consumed. Cool, weigh and report the per cent ash.

Drying Time. Flow the oil out on a glass panel and allow it to dry in a vertical position at 30 ± 2°C and at a relative humidity of 32 ± 4 per cent. Test the film at intervals and report as the drying time, the time when the film no longer adheres to the finger and does not appreciably rub up when gently rubbed across the surface.

Resins

The characteristic properties and composition of the resins used in the protective-coatings industry vary so widely that the same series of tests is not generally applicable to all resins. Each class of resins, due to composition and physical characteristics, requires special tests suitable for that particular class. However, a few tests do have fairly general application to a considerable number of resins and resin classes, and these will be discussed briefly. No consideration will be given to detailed tests for specific resins. For detailed information on this subject reference is made to the literature of the various resin manufacturers, and also to Volume 5 of "Protective and Decorative Coätings," by J. J. Mattiello.

Resin tests of general application are: specific gravity, softening point, acid number, color, viscosity.

Specific Gravity. The specific gravity of liquid resins and those normally supplied and handled in solution may be determined in the same manner as that of drying oils, that is, by means of a specific bottle, or pycnometer. As the procedure has already been discussed, no further mention is necessary.

Acid Number. This value is frequently run by dissolving a sample of 1 to 2 grams in a suitable solvent, usually toluene, diluting with neutral alcohol, and titrating the free acid with 0.1 normal KOH using phenolphthalein as indicator. The result is calculated as mg of KOH per gram of sample. In the case of resins already in solution, the acid number is calculated on the solid portion of the sample and therefore the per cent of non-volatiles must be determined.

Non-volatiles: The methods of running this test are legion. The details of the method used are not important provided they give reliable and consistent results. One method generally acceptable is as follows:

A 1-gram sample ± 0.1 gram is weighed by difference from a stoppered weighing bottle into a tared shallow dish. A 2½ to 3″ friction can lid is satisfactory. The weighed sample is then placed in an oven and the volatile evaporated at 105–110°C for 3 hours. The non-volatile content of the sample is calculated from the weight of the dried residue and the weight of the sample.

Color. Manufactured resins are generally compared with the 1933 Gardner scale of color standards. Solid resins being put into a 50 per cent solution and those in solution compared at the normal solids as supplied. Samples are put into standardized glass tubes and compared with standard tubes or with glass standards under uniform lighting conditions. Care must be used to avoid side light, as this may change the apparent color. Other color comparison methods are frequently used as well as other color standards. There seems to be no common ground on this matter.

Viscosity. Viscosity, like color, is another characteristic in which there is a wide difference in the type of equipment. The one method, however, which seems to have the widest general acceptance is the use of the Gardner-Holdt viscosity tubes and standards. The standards are a series of water-white oils of relatively good stability permanently sealed in standardized tubes. The sample is placed in a similar tube and both tubes brought to 77°F. The tubes, held in a vertical position, are quickly inverted and the rates at which the bubbles rise are compared. The viscosity is reported by the letter designation of the standard tube which most closely equals the sample.

Instruments of the efflux type, such as the Ford Cup, the ASTM Cup, the Zahn Cup or the Saybolt viscosimeter are sometimes used, as are also rotary instruments such as the MacMichael and Stormer viscosimeters.

Pigments. The variety in pigments in regard to chemical composition and color almost defies imagination. A factory making organic protective coatings may readily have a larger number of pigments in stock than it has of all other ingredients combined. The discussion of pigment testing, therefore, must of necessity be limited to the ordinary tests applicable to pigments in general, such as tests for: moisture and volatile matter, coarse particles, oil absorption color, and tinting strength.

Moisture and Other Volatile Matter. Excessive moisture in pigments is undesirable and may result in puffiness or seediness in pigmented products. To determine moisture and other volatile matter, 3 to 5 grams of sample are weighed in a wide, flat, covered weighing bottle or covered aluminum moisture dish. Remove the cover and place in an oven for two hours at a temperature of 105–110°C. Replace the cover cool in a desiccator, and weigh. The loss in weight multiplied by 100 and divided by the initial weight is the percentage of moisture and other volatile matter.

Coarse Particles. In the manufacture of colored protective coatings the dispersion of finely pre-ground pigments is much easier than is the grinding and dispersing of coarse pigments. Frequently excessive coarse particles increase the time necessary to prepare a satisfactory product to prohibitive limits. It is therefore desirable that pigments contain a minimum of oversize.

To determine the percentage of coarse particles, a 3″ diameter 325-mesh sieve is dried in an oven at 105–110°C and cooled. A sample of pigment ranging from 2 to 25 grams, depending upon its specific gravity, is weighed into the sieve and washed with a stream of 300–500 ml of water per minute, slightly shaking the sieve or gently brushing with a soft camel-hair brush. When most of the pigment is washed through (in from 2 minutes to 1 hour) the sieve is placed in 250-ml of water in an 8″ porcelain dish. The remaining pigment is gently brushed 20 strokes in 10 seconds; the sieve is then lifted out of the dish to allow the water to drain, and then replaced. This brushing and draining cycle is repeated, changing the water after each 2 cycles until no pigment particles are seen in the water after draining the sieve, when 200 ml of water is poured through the sieve and collected in a 400-ml beaker. Stir rapidly and examine over a black or white background contrasting with the pigment. The wash shall be continued until no pigment particles are observed in the center of the beaker. When washing is complete, dry in an oven at 105–110°C, cool, weigh and calculate the percentage of coarse particles. Rinsing the moist residue with a few drops of alcohol followed with ether will facilitate drying. In the case of pigments which foam when nearing the end of the washing period a small amount of alcohol will usually help to stop foaming.

Oil Absorption. This characteristic is determined by adding raw linseed oil drop by drop to a weighed quantity of pigment sample on a marble or glass slab, rubbing the pigment and oil together with a sharp-edged spatula after each addition until a stiff, putty-like mass is obtained which does not separate or break up. From the weight of oil used and the weight of pigment sample report the results as pounds of oil per 100 pounds of pigment.

Color. In view of the fact that many pigments are used for their color rather than other properties, a means of comparing the color of the sample with a standard is necessary. Comparisons of the powdered dry colors are not satisfactory, so pastes of thin consistency are prepared, usually in white refined linseed oil, of an acid number of approximately 4.

The pastes are prepared by rubbing carefully weighed quantities of pigment and oil on a ground glass or lithographers' stone slab with a 3″ beveled-edge glass muller. An oval or rectangular pattern of rubbing is used, the strokes being 12 to 15″ in length and 3 to 4″ apart. After a definite number of "rubs" or strokes, depending upon the pigment, hard-grinding pigments requiring more rubbing than soft ones, the paste is gathered together from the muller and the slab and the whole cycle repeated 4 to 6 times, or until the total number of rubs required has been reached.

Pastes of the Standard and sample are then placed side by side in contact on a glass or tin panel and a scraper drawn lightly over them to produce a smooth level surface for examination, which should be made immediately.

Tinting Strength. As many of the dry colors used to make light shades and tints are much more expensive than the white base used for these shades and tints, examination for tinting strength is desirable. This test is run by reducing weighed portions of the color pastes of a standard and sample, prepared as just described for the color test, with proportionate parts of an appropriate white paste similarly prepared. Each reduction is carefully mixed with a spatula on a glass plate until uniform and until no streaking is evident, and then comparison is made on a glass or tin panel as described for color.

The test for color and tinting strength is one of many in which the personal equation is a factor. Every effort must be made to obtain, as nearly as possible, absolute uniformity. The number of rubs, the length of stroke, the pressure used on the muller and the size of the batch all influence the results. Here, as in many other tests, uniformity and reliability can be obtained only with experience.

The tests given frequently are sufficient for many routine examinations of the raw materials most commonly used in the protective-coating industry. In some cases additional examination may be desirable or required. In this case, reference is made to literature and technical bulletins of the raw materials suppliers and to additional references, such as "Standard Methods of Chemical Analysis," by Scott; "The Examination of Paint, Varnish and Lacquer," by Gardner; "Protective and Decorative Coatings," by Mattiello; and to the following specifications:

Federal Standard Stock Catalogs
  TT-P-141a Paint, Varnish, Lacquer and Related Materials—General Specifications and test methods.
  VV-L-791b Lubricants and Liquid Fuels—General Specifications and test methods
  U. S. Army 3-1F Paints and Related Materials—General Specifications and tests
  ASTM Standards on Paint, Varnish, Lacquer and Related Products

There are many materials which have not been discussed such as lacquer plasticizers, the various cellulose esters and ethers, metallic driers, dispersing agents and many others. These have not been mentioned:

(1) Because these groups are so varied that no generalizations can be made.

(2) The technique involved or the equipment required is not generally available in the average laboratory.

(3) Only a brief generalization has been attempted in this chapter.

Conclusion

It is recommended that the analyst understand what he is doing and why he is doing it. Many of the tests described here in brief are given in considerable detail in the literature referred to. Details should be followed completely and to the letter, since many of the tests are undependable when the conditions of tests are changed, while most of them give very reliable results when the method is carefully followed.

Chapter 18

Principles of Paint Formulation

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The subject of this chapter covers a broad field and of necessity will have to be limited to an outline of definite principles to be followed in the formulation of various types of paint materials based on research experience gained by the profession largely during recent years.

As the performance characteristics of any paint are primarily influenced by the ratio of pigment to non-volatile vehicle in the dried paint film, let us first define two means of designating this ratio. (1) The ratio may be given as a definite pigment volume percentage or pigment volume concentration. This term is commonly designated as per cent P.V. or per cent P.V.C. (2) The ratio may be given as a simple ratio of pigment volume to non-volatile vehicle volume. This term is commonly designated as the P/B ratio. In the determination of the per cent P.V. or per cent P.V.C., it is necessary to calculate the total pigment volume in the paint and divide this by the total pigment volume plus the total non-volatile vehicle volume. In determining the P/B ratio, it is still necessary to calculate the total pigment volume and the total non-volatile vehicle volume; however, the ratio is normally expressed by using unity for the P figure and calculating the pigment to binder ratio on this unity figure. Thus, in expressing P.V. or P.V.C. it is simply a whole number such as 28.0 per cent, but in expressing P/B ratio it is expressed as 1/2.57.

To determine pigment volumes in a given paint, it is first necessary to know the bulking values of the various pigments used. The bulking value of a pigment is expressed in gallons per 100 pounds of pigment. This means that when the pigment is ground into a paint with oils or other types of vehicles, the pigment occupies a certain definite volume in the paint. Bulking values may be calculated by first determining the specific gravity of the pigment in question, and then calculating the weight per solid gallon of pigment by multiplying the specific gravity by the weight of a gallon of water, 8.33 pounds. The reciprocal of the weight per solid gallon of pigment is the bulking value in gallons per pound of pigment.

Table 41 shows the specific gravity, weight per solid gallon, the bulking value, fineness, oil absorption and composition of some of the commonly used paint pigments. These values are as given by the pigment manufacturers themselves.[28*]

To demonstrate the effect of pigment volume in various types of paints, we shall first take up house paint formulations. Chapters 4, 5 and 6 have described in some detail the characteristics of the white and colored pigments, and of the extenders used in paints; on that account we shall not go into any detail here as to their specific properties. Prior to World War II, exposure tests run by many paint and pigment manufacturers showed that the volume relationships of pigment to binder or the P.V. (pigment volume) may vary over relatively wide limits without serious effects. Generally, however, pigment volumes of about 28 to 30 per cent were considered most acceptable because of the fact that high pigment volumes tend toward chalking, which results in failure by erosion, whereas low pigment volumes give more dirt collection and mildew and tend toward plastic checking, or an "alligator" type of cracking.[2] During World War II the world-wide shortage of fats and oils made itself felt as far as paint manufacturers were concerned and it was necessary for the U. S. Government to issue many orders through its agencies conserving the amounts of oil used in various types of paint. House paints or paints of the exterior oil type were limited to 3.75 pounds of oil per gallon of finished paint. This is in contrast to the 5.0 pounds of oil per gallon of finished paint which was the average amount of oil in pre-war house paints. This reduction in the amount of oil meant a corresponding increase in the pigment-volume relationship. Thus pigment volumes were increased from 28 or 30 per cent to 35 or 40 per cent. An explanation of how this was accomplished is as follows.

The binder or non-volatile vehicle in the pre-war house paint was generally composed of linseed oil. A combination by weight of 92 per cent alkali-refined linseed oil and 8 per cent kettle-bodied linseed oil (body "Q," 4.35 poises) was known to give good results. This oil combination was used in the vehicle at the rate of 85 to 90 per cent by weight, the remainder being volatile matter, mineral spirits, turpentine or similar solvents. Using a pigment percentage by weight of 60 to 70, pigment volumes of 28 to 30 per cent result using, of course, the vehicle combination as given above. To increase the pigment volume in the oil-conserva-

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* Refer to *Scientific Bulletin* for more complete list.

Table 41. Bulking Value Chart.

Pigment Trade Name	Producer	Sp. Gr.	Weight per solid gallon (pounds)	One pound bulks (gallons)	Fineness residue on 325 mesh screen %	Oil Absorption	Composition
Timonox "White Star"	Texas Mining & Smelting Company	5.73	47.73	.02095	0.13	11	99.7% Sb_2O_3 (Antimony Oxide)
Eagle #40 Super Sublimed	Eagle-Picher Lead Co.	6.50	54.15	.01847	0.1	9–11	20% PbO (Basic Lead Sulfate)
Euston Standard	Euston Lead Co.	6.80	56.64	.01766	0.07	9	$2PbCO_3$—$Pb(OH)_2$ 99.8% (Basic Lead Carbonate)
XX-50	New Jersey Zinc Co.	5.61	46.73	.02140	0.01	—	98% ZnO (Zinc Oxide)
Ozlo 65/35, 412	Sherwin-Williams Company	5.92	49.31	.02028	—	15	35% $PbSO_4 \cdot PbO$ (35% Leaded Zinc Oxide)
TiPure LO-CR	DuPont	3.88	32.32	.03094	—	18–19	97% TiO_2 (Anatase Titanium Dioxide)
TiPure R-610	DuPont	4.20	34.99	.02858	—	19–20	94% TiO_2; 0.8–1.2% ZnO; 1.8–2.4% Al_2O_3; 0.6–1.0% SiO_2 (Rutile Titanium Dioxide)
Sunolith Low Oil	Chemical & Pigment Company	4.29	35.74	.02798	—	17–19	28% Min. ZnS Balance $BaSO_4$ (Lithopone)
No. 1 Barytes	C. K. Williams Company	4.40	36.67	.02729	0.025	11	98–98.5% $BaSO_4$ (Barytes)
Atomite	Thompson-Weinman Company	2.71	22.57	.04431	—	30	98% $CaCO_3$ (Calcium Carbonate)
Isco Carrara O	Innis Speiden Co.	2.65	22.07	.04531	0.5	30–35	99.5% SiO_2 (Silica)
#610 Talc	W. H. Loomis Talc Corp.	2.85	23.74	.04212	2.0	48–52	94% $MgSiO_3$ 4.0% CaO (Asbestine)
Dark Indian Red	Synthetic Iron Color Company	5.02	41.82	.02391	0.5	40	99% Fe_2O_3 (Iron Oxide)
Persian Gulf No. 438	C. J. Osborn	4.14	34.49	.02899	0.1	11	71.7% Fe_2O_3; 23.8% SiO_2; 2.5% CaO; 1.9 loss on ignition (Iron Oxide)
Mapico Lt. Lemon 100	Columbian Carbon Co.	4.05	33.74	.02964	0.01	70	87% Min. Fe_2O_3 98% Min. Fe_2O_3: H_2O (Ferrite Yellow)
Monarch #80	Godfrey L. Cabbot Inc.	1.81	15.08	.06631	—	75	95% Fixed Carbon (Carbon Black)

tion type of formula, the pigment percentage by weight remained essentially the same, but the vehicle composition was altered markedly. In this case the vehicle was composed of one-third alkali-refined linseed oil, one-third kettle-bodied linseed oil (body Z2-Z4, 36.2–63.4 poises), and one-third volatile thinner. This results in pigment volumes of 35 to 40 per cent, depending, of course, upon the pigment combination used.

In order to demonstrate this change a typical pre-war formulation on an outside white house paint in comparison with a typical oil-conservation type formula is given in Table 42. As stated before, higher pigment volumes lead to chalking. In the oil-conservation type of formula this is counteracted by the use of the proper kettle-bodied linseed oil. Exposure tests run some years ago, again by paint and pigment manufacturers, showed that varying amounts of kettle-bodied linseed oil could be incorporated in exterior oil paints by proper adjustment of the vehicle. Optimum results were obtained when using a Z2-Z4 kettle-bodied oil with an acid number of 8 to 10. The results showed that best durability and best can stability, *i.e.*, most exterior-type oil paints, contain a certain percentage of zinc oxide, either as such or in combination with basic lead sulfate as in 35 per cent leaded zinc oxide. The acid number of the bodied oil is kept at 8 to 10 to prevent harmful zinc soap formation and consequent bodying of the paint.

Table 42. A Typical Oil-Conservation Paint Formula.

White Outside House Paint	Pre-War Type		Oil Conservation Type	
	Weight (Pounds)	Volume (Gallons)	Weight (Pounds)	Volume (Gallons)
Anatase type titanium dioxide	127	3.92	127	3.92
35% Leaded zinc oxide	424	8.65	424	8.65
Magnesium silicate	297	12.50	297	12.50
Alkali-refined linseed oil	435	56.05	187.5	24.16
"Q" body linseed oil	38	4.77	—	—
Z2-Z4 linseed oil	—	—	175.5	21.94
Lead-manganese drier	25	2.83	19	2.15
Mineral spirits	74	11.28	175	26.68
	1420	100.00	1405	100.00

Properties	Pre-War Type	Oil-Conservation Type
Consistency	90 K. U.	82 K. U.
Pigment Volume	28.5%	34.5%
Oil/Gallon	4.89#	3.75#

Consistency of most exterior house paints and enamel-like paints is given as so many K.U. (Krebs Units) and is determined in accordance with the A.S.T.M. Method. Reference should be made to A.S.T.M. Designation; D–562–44 for details of this test.[25] In Table 43 is a viscosity chart on Krebs Units showing the relationship of Krebs Units as far as time and weight in grams on the instrument are concerned. The re-

Table 43. Stormer Consistency Time—Weight Krebs Units.

TIME								WEIGHT (GRAMS)							
	75	100	150	200	250	300	350	400	450	500	550	600	650	700	750
(SECONDS)								Krebs Units							
24	42	52	65	75	83	90	95	99	103	108	111	115	118	122	125
25	45	54	66	76	84	90	95	100	104	109	112	116	119	122	125
26	47	56	68	78	85	91	96	101	105	110	113	117	120	123	126
27	49	57	69	79	86	92	97	102	106	111	114	118	121	124	127
28	51	59	70	80	87	93	98	102	107	112	115	118	121	124	127
29	53	60	71	81	88	94	99	103	107	112	115	119	122	125	128
30	54	61	72	82	89	95	100	104	108	112	116	120	122	125	128
31	55	62	73	82	90	95	100	104	108	113	116	120	123	126	129
32	56	63	74	83	90	96	101	105	109	113	116	120	123	126	129
33	57	64	75	84	91	96	101	105	109	114	117	121	123	126	129
34	58	64	75	84	91	97	102	106	110	114	118	122	124	127	130
35	59	65	76	85	92	98	102	106	110	114	118	122	124	127	130
36	60	66	76	85	92	98	103	107	111	115	118	122	125	128	130
37	61	67	77	86	93	99	103	107	111	115	119	123	125	128	131
38	62	68	78	87	93	99	104	108	112	116	119	123	126	129	131
39	62	68	78	88	94	100	104	108	112	116	120	124	126	129	131
40	63	69	79	88	94	100	104	108	112	116	120	124	127	130	132

lationship between these arbitrary units and the expression of viscosity in poises has been investigated by Geddes and Dawson for truly viscous liquids. They report the relationship:

$$\text{Viscosity in poises} = \frac{t\left(F - \dfrac{27500d}{t^2}\right)}{610}, \text{ where}$$

t = time in seconds for 100 revolutions of the paddle.
F = driving weight in grams.
d = density in grams per milliliter.

However, this relationship has not yet been investigated for liquids which are not truly viscous (such as pigmented coatings) and any expression of the viscosity of pigmented coatings in poises by use of this method and the above conversion must be at present considered as an approximation only. The same consideration, in general, applies to other instruments used to measure viscosity of pigmented coatings.

As examples, exterior oil-type paints show an average K.U. reading of 90 to 100. Exterior oil-type primers show an average K.U. reading of 65 to 75. Flat wall paints have an average K.U. reading of 90 to 95. Enamels, glosses and semi-gloss paints vary in K.U. readings depending upon the specific formulation used. However, averages will be close to the range shown for exterior-type primers.

Let us examine in more detail the paints given in Table 42 as far as the function of each raw material in the formulation. In Table 44 a comparison of the volume percentages of the two paints is given.

Thus it may be seen that the pigment occupies the same volume in the two paints, but the volume of oil is almost 50 per cent greater in the prewar type than in the oil-conservation type.

Table 44. Volume Percentages.

	Pre-War Type (per cent)	Oil-Conservation Type (per cent)
Anatase type titanium dioxide	3.92	3.92
35% Leaded zinc oxide	8.65	8.65
Magnesium silicate	12.50	12.50
Alkali-refined linseed oil	56.05	24.16
"Q" body linseed oil	4.77	—
Z2-Z4 linseed oil	—	21.94
Lead-manganese drier	2.83	2.15
Mineral spirits	11.28	26.68
	100.00	100.00
Total pigment volume	25.07	25.07
Total oil volume	60.82	46.10
Total drier volume	2.83	2.15
Total thinner volume	11.28	26.68

In the pigmentation we have anatase titanium dioxide. This pigment is used for several reasons: (1) it has high hiding power; (2) it is a chalking type of titanium dioxide, and as such aids in presenting a clean surface film; (3) due to its chalking it aids in prevention of dirt collection. 35 per cent leaded zinc oxide is also used for several reasons: (1) the zinc oxide portion of the 35 per cent leaded zinc inhibits mildew; (2) it produces a hardness of film which is resistant to chalking and as such may cause cracking or checking; (3) the lead sulfate portion aids in preventing this cracking and checking and contributes to the ease of brushing; (4) lead and zinc soap formation with the oils present aids in brushing; however, the lead soaps produced are the contributing factor as they are soft and buttery in nature, whereas the zinc soaps are hard and stringy; (5) the zinc oxide portion contributes to the flow of the paint.

The magnesium silicate present is fibrous in nature and is present (1) to aid suspension of the paint by preventing hard settling; (2) due to its structure it aids in resistance to checking and cracking; (3) it aids in brushing, giving some slip under the brush.

In the vehicle is refined linseed oil because (1) this oil gives color, as it does not stain the pigment sufficiently to affect the white color; (2) it does react to a certain degree to form soaps; as stated under the pigments, this soap formation contributes to ease of brushing and also to ultimate durability. The hiding power of whites will be taken up later, but let it suffice to say here that the higher index of refraction of the pigments over the index of refraction of the oils and thinners is the controlling factor in hiding. The bodied linseed oils are present largely to aid durability and flow. In the case of the conservation-type formulation a much higher percentage of bodied oil is used, due to the higher pigment volume, necessitating better flow, and also as an aid to body of the finished paint due to the higher volatile vehicle volume; this oil of necessity must be of controlled acid number to prevent package instability where a high amount of bodied oil is used. The mineral spirits portion of the vehicle is present (1) to aid brushability by reducing the viscosity of the paint to the proper brushing body; and (2) to aid flow to a certain extent by remaining in the film sufficiently long to prevent any tendency to set up under the brush.

In exterior oil-type paint tints similar pigment volumes are used. Pigmentation is varied, however, a rutile type of titanium dioxide being used instead of the anatase type. Pigment percentage by weight of a typical exterior tint base would be 12.5/45/42.5 of rutile titanium dioxide / 35 per cent leaded zinc oxide / magnesium silicate. Permanent pigment colors are used in tinting. These include among many others: iron oxide pigments, natural and synthetic; chrome greens and yellows; hydrated chromium oxide; phthalocyanine greens and blues; iron blues and lampblack. These pigments have been discussed in more detail in Chapter 6.

Exterior trim paints were originally made on an oil-type base similar to the paints discussed above. These paints in solid shades are still used to some extent, but for the most part have been replaced with trim paints made on an oil-modified glyceryl phthalate base. These paints are high-hiding permanent pigment color combinations and include pigments as given above for use in house paint tints. The pigment volume averages 15 per cent for this type. The vehicle is usually composed of long-oil alkyd resin varnish, with or without the addition of drying oils. This type is also used on advertising sign boards where a durable material is necessary. Ease of brushing, holding a sharp line for lettering and fairly fast drying are essential for these sign colors.

General principles involved in the formulation of interior paints and enamels will be discussed next. Four major classifications based on the surface characteristics of the dried films may be listed.[2] These consist of flat paints, semi-gloss paints, gloss paints and enamels. Here again the relationship of binder to pigment (P/B) is of paramount importance because of its predominating influence on the physical and visual properties of any given pigmented system. The P/B ratio here is an accurate means of expressing the true relationship that exists between the pigment and binder in the dried film. In addition, of course, inherent oil requirements of the pigments used, specific film characteristics and attributes of the vehicles used all affect the amount of binder to be used per unit of pigment volume. The pigment concentration is necessarily the limiting factor in the four classes given above. For example, in flat paints it may fall within the range of 71.5 to 52.5 per cent by volume based on the total solids; this will mean a P/B ratio of 1/0.4 to 1/0.9. Semi-gloss and gloss paints may fall within the range of 52.5 to 33 per cent by volume based on the total solids; this means a P/B ratio of 1/0.9 to 1/2.0. Enamels may fall within the range of 33 to 20 per cent by volume based on the total solids; this again means a P/B ratio of 1/2.0 to 1/4.0. Obviously these limits are not closely defined and there is no sharp line of demarcation between adjacent groups. In general, as the pigmentation is increased, the gloss decreases proportionately; as a result, the amount of binder used per given unit of volume of pigment is determined by the film surface characteristics desired. Other film properties and paint characteristics are also influenced by these ratios. Suspension, consistency, brushing, leveling, hiding power and color are among the properties affected.

Some definition of terms used should be given. First we give a definition of brightness[26] as applied to a paint film; this is the same as the "coefficient of reflection." The *brightness* of a surface giving out light is the quantity of light emitted in the direction perpendicular to the surface, per unit area of surface; also it is the attribute by which a bright shade is distinguished from a darker shade of the same hue. The term is sometimes incorrectly used to indicate that a transparent material is free from turbidity or suspended matter. *Gloss*[27] as applied to a paint film may be defined as the luster, shininess, or reflecting ability of a surface, or the ability of a surface to reflect light regularly. It is based on the degree of optical smoothness of a surface, variations in smoothness being microscopic. Means of determining the gloss of paint finishes are given under A.S.T.M. Designation—D-523-44-T.[28] Gloss readings as given in detail in the A.S.T.M. Specifications are classified as in Table 45.

Table 45. Gloss Classifications (A.S.T.M.).

Surfaces having Gloss Values	Classed as	Usually referred to as
Above 70	A	High or full gloss
70 to 30	B	Semi-gloss or medium gloss
30 to 6	C	Eggshell
6 to 2	D	Flat to eggshell (Intermediate)
2 and under	E	Flat

An example of an interior paint formulation is given in Table 46. This formulation is made to meet the Federal (U. S.) Specification TT-E-506-A Amendment #1 (Gloss White).[24]

It may be seen from the constants on the paint mentioned in Table 46 that it falls in the gloss paint class, referring to the pigment volume and the P/B ratio. In this formulation the pigment is composed of a titanium rutile calcium pigment, which is a combination of 30 per cent rutile titanium dioxide and 70 per cent calcium sulfate. This pigment gives whiteness of color, brightness, hiding, ease of brushing, and a tendency toward a thixotropic body in the paint. The precipitated calcium carbonate is transparent in oil, *i.e.*, it has an index of refraction close to that of the vehicle, has no appreciable hiding power. It does aid in giving body. It does not detract from the gloss and does not affect leveling of the finished paint. Aluminum stearate or soya lecithin, as the case may be, is added to aid in suspension properties and also in preventing sagging of the paint when applied. The varnish, of course, supplies the non-volatile binder for the paint. In addition it contributes to the proper consistency, brushing, leveling, gloss, drying and flexibility of the finished paint. The mineral spirits is added to facilitate the above vehicle characteristics, such as consistency, brushing and leveling. Cobalt and lead naphthenates are added to facilitate drying of the finished paint in a reasonable time, usually 16 hours under normal conditions. This paint is typical of an interior gloss paint used by the Federal Government in emergency housing and is also similar in construction to interior gloss paints used by the home owner, master painter or maintenance painter.

Table 46. Interior Paint Formulation.

	Pounds	Gallons
Titanium rutile calcium pigment	392	14.48
Precipitated calcium carbonate	110	4.93
Aluminum stearate*	1.2	.12
Ultramarine blue	.078	—
40 Gallon ester gum dehydrated castor oil varnish (55% N.V. by wt.)	540.8	72.72
Mineral spirits	54.2	8.35
6% Cobalt naphthenate drier	1.9	.24
24% Lead naphthenate drier	3.2	.33
	1,103.378	101.20

Gallon weight	11.03#	Brushing	Good
#Oil/gallon	2.21#	Leveling	Good
Pigment volume	34.8%	Sagging	None
P/B ratio	1/1.88	Gloss	OK
Pigment weight	45.62%	Drying	OK
Vehicle weight	54.38%	Flexibility	OK
N.V. in vehicle	50.0%	Brightness	84.0%
Consistency	73 K.U.	Contrast ratio at .003" film thickness	92%

* Soya lecithin (2.5#/100 gal.) gives better gloss than aluminum stearate when used as a suspending agent.

Some mention should be made of hiding power, as it affects film properties of both interior and exterior paints. In speaking of hiding power,[8] reference is usually made to dry film hiding; however, in many instances, the wet film hiding is equally important. Both wet and dry film hiding power will vary appreciably depending upon the pigments used and the paint composition involved. High oil absorption (high consistency) pigments offer distinct advantages in hiding power at low binder contents at the expense of film properties. This advantage is minimized at higher binder contents. Other factors, the most prominent of which is film thickness, also have a direct bearing on hiding power. This does not mean that increasing film thickness is directly proportional to the hiding power, but it does minimize differences in relative hiding power between pigments and emphasizes the necessity of controlling spreading rates when hiding comparisons are made. According to Rhodes and Starr,[4] the addition of small quantities of carbon black or Prussian blue to white paints definitely increases the hiding power while decreasing the brightness only slightly. Larger amounts of colored pigments have a more pronounced effect. It was also found that with very small quantities of Prussian blue the ratio of the increase in hiding power to the decrease in brightness is greater than with carbon black. The addition of aluminum powder greatly increases the hiding power but lowers brightness and causes the dry film to have a flecked appearance. Rhodes and Starr suggest as advantageous the use of aluminum powder in undercoats for white finishing coats.

Table 47 shows the hiding power in square feet per pound of white pigment as determined by various investigators.[5,6,7]

Table 47. Hiding Power of Whites.

Material	Pigment % for #1	Hiding Power (Square Feet per Pound) 1	2	3	4	5	6
Titanox A	50	57.9	93.6	115.0	51.2	58.7	180.
Zinc sulfide	70	35.2	56.2	58.	26.5	42.8	108.
Titanox C (25% TiO_2)	50	26.4	32.8	48.	26.1	37.9	74.
Titanated lithopone	60	27.3	32.8	44.	—	—	67.
Hi Strength lithopone	60	27.8	32.8	44.	23.8	33.9	67.
Titanox B (25% TiO_2)	60	22.9	28.3	40.	23.1	31.8	58.
Lithopone	60	23.4	23.4	27.	24.	30.	43.
Antimony oxide	—	—	—	—	22.1	30.9	—
Calcium base lithopone	60	24.4	30.5	—	—	—	—
American zinc oxide	60	22.5	—	—	25.2	30.2	—
French zinc oxide	60	17.8	—	20.	—	—	—
35% Lead zinc oxide	60	20.0	—	—	17.8	23.6	—
Lead carbonate	77	13.2	—	15.	14.	22.9	—
Lead sulfate	77	11.9	—	13.	12.7	14.3	—

1. R. A. Morrison (Western P & V), Cryptometer Refined Linseed-Pigment Percentage given before each one.
2. Krebs; their relationships recalculated with lithopone 23.4.
3. (A.S.T.M.) R. L. Hallett; Proceedings American Society Testing Materials 30, Part 2, (1930). Brush-out test over black stripe.
4. Gardner Manual: Cryptometer.
5. Gardner Manual: Lino brush-out.
6. Analytical Edition *Industrial & Engineering Chemistry,* Volume 6, p. 393 (Nov. 15, 1934) Titanium Pigment Company. Brush-out over checker board of black 5% and gray 25% brightness, 28% pigment volume in all cases except first two which are 15% pigment volume.

Floor, porch and deck enamels are also influenced by the P.V. (pigment volume) ratio. In these enamels, the P.V. ratio may vary from as low as 6 per cent to as high as 35 per cent, depending upon the pigmentation used; that is, a pure rutile titanium dioxide tinted to the ordinary grays used to such a large extent for floor, porch and deck enamels would be formulated at 6 per cent P.V. The introduction of other hiding pigments such as lithopone, leaded zinc, and the reduced titanium barium or calcium-base pigments, or the addition of extender pigments such as magnesium silicate, calcium carbonate or barium sulfate will alter the P.V. and will of necessity raise it toward the high level of 35 per cent. The vehicles used in floor, porch and deck enamels also vary depending upon the properties desired. Tests run comparatively have shown that a glycerylphthalate type vehicle of medium oil length gives the best general performance. This is followed by modified alkyd combinations, then modified synthetic resin vehicles of 25 to 35 gallons in oil length. Such statements are based on tests run by various manufacturers and there may naturally be differences in opinion. Let it suffice to say that generally the above vehicles will rate in the order given.

Exterior enamels follow in much the same classification as interior enamels as far as pigment volumes are concerned, *i.e.*, they may fall within the range of 20 to 33 per cent by volume based on the total solids. This means a P/B ratio of 1/2.0 to 1/4.0. There are certain exceptions to this classification; in black enamels, for instance, which contain a very low percentage of pigment (2 to 4 oz. of black per gallon of vehicle), the P/B ratio is considerably higher. Exterior enamels, in addition to being influenced by pigment volume, are quite naturally affected by the type of pigment used and by the nature of the binder in the vehicle. Exterior architectural enamels in white and light tints are usually made with rutile type titanium dioxide in the white and tints, and with permanent colors such as those given for house-paint tints. The binder portion of the vehicle usually consists of a long-oil glyceryl phthalate type resin modified with soya, dehydrated castor or linseed oils. In darker shades these enamels are practically the same as the trim paints given previously. Enamels other than for architectural usage are designed for the purpose intended, pigmentation and vehicle binder being chosen to suit any given need. Pigment volumes follow the general limits as given.

The automotive enamel field is a highly specialized one where various rigid requirements must be met. There are two broad types of automotive enamels; one is the air-dry type made largely for refinishing passenger cars, trucks and busses. This type is largely applied by spraying and is made to dry as rapidly as possible in order that two coats may be applied within 15 to 30 minutes, *i.e.*, it should be set up sufficiently to take a second coat immediately after the first coat has been applied. Pigmentation is generally rutile type titanium dioxide for white and light tints. Darker colors use permanent pigments alone or in combination in order to obtain the many shades desired in the automotive industry. The binder portion of the vehicle ranges from a short-oil glyceryl phthalate type resin to a long-oil glyceryl phthalate, depending upon desired speed of drying. Present types on the market dry to take two coats as stated above, and may be masked with masking tape within 4 to 6 hours. This is necessary in a two-color job. These enamels dry hard overnight. Automotive enamels of the air-dry type also find many other uses by a change in the solvents in the vehicle to enable them to be applied by brushing. These uses include refinishing store fronts, gasoline pumps, implements and tractors, structural steel, tanks for storage, and numerous other items.

The second type of automotive enamel is the baking type used primarily in production finishing of new automobiles, trucks and busses. Here again the pigmentation is similar to the air-dry type. The vehicle is usually shorter in oil length, and medium to short-oil alkyds are used. The vehicle may be modified with urea, melamine or urea-melamine resin combinations. The amount used depends largely upon the hardness of dried film desired. Generally the percentage of modification is 25 per cent based on the glyceryl phthalate resin solids. Percentages up to 25 have given very satisfactory exterior durability. Baking schedules vary, but one hour at 250°F is used by a number of concerns.

Another large field for the use of paint products is the refrigerator, washing machine, stove and kitchen cabinet lines. These materials are largely finished in white, and they also require highly specialized finishes which must stand up under rigid test conditions set by the manufacturers of the various materials. Enamels of this type may be pigmented with anatase or rutile type titanium dioxide and tinted to off-white shades with ultramarine blue, mineral violet toners, indanthrene blue, lampblack, cadmium reds and bordeaux red. These colors may be used alone or in combination, depending upon the shade desired. The P/B ratio is similar to that encountered in most enamel formulations, *i.e.*, 1/2.0 to as high as 1/6.0, depending upon the finished requirements of the enamel. The binder portion of the vehicle usually consists of a medium to short-oil glyceryl phthalate-type resin in combination with urea, melamine or urea-melamine resins. The oils used in modifying the glyceryl phthalate are of the drying oil and non-drying oil type, which are noted for their pale color and color retention both in the baking process and subsequent exposure to the light, heat or other atmospheric conditions encountered in service. The ratio of glyceryl phthalate resin solids to amine resin solids varies from 1 to 1 to as high as 4 to 1, depending upon specific requirements. These finishes are largely applied by spraying and are baked at temperatures from 250 to 350°F and at times of 1 hour to as low as 10 minutes, depending upon specifications. Some of these finishes are baked under infrared lamps at times as low as 2 to 3 minutes up to 10 minutes and peak heats up to 400°F.

Primers are often used under the above enamels, especially where severe conditions are encountered in tests and in service. These primers use pigments similar to the enamels; however, inert pigments are added to provide additional desirable characteristics, such as a lower luster, which should be of a flat to eggshell sheen in order to take the finish coat satisfactorily. Here again the primers are baked after spraying under conditions similar to the enamels. Some flash-dry primers are being used; in this case the primer is sprayed and allowed to air-dry, usually up to a maximum of 10 minutes. The solvents are allowed to evaporate and then a second coat of the finishing enamel is applied without baking the primer first. The binder in the primers is glyceryl phthalate resins similar to those in the enamel. In some cases amine resins are added but generally in much lower amounts. Pigment binder ratios are higher than those in the enamels and follow more closely the ranges given for interior flat and semi-gloss paints.

A large field for paint use is the farm, *i.e.*, exterior house paint, trim colors, and exterior enamels, including farm implement and tractor enamels. Red barn paints are possibly one of the largest requirements. These have been formulated in numerous qualities depending upon consumer requirements. Here again a first-quality barn paint will usually be made from high-grade iron oxide pigments such as Venetian Reds and/or Persian Gulf Oxides in combination with extender pigments such as calcium carbonate and/or magnesium silicate. The optimum ferric oxide content ranges between 24 to 45 per cent by weight of the pigment. Pigment binder ratios vary widely; however, the range is within that of the pre-war type exterior oil paints for maximum durability. Vehicle binder again varies widely; linseed oil vehicles give best durability. Many vehicles are composed of the various drying oils, such as linseed, fish or soya, in combination with oleoresinous varnishes based on lime-hardened rosin.

A discussion has been given on some principles of formulation of the major paint materials used in the home and on the farm, as well as of some of the industrial paint materials used in large volume. There are numerous special industrial finishes that have not been mentioned; these include railroad finishes for both station and rolling-stock use, chemical-resistant and fume-resistant finishes for maintenance use in chemical plants, bakeries, dairies, etc., marine finishes, office-equipment finishes, and various specialty finishes such as wrinkles, metallic type, spattered and veiled finishes.

As mentioned above, railroad finishes may be divided into two classes —for station use and for rolling stock use. For station usage the finishes are similar to those used in the home, *i.e.*, exterior type oil paints, trim paints and interior paints and enamels. As a rule the quality of station paint finishes is of the best, as the upkeep of any large railroad is tremendous and the less painting required the lower the upkeep charged to painting will be. For rolling stock use the interior finishes of coaches, Pullmans and baggage cars are similar to the interior finishes discussed. They are usually furnished in a semi-gloss to eggshell sheen. The exterior finishes on the same cars are usually high grade glyceryl phthalate enamels similar to the exterior architectural enamels discussed previously. Colors are usually dark, *i.e.*, olive greens, maroons, etc. Newer cars are coming in, however, made of the non-ferrous metals such as aluminum alloys. These are being finished with enamels more on the automotive type, and colors are lighter and brighter than those used on the older cars. On freight cars and gondola cars, both wood and metal, red or brown metallic paints and black paints are used. Originally these were made as paste paints in linseed oil and reduced by the railroad or car builder with a reducing oil. In the years before the last war, however, ready-mixed freight-car paints of the quick-drying type came into use. These paints permit the application of two coats a day, allowing the first coat to dry up to 4 hours before recoating; the two-coat system must be able to take a stencil the following day. These formulations are made using iron oxide pigments, synthetic or natural, and carbon blacks either alone or in combination with extender pigments. As a rule the P.V. is in the enamel range. The percentagé of iron oxide used is close to that recommended for barn paints. The black pigmentation varies from straight black to as high as 80 per cent extender pigments by weight with the black. Vehicles may be long oil glyceryl phthalate, modified phenolic, or long oil oleoresinous types.

Marine paints include bottom paints of the anti-corrosive type as a primer for use on steel hulls and of the anti-fouling type as a finish coat on steel hulls and as a primer and finish on wooden hulls. Anti-corrosive paints must dry rapidly, reduce corrosion to a minimum, provide a suitable surface for succeeding coats, and have good resistance to corrosion. Pigments used include chrome yellows, zinc yellow, zinc oxide, zinc powder, basic lead chromate, red lead, iron oxide and blue lead.[8] The vehicles used include a combination of rosin, coal tar, manganese linoleate and thinners; a combination of shellac and pure oil thinned with alcohol;[9] chlorinated rubber vehicles; and more recently, medium oil length spar varnish types.[8]

Anti-fouling paints are used essentially to prevent the growth and collection of marine fouling organisms. Toxic ingredients are used in the pigmentation. Many different toxics have been tested but the most effective materials used are cuprous oxide and mercuric oxide. Recent work by Ketchum, Ferry and Burns[10] indicates that 30 per cent of cuprous oxide by volume is necessary, and that in order to prevent fouling the copper leaching rate should be of the order of 10 mg/sq cm/day. Iron oxide, zinc oxide and extender pigments are added to secure proper viscosity and other physical characteristics. Vehicles include shellac, pine tar and alcohol; rosin, coal tar, manganese linoleate, and thinners; recently, a vinyl-type resin base has shown exceptional results.

Boot-topping paint is applied to the hull of the vessel between the light load and deep load line. Conditions of exposure are severe and add abrasion and erosion failures to the finish. Topside paints are applied to the hull above the deep load line. They are subjected to severe conditions also. The vehicles used in both cases are phenolic-base varnishes with tung oil in medium to long oil lengths. Recently waterproof alkyd resin vehicles have been used successfully. Pigmentation is unlimited and selection depends upon color desired and durability characteristics such as light fastness, chemical inertness and chalking resistance.

Deck and superstructure paints are formulated like standard industrial protective paints. Reference has been made previously to floor, porch and deck enamels and exterior architectural enamels, which may be used satisfactorily. Interior ship paints are very similar in construction to the interior finishes discussed. Fire retardance came to be of considerable importance during World War II, however, and various pigments and some special vehicles have been used for this purpose. Pigments include antimony oxide and calcium carbonates. Vehicles include chlorinated resins, such as chlorinated rubber resins and chlorinated oils and plasticizers, such as chlorinated paraffins and diphenyls.

In wrinkle finish formulation pigments control the "texture" of the wrinkle to a marked degree. The general rule is that as pigment volume is increased the texture of the wrinkle becomes finer until a small wrinkle pattern, dull in sheen known as "suede," is developed. Pigment volume accordingly follows the ranges set up for interior finishes through enamel to semi-gloss. Various pigments, such as lithopone, titanium dioxide, and zinc oxide, are listed as stabilizers[11] by Toll; these produce substantially uniform patterns in wrinkle finishes of all colors. In the matter of producing uniform texture with extender pigments, interesting results were obtained recently[12] by using a colloidal calcium carbonate having an average particle size less than one-tenth of a micron. It is claimed that low sheen finishes of the suede type are readily produced by increasing the ratio of this extender to hiding pigment. The hiding pigments used are not limited except as to desired color and color retention under heat, depending upon the maximum temperature used in baking the wrinkle finish and in actual service conditions. The vehicles used include both oleoresins and glyceryl phthalate. Tung oil is largely used, although others have been employed, including oiticica oil. The wrinkling mechanism is supposedly due to tung oil frosting in drying; genuine wrinkling is due to the extreme film thickness employed. Various theories have been proposed[13,14,15,16,17] to explain wrinkling. Hyman and Greenfield state that wrinkling of tung oil is due to minute quantities—four to five parts per million—of nitrogen dioxide in the atmosphere. The polymer size of the varnish used must also be taken into account. Root and Moore[14,17] have shown that aeration or blowing of oleoresinous and alkyd polymers intensifies wrinkling. This may be due to the fact that large polymers are formed by the fixation of oxygen, and these associate to give higher molecular weight polymers, which show improved wrinkling tendencies because of their size.

So-called "top" driers are always used with wrinkle finishes. These are cobalt and manganese types. High concentrations are usually employed—0.2 to 1.2 per cent of manganese or cobalt as metal and sometimes lead at 2 to 4 per cent, all based on the varnish solids used.

Throughout this chapter very little mention has been made of primers for wood and metal; undercoaters for wood; primer-surfacers for metal; special primers for use on non-ferrous metals; and primers for concrete, brick, stucco, plaster, etc.

Wood primers as used in two-coat house paint systems[18] are usually formulated with pigment volumes varying from 35 to 40 per cent. The penetrating power of the vehicles is controlled by proper selection of the oil-varnish combination. Pigmentation in this type of primer is generally white lead carbonate, anatase titanium dioxide and siliceous extender pigments. Percentages by weight are approximately 35 to 40 per cent of white lead, 10 to 15 per cent of titanium, and the balance extenders.

By wood undercoaters, reference is made to those used largely in interior enamels. In this case we may refer again to the pigment-binder relationships as given for interior paints and enamels. Specifically, enamel undercoaters should fall between the flat wall range and the semi-gloss range. At that pigment-binder ratio, optimum holdout of enamels is obtained. This means that the P/B ratio would fall close to 1/1. Enamel holdout is obtained largely through the vehicle effect plus proper selection of the pigments used.

Primers for concrete, brick and stucco are usually similar in composition to the primers used for wood. Satisfactory durability has been obtained in their use.

Primers for plaster as used on the interior of buildings and homes vary widely in their composition. Pigment volumes or pigment-binder ratios follow those given under interior finishes and fall in the range of semi-gloss to gloss paint finishes. The pigments used are orthodox types, and include lithopone and titanium pigments with extenders of the silicate and carbonate types. Vehicles cover a wide range, the common types being long-oil resin varnish combinations with blown oil added. Newer varnish combinations include short to medium phenolic tung oil combinations plasticized with methyl abietate. Rubber-base paints have also been used to some extent on plaster walls due to their high degree of alkali-resistance.

Metal primers and primer-surfacers for use on ferrous and non-ferrous metals cover a specialized field. Metal primers for iron or steel were originally red lead oil-type primers, and they are still used to a large extent on structural work. Pigment volumes on pure red lead paints range from 25 to 35 per cent. This is lowered correspondingly when silicate extenders are added up to 40 per cent by weight of the pigment, or when the linseed oil is replaced in whole or in part with oleoresinous, phenolic or glyceryl phthalate varnishes. Pigment combinations have been developed in recent years using red lead, basic lead chromate, blue lead, and zinc yellow combined with iron oxide pigments and silicate extenders, using the above-mentioned vehicles. In these formulations pigment volumes vary from 25 to 45 per cent, depending upon the combination of pigments.[19,20] Under non-ferrous metals, galvanized iron requires special primers. Zinc dust primers[21] are used largely for this purpose. Pigment volume varies depending upon the color desired. The most common formula is gray in color and contains 80 per cent zinc dust and 20 per cent zinc oxide in the pigment by weight and 90 per cent raw linseed oil and 10 per cent lead-manganese drier and thinner in the vehicle by weight; the total pigment is 80 per cent and the vehicle 20 per cent by weight. This would mean a pigment volume of 35 per cent. In other colors the zinc dust is reduced correspondingly and replaced with iron oxides, iron blues, or chrome greens, depending upon the shades desired. In these cases the pigment volume may vary from 20 to 30 per cent. Zinc dust paints may be used both as primer and finish coats over galvanized iron.

Primers for aluminum alloys gained in usage during World War II due to the wide employment of aluminum in aircraft and other fields. These primers are largely based on zinc yellow in combination with silicate type pigments. Vehicles vary widely, but the commonly used type for aircraft is based on phenolic alkyd resin combinations. Pigment volumes in these formulations vary from 30 to 35 per cent. Similar zinc chromate primers have been developed for use on steel hulls and interior steel of ships. These primers are of the brushing type, and have titanium dioxide plus raw sienna pigments in addition to the zinc yellow–silicate extender used in the aircraft type primers. Zinc yellow is reduced to approximately 50 per cent by weight, and extender pigment is increased to 30 per cent by weight. Pigment volumes in this type of primer average 40 per cent. Recent uses of aluminum in the manufacture of metal roofing and siding for homes require a primer of known durability; the above-mentioned primer would be satisfactory. Zinc yellow primers of widely different compositions have also been used as priming coats on aluminum in the past.[22]

Primers and primer surfacers in the industrial field may be of two distinct types depending on whether they are applied under air-dry or baking automotive finishes. In the air-dry types the primer is usually a neutral gray in color or is made somewhat lighter in color than the finish coat of enamel. These air-dry materials are made largely on short to medium-oil glyceryl phthalate-base vehicles, alone or modified with resins. The primers are usually sprayed and dry sufficiently fast to be recoated in 1 hour to 24 hours with the primer surfacers. In some cases the primer is omitted and the primer surfacer used alone. Pigmentation in the primer may contain some rust inhibiting pigments. The primer surfacer contains pigments which make for ease of sanding as well as enamel holdout of the finish coats. Pigment volumes in the primers usually follow those given for semi-gloss to flat finishes. This is also true of the primer surfacers, although the majority will range toward the flat wall finish pigment volume.

Baking types as used in production are based on either glyceryl phthalate vehicles or oleoresinous vehicles as far as both primers and primer surfacers are concerned. Pigment volumes will follow the same general pattern as given for the air-dry types. Pigmentation is again similar to that encountered for the air-dry types. Specifically, iron oxide pigments plus some rust inhibiting pigment and extenders are used in both kinds of primers. In the primer surfacers, the colors used are usually gray or red, and in these materials the pigments are largely iron oxide with extenders or lithopone and/or titanium dioxides with extenders.

In the material given in this chapter the influence of the pigment volume or pigment-binder relationships to paint characteristics has been stressed. However important these may be, the various pigments and vehicles used in formulations will alter paint properties so that there is a definite interrelation or overlapping. That is, regardless of pigment volume or pigment-binder ratio, it is necessary to dovetail exactly the pigments and vehicles used in order to obtain the desired physical and chemical properties in the finished paint product.

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Chapter 19

Resin and Varnish Manufacture

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"Varnish" is defined by the American Society for Testing Materials as a liquid composition which is converted to a transparent or translucent solid film after application as a thin layer. "Resin" is defined by the same Society as a solid or semi-solid, water-insoluble, organic substance, with little or no tendency to crystallize. Other definitions of resin may include breaking with a conchoidal fracture. The two words are continually confused. The ultimate user refers to the clear coating on his furniture as varnish when it is obviously solid and therefore a resin. Conversely, some manufacturers refer to certain types of varnishes, particularly glyceryl phthalates, as resins, when obviously they are liquids and in some cases would not be particularly solid even without their volatile solvent.

The origin of the word "varnish" is obscure, but it was apparently one of the names for the natural resin which we now call amber, which was one of the early coating materials. The word varnish in legend goes back through a series of translations including Verenice to Berenice, which was supposed to have been the name of an Egyptian queen whose beautiful golden tresses were matched in hue by the color of amber resin brought back by returning warriors. Varnish and resin are therefore interrelated terms and form the principal components of almost all coating vehicles.

The process of transforming liquids of as low a viscosity as linseed oil to solids in a dry paint film is obviously accompanied by a very great increase in viscosity. Viscosity changes and control are therefore a primary part of varnish formulations and manufacture. Viscosity increase in either the manufacturing process or in the drying of a film is usually gradual, with no sharp increases comparable to that which accompanies the solidification of an inorganic salt. Organic varnish molecules, being very large and irregular, develop no crystallization; the increase in viscosity of varnish upon drying may be due both to increase in molecular weight by chemical transformations and to building up of secondary valence forces when solvent evaporation permits.

Film formation from such molecules cannot have much regular orientation but only a random arrangement. Since the desirable property of toughness is related to good chemical orientation in linear, planar and even three-dimensional systems, such structures have to be built into molecules present in the varnish, leaving only a minor amount of building to be done during the drying of the film. For this reason the character of the oils and primary resins going into varnishes is of utmost importance in relation to the varnish maker's two principal problems. These are (1) Viscosity control during manufacture and application, which for varnishes range from 0.1 to 1,000 poises for various special purposes; and (2) attainment of desired physical and chemical properties of the ultimate film by proper selection and processing of varnish raw materials.

The complexity and importance of this problem may be judged by noting that varnishes are the principal components of coatings, which are produced with a value of about $750,000,000 annually in the United States. Although consumption data on all varnish materials are not readily available, it is reported by the Bureau of Census that about 500,000,000 pounds or 65,000,000 gallons of drying oils are consumed annually in coatings. Approximately half of this is the amount of resins or resin-forming materials which would be combined with most of the oil, exclusive of oil in house paint, to produce somewhere between 100,000,000 and 200,000,000 gallons of varnish a year.

Complexity of use, although impossible to cover in complete detail, can be illustrated by a tabulation of some important types of uses; these account for the vast bulk of actual coatings produced and can be used for discussion as examples of varnish formulation problems. Such an outline follows:

Trade Sales
  (1) Pigmented interior wall finishes.
      Gloss
      Semi-gloss
      Flat
  (2) Trim and furniture
  (3) Floor and deck (interior and exterior)
  (4) Misc. screen enamels
  Unpigmented roof coatings; putty
Transportation
  (1) Automotive (formerly coach)
  (2) Railway freight car
      Passenger car (interior and exterior)
  (3) Airplane
  (4) Tractor and farm implements
  (5) Ships (marine)
Household Appliances
  (1) Refrigerators, stoves, washing machines
      kitchen cabinets

Furniture Varnish
Maintenance Factories' mill whites,
  oil tanks
Graphic Arts
  Exterior signs
  Interior signs
  Inks
  Label varnishes
Can Coatings
Electric Insulation
Textile Printing

Materials and their properties for meeting performance requirements of these products offer a wide variety of choices in formulation with due regard to raw material costs, varnish equipment availability, application method (brushing, spraying, dipping, roller coating) and performance requirements of the dried film. Materials of commercial importance include the following:

Drying oils, in order of hardness
  Tung
  Oiticica
  Fish oil fraction, high iodine value
  Perilla
  Linseed
  Dehydrated castor
  Fish
  Corn and cotton oil fractions
  Soya
  Tall (½ is fatty oil)
  Plasticizers, non-drying

Resins, in order of toughness
  Cellulose esters and ethers
  Vinyls, acetate, chloride, butyral
  Styrene and other substitutes

  Phenolic
  Phthalate
  Rosin esters modified with phenolic or maleic anhydride
  Hydrocarbons: coumarone, indene, terpene, etc.
  "Natural": Congo, Kauri, East India
  Rosin esters
  Rosin

Driers, in order of top drying
  Cobalt
  Manganese
  Lead
  Zinc
  Calcium

Volatile solvents, including aliphatic, naphthenic and aromatic hydrocarbons; alcohols, esters and ketones, all of various evaporation rates.
Anti-skinning agents
Miscellaneous

The performance expected of these materials will include a wide variety of requirements such as:

(*a*) Drying times *without* heat, ranging from a few minutes for lacquer to a few hours for trade sales enamels and to several days for cheap barn paint.

(b) Drying times *with* heat ranging from a few seconds at 700°F for insulating varnishes on wires, to an hour or so at 250°F for many general industrial enamels, down to several hours at 120°F for forced drying of varnishes on wooden furniture.

(c) Toughness, for actual flexing of wire coatings, impact in floor varnishes, or simply as an indirect measure of weather resistance.

(d) Color, which really means paleness and its retention.

(e) Resistances of various sorts, including resistances to hot and cold water, to alkali (soaps), sunlight, oxygen and various specialized reagents.

(f) Surface texture with respect to high or low gloss and to relief patterns, as in wrinkle finishes.

(g) Stability of the liquid prior to use including:

  (1) Clarity initially and in storage.
  (2) Viscosity stability in storage; one indication of probable instability is the appearance of a tail on the bubble, in a bubble-tube viscosimeter. This is apparently the beginning of gelation.
  (3) Lack of skinning in full or partly full closed packages.

(h) Miscibility with other oils, varnishes or solvents which may be encountered in either formulation or application by the consumer.

(i) Lack of undesirable characteristics such as:

  (1) Gas checking on drying in atmospheres fouled by incompletely burned fuels, producing an irregular, semicrystalline pattern from some combinations using the conjugated oils, *i.e.*, tung, oiticica and dehydrated castor oils.
  (2) Wrinkling in either air draft or direct sunlight, due largely to too rapid dying of the surface of a film which remains liquid underneath.

Any varnish-formulating problem involves balancing a given set of desired performance requirements against the costs of available oils and resins and their processing, and then choosing, combining and testing the proportions of materials needed to fit the requirements. World War II gave us much practice in this.

Experimental batches are made in a manner approximating as nearly as possible the manufacturing methods available on a large scale. Aside from a few important and more or less special resins and varnishes, such as cellulose lacquers, vinyl coatings, etc., most coating vehicles are combinations of resins and oils under heats ranging up to 330°C or 626°F. Heat is needed for several essential purposes:

(1) Polymerization of oils
(2) Isomerization of oils (thermolizing tung oil)
(3) Dispersion of resin in oil
(4) Cracking or running of resins for soil solubility
(5) Esterification
(6) Distillation of drying components, as in the low acid value bodied oils and the removal of oils resulting from the cracking of resins.

All these processes are carried out in essentially the same simple type of equipment, which is often without mechanical agitation. Older types are portable kettles on wheels which are only slight improvements over a bucket and stirring paddle. They are commonly heated directly by coke, oil or gas fires. The sizes of these portable kettles range up to 250 gallons, a common size being 38 inches high and 38 inches in diameter, with a gross volume of 190 gallons and a net working volume of about 150 gallons. These portable kettles often lack mechanical agitation and therefore are limited to simpler operations, since they cannot produce the thorough agitation needed to promote the alcoholysis of an oil which often precedes an inter-esterification reaction.

Portable kettles are gradually being replaced for reasons of economy, versatility and quality by larger, mechanically agitated kettles, holding up to 8000 gallons, the 1000-gallon size being common. The size is limited by diminishing heating rates and difficulty in cooling to counterbalance exothermic heats of reaction. The larger kettles are most often heated, either directly by oil, gas or electricity or indirectly through the medium of Dowtherm, high-pressure steam, or circulating oil. Of the indirect media, Dowtherm is finding favor in the United States; Germany is reported to have used steam at about 1000 lbs. pressure in coils welded to the outside of the kettle. Kettles are commonly made of stainless steel, Inconel and related nickel alloys, aluminum, copper and carbon steel in about that order of preference.

Cooling means may be built into the kettle, either coils inside or outside, or an outside jacket to provide circulation of oil, Dowtherm or water. Water may also be sprayed directly into the varnish batch for cooling. Cooling is necessary both for control of exothermic reactions and for reducing the temperature of the varnish base to a safe and practical point for dilution with volatile solvents.

Dilution, or thinning of the varnish base, as it is commonly called, is somewhat hazardous, particularly in the older style portable kettles, where it is necessary to cool the varnish base to near the boiling range of the solvent and then add the solvent, with judicious manual stirring and with some solvent loss due to volatility. The larger kettles usually discharge their finished varnish base into a separate thinning tank, usually fitted with a tubular condenser or a water jacket around the tank, or both.

Driers may be cooked in, using the metal salts or oxides, or may be added as soluble soaps in the thinning operation.

A continuous process for making varnishes and resins is an ideal possibility that is not yet too practical because of the small volume of individual varnishes, which in turn is due to the thousands of specialized uses of coatings. Representative processes of manufacture can best be shown by examples.

(1) Tung Oil

Tung oil is polymerized by heat in at least three different ways:

(a) Simple heat-bodying (polymerization) at 350 to 450°F for an hour or so to yield a bodied oil which is not gas-proof.

(b) Partial gas-proofing by rapid heating to 560 to 600°F, holding this temperature just a few minutes and then quenching by very drastic cooling, either with water inside or outside the varnish kettle, or with some cold material which is desired in the finished product. This can be cold but previously polymerized tung oil, or some other oil, or a readily soluble resin.

(c) Practically complete gas-proofing is attained by a continuous process in a pipe coil system where the tung oil is heated to the range of 650 to 725°F and cooled again, both with extreme rapidity.

Gas-checking is thought to be associated with conjugated double bonds, which in tung oil are believed to be in the 9, 11, 13 positions on its elaeostearic acid. Gas-proofing of tung oil probably involves the shifting of some of these bonds to isomeric and non-conjugated positions; by analogy to other oils this makes for slower polymerization and surface drying. The conjugated positions, on the other hand, account for the extreme rapidity of polymerization of tung oil. These three types of cooking then illustrate the competition between polymerization and isomerization. Furthermore, polymerization rate is directly proportional to temperature only up to a peak in the vicinity of 600°F, above which the polymerization rate diminishes.

Viscosity measurement during polymerization is of primary importance in manufacturing control. Traditional methods in the varnish maker's art include rule of thumb methods in judging the length of string of the oil as it drops from the *hot* spade, used in stirring the batch, or the length of string obtained from a *cold* drop upon withdrawal from the drop by the varnish maker's skilled finger. The more modern and most commonly used method is the bubble-tube viscosimeter, which permits determination in a few minutes with simple, inexpensive apparatus and with errors of about 10 per cent, which accuracy is quite adequate in consideration of the wide range of 0.1 to 1000 poises with which the varnish maker is concerned.

Gelation is the end product of these polymerization processes, and accidental gelation may represent a real economic loss, since the gelled mass is of little use except where it can be redissolved with a substance such as rosin to give a product that has some salvage value.

(2) Oiticica Oil

Oiticica oil behaves somewhat like tung oil, but the carbonyl group on the fourth carbon atom of the licanic acid in it makes it unstable at high heat, so that only temperatures below about 525°F are practical.

(3) Perilla and Linseed Oils

Perilla, linseed and the high iodine value fraction of fish oil are similar to one another in being substantially non-conjugated, and therefore require several hours at 575 to 600°F to gel. Control is therefore much easier with these than it is with tung oil, unless the amount of oil is so large that the heat from the exothermic reaction raises the temperature above 600°F. Polymerized linseed oil is used regularly in a wide variety of viscosities up to about 1000 poises for use in printing inks.

Acid values may increase in this slow polymerization from substantially zero in the original oil up to about 25 in the extreme viscosities. This represents up to 12 per cent dissociation of the oil, due to long exposure to high heat. This acidity may be objectionable in some products, such as those which use basic pigments, zinc oxide for instance, as it may cause gelling by formation of poorly soluble zinc soaps and make the varnish unusable. Control of acid value is therefore important; it is commonly done by keeping the holding temperature down to a practical balance between slow dissociation and slow polymerization. Acid value may also be kept down by application of either vacuum or an inert (non-oxidizing) gas to sweep out fatty acids, which may be recovered in a separate condenser.

(4) Other Oils

Dehydrated castor oil has a lower iodine value than the above oils, but it is partly (about one-third) conjugated and so is rather fast in polymerization rate, particularly since some grades are partially polymerized in the dehydration process.

Soya and walnut oils, with still lower iodine values, polymerize so slowly that extremely high viscosities are not practical without the aid of polymerization catalysts, of which anthraquinone and sulfur dioxide are two practical types.

Corn and cottonseed oils are substantially non-drying and not readily polymerized, but these oils or fractionated oils from them are used in phthalate varnishes, of good color retention.

Coconut oil and its acids are even better for non-yellowing phthalates.

(5) Oil-Resin Combinations

Oil and resin combinations may in many cases be considered as similar to the above types of oil polymerization, with sufficient modification to accomplish: proper dispersion of the resin, inter-reaction with the oil, and resin formation during the heating process.

The dispersion problem is clarified somewhat by recalling that oil molecules are relatively small—of about 1000 molecular weight for monomers and 2000 for dimers—whereas resins may vary in molecular weight from as low as 330 for rosin and 1000 for the glycerin ester of rosin up to extremely high values for alkyds (in the general sense), phenolic resins and other three-dimensional polymers. General practice for complex phenolic resins and phenolic and maleic-modified rosin esters is to heat 2 parts of resin with 1 part of oil to about 560 to 580°F and hold 15 minutes or longer to attain clarity not only of the hot batch but of a cooled sample.

Further amounts of oil are added and the heating process is repeated until all the oils and resin are combined and clear. This process is probably analogous to the sorption of water by gelatin, wherein gelatin first swells gradually as the water penetrates into the complicated structure. This resin dispersion does not involve any great loss of materials and is very necessary, for if dispersion of the resin is not sufficient, the combination may yield a cloudy solution in volatile solvent or even a cloudy film on drying.

Natural resins, such as Kauri and Congo gums, may be so insoluble in drying oils that they must be cracked ("run"), or decomposed to simpler molecules that are oil-soluble. Much ancient art and tradition in "running" resins involved separate heating of the resin in one or more cycles to 625°F, with or without condensation of cracking products, which can give losses of 5 to 35 per cent. These losses, along with the extra bother of the cracking operation, are a part of the reason for the declining use of the natural resins.

Inter-reaction of resin with oil includes both phenolic condensations and ester interchanges. Some phenolic resins have residual reactivity, probably methylol groups which are capable of reacting with hydrogens made active by proximity to double bonds in the drying oil, or with the double bonds themselves. This type of reaction requires the relatively low varnish-making temperatures of about 300 to 400°F, and gelation is all too easily attained. Ester interchange is claimed to occur at about 575°F between neutral oils and previously prepared neutral resins, such as those of rosin with glycerin or pentaerythritol.

Varnish manufacture by resin formation in the presence of the oil is practical and may be desirable if agitated equipment is available. The various solid glycerin and other esters of rosin are conveniently produced at about 525°F, but since many hours are required for ester gums of low acid value, it is economical to make these only in large kettles so that manufacturers who have only small portable kettles may prefer to buy solid ester gum for use in their varnish. Conversely, manufacturers with large kettles may find it economical to eliminate the intermediate step of solid resin formation and may cook rosin, glycerin and oil or oil acids together to form a varnish base in one operation. An interesting variation is esterification of tall oil (from the kraft paper industry), which consists of about equal parts of rosin acids and semi-drying fatty acids. The tall oil ester makes a rather brittle and slow-drying varnish base, which can be fortified with higher-quality resins and oils.

Congo resins are also capable of esterification in about the same fashion as rosin, after they have been run. This includes decarboxylation down to approximately a monobasic acid.

Phthalic anhydride is representative of another class of materials which are readily adaptable to resin formation in the presence of oil. Because it is an anhydride of a dibasic acid of low molecular weight, its esterification rate is much greater than that of rosin; temperature ranges between 400 and 525°F are common.

Since simple glyceryl phthalate is not readily soluble in drying oils, there must be inter-esterification to attain good solubility in oils and volatile solvents. This is accomplished either by starting with fatty acids, plus phthalic anhydride and glycerin (or related polyacids and polyalcohols), or by first alcoholyzing the oil. This alcoholysis is commonly attained by holding oil and glycerin for about one hour near 460°F, which is conveniently below the boiling point of glycerin. This heating is done in the presence of some alkaline alcoholysis catalyst, such as the oxide or hydroxide of calcium, barium or lead. Sufficient combination of oil with polyalcohol is conveniently tested, either by some degree of solubility in anhydrous methanol or ethanol or by a test addition of the phthalic anhydride or other acidic materials.

Glycerin may be replaced by other commercially available polyalcohols such as ethylene glycol and other glycols, by mannitol, by sorbitol, and by pentaerythritol or its ethers. Phthalic anhydride can be replaced by maleic anhydride or by the adducts of maleic anhydride to rosin, to a terpene ("Petrex"), to cyclopentadiene ("Carbic" anhydride), or to other compounds containing active double bonds. The general principles of esterification are largely the same, but the optimum conditions and the most economic and best-performing materials will depend on specific requirements for individual products.

Spar Varnishes

These very general observations on practical varnish and resin manufacture can be made more meaningful by illustration with typical varnish requirements.

Spar varnishes can be formulated from a wide variety of raw materials according to specific needs. In general they should give protection for a year or so of continuous exposure in Florida as a test of general quality in the United States. An alternate and preliminary exposure test would be about 400 or 500 hours in a carbon-arc type of weathering machine. In addition to good weather resistance, a spar varnish ought to dry in from 8 to 18 hours. It should be moderately pale so that it will have good appearance over wood. It should not gas-check when applied to a window sill within a home and should not wrinkle from too rapid surface drying. Since it may be pigmented for paint used for porch floors, it ought to be reasonably neutral on the chance that zinc oxide may be a part of the pigmentation.

Linseed oil would give good protection but its drying would be inadequate. Tung oil would dry well and have reasonable durability, but would tend to wrinkle on drying and probably skin in the package. Addition of a very soluble resin would help both of these troubles. This brings up a time-honored spar varnish formula, which consists of heating 40 gallons of tung oil very rapidly to about 575°F to gas-proof the oil and to body it a little. One hundred pounds of ester gum are then added, thus cooling the oil considerably and slowing and controlling its tendency to gel rapidly. The varnish base is then cooled further to about 400°F, at which temperature it is safe to stir in enough mineral spirits (having a boiling range of 300 to 400°F), so that the finished varnish has a viscosity of about one to two poises and a non-volatile (varnish base) content of about 50 to 60 per cent. Anti-skinning agents, such as guaiacol or butyraldoxime, are added to the extent of a few tenths of a per cent and also driers which might be 0.2 per cent lead and 0.1 per cent cobalt, based on the oil. Some such varnish was probably typical about 25 years ago.

Replacement of the ester gum by a pure phenol-formaldehyde added substantially to the durability, possibly because the rosin in the ester gum has unsaturation, which permits slow oxidation and disintegration, whereas the phenolic resin is not only more stable in itself but probably exerts an antioxidant effect on the oil and retards its degradation in the film.

Still other modifications of this spar formula are possible. Replacement of the glycerin ester of rosin by the pentaerythritol ester improves not only the drying but the durability of the varnish; further modification of this ester by addition of maleic anhydride or fumaric acid will give an even greater improvement, and durability may approach that of the phenolic type.

Phthalate varnishes may also be of spar quality and under some market conditions may offer economy over the tung oil type. Whereas the varnish base of the 40-gallon tung oil type would contain about 75 per cent of oil, the phthalate varnish need contain only 60 to 65 per cent by weight of oil. This lower oil content is partly because of the great functionality of the phthalates; it is also partly an illusion, since our calculations are conveniently based on weight percentages, whereas it is volume percentage that is of significance. Pure glyceryl phthalate has a specific gravity of about 1.5 as compared to about 1.1 for phenolic rosin and other conventional resins.

Phthalate spar varnishes need use only linseed and soya oils, since adequate drying is attained and since tung oil in such a combination would give too great a viscosity at the desired non-volatile content.

Floor Varnishes

Floor varnishes would be made along somewhat similar lines, but the need for exterior durability is replaced by the requirements of faster drying speed and greater resistance to alkaline soaps and other materials used in the home. The varnish should be dry enough to walk on in 6 or 8 hours. Varnish for linoleum ought to meet all these requirements, as well as those of initial paleness and non-yellowing. Furthermore, the dried films should be hard enough not to print and yet tough and elastic enough to withstand rigorous wear. Since these same varnishes could be pigmented as floor and trim enamels for similar uses in industrial products, the varnish should be non-reactive with pigments and should give a desirable rate of flow in the film to level out brush marks.

Formulating and manufacturing principles are the same as for the spar varnishes; however, a higher percentage of resin is used, the usual range being 20 to 25 gallons of oil per 100 pounds of resin, which is 60 to 67 per cent of oil in the varnish base, where the rosin or phenolic resins are used. Phthalate varnishes for this purpose would contain 50 to 55 per cent of oil.

Furniture varnishes require still higher percentages of resin, both because they do not meet the wear requirements of a floor varnish and because their use in furniture factories demands still faster drying times, not only to handle but to sand and rub to a very smooth finish.

Application Methods

Whereas brushing is the usual mode of application of the varnishes already discussed, most industrial finishes are applied by either spraying or dipping, and the general drying requirements are usually more strict. Weathering requirements may be less stringent than for external varnishes, but abrasion resistance should be higher. Again the same general principles of selection of oil and resin apply, but instead of using mineral spirits as a solvent, a faster-evaporating solvent is necessary in order to control the flow of the film before drying on a vertical surface and to increase the general rate of drying. Dipping of long pieces such as metal locker doors in enamels may require long drainage times to attain a reasonably even thickness of coat, and varnishes so used will probably require solvents of relatively slow evaporation rate.

Baking of industrial finishes requires adjustment of drier contents downward from the amounts used in air-drying varnishes. The proportion of lead may be reduced sharply, leaving only manganese and cobalt as the principal driers. Iron drier is very effective in high-temperature bakes, such as 400°F, where color retention is of no importance.

In addition to these general observations, certain specialty finishes deserve some attention. Among these are so called wrinkle finishes, which are used both clear and pigmented; for example, these can be produced from tung oil and one of the harder resins cooked to near the gel point with a large amount of cobalt as the sole drier. Many variations of size, relief and gloss of pattern are attained by various proportions and treatment of the oils and resins.

Refrigerator finishes are examples of a class of finishes where extreme paleness and non-yellowing of the vehicle is of paramount importance. Tung, linseed and related oils have no place here, and even soya oil is not too good. The complete absence of linolenic and other acids of unsaturation higher than linoleic is required, the oils are thus limited to castor, sunflower and fractions of cottonseed and corn oils. Still better whiteness is attained by urea-formaldehyde resin solutions plasticized by non-drying phthalate varnishes made from coconut oil and glyceryl phthalate.

Coatings for food cans require not only slow thinners for application by roller, but extreme resistance to steam used in processing of the foods and to the foods themselves, as well as the complete absence of lead in any material in contact with food.

These several examples are intended to show that out of a relatively small number of raw materials and a few chemical and operating principles, literally thousands of product requirements can be met. Because of this complexity a varnish chemist's work is never monotonous, as new problems are always a challenge to his ingenuity.

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Chapter 20

Industrial Finishes

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A definition invariably suggests exceptions, but in the majority of cases we may define industrial finishes as the paint products used by industry to protect, decorate and/or augment the function of its product. Protection and decoration are closely related, and we usually strive for the maximum in each property, although in some cases the requirements may be such as to indicate only a short-lived coating for appearance, and protection may be sacrificed. An example of this type may be found in the case of identification paints, applied to semi-finished products for easy and rapid identification, but no longer serving any useful purpose after the part is assembled into the finished product. Again, protection may be the dominant requirement and appearance may be secondary. Examples of this type are red lead paints used for their corrosion-resisting properties, and stripping finishes which are used to protect products in transit and during storage, but which are removed before the product is put into use. Certain finishes are primarily essential to the function of the product; among these may be listed the chemically resistant, light-reflecting, light-absorbing and insulating types.

A brief reflection on the vastness of industry and its multitude of products makes it apparent that the field of industrial coatings is a large one. Its products are highly specialized and require a broad background of experience in their use and application, and a wide knowledge of their component parts. These two factors make it impossible to cover the subject in such a way that exceptions cannot be found. Cases exist wherein exactly opposite products or procedures may be employed in identical situations to produce the desired results. To include all of these is beyond the scope of this work. Instead a more general treatment has been followed covering the information presented from the approach of the industrial finish formulator to his problem

(1) by classifying industrial finishes;
(2) by discussing factors which influence the formulation;
(3) by discussing factors other than those influencing the formulation which are also related to industrial coatings.

Classification

Industrial finishes are frequently classified in two separate and distinct ways. One of these is by vehicle composition and the other is by type of product.

(1) Under the classification by vehicle type therefore are found: (A) Oleoresinous-type finishes, (B) Alkyd-type finishes and (C) Solvent-type finishes. Since the information given in earlier chapters devoted to these vehicles also applies when they are used in industrial coatings, nothing further will be said here about this classification.

(2) Under the classification of industrial coatings by type may be listed: (A) undercoats and (B) topcoats. Undercoats are subdivided into two groups, those used over metal and those used over wood. The undercoaters used over metal include primers, primer surfacers, surfacers and miscellaneous others, including sealers and ground coats. The undercoaters used over wood include all those just mentioned and in addition several others which are infrequently called undercoaters by the trade, but are included here since they serve that purpose. Such coatings include stains, rot-inhibiting sealers, wood fillers and wood sealers. Top coats include flat or lusterless, semi-gloss, gloss and miscellaneous other coatings having special properties. Included in this last group are clear finishes for both metal and wood, wrinkle finishes, chemical resisting finishes and the finishes containing powdered metal such as aluminum paints, iridescent finishes and hammered effect finishes.

(A) *Undercoaters* are finishes used exactly in the manner implied by the name. In general they are found with oleoresinous or alkyd resin vehicles although products with solvent resin vehicles account for a small proportion of the total undercoat produced. They are most often gray or red (the color of red iron oxide) although they may be other colors, including the yellow of zinc chromate primer and the orange of red lead primer. They function as the base for the whole finishing system. In so doing they provide bond between the substrate and the rest of the finishing system; they supply filling to the substrate and they frequently supply properties required in service (such as water and corrosion resistance) which could not be obtained without their use. These products are of particular value in supplying bond when top coats with solvent-type vehicles are used. For example, in truck and automobile finishing, nitrocellulose coatings are always applied over an undercoat, never directly to the metal.

Similarly with other solvent-type topcoats more satisfactory results are often obtained if an undercoat is used. They may also be necessary for another purpose in the case of vinyl and chlorinated rubber topcoats applied over metal, since on drying these may produce minute amounts of chlorine or other corrosive products, which often destroy bond and facilitate corrosion. In the case of metal substrates filling is supplied by the undercoat. In the postwar period of insufficient steel supply filling the pores of this metal has become a major requisite of the undercoat, since steel with the highest grade metal finish requiring little or no filling is not available in the tonnages needed. Filling the metal by applying heavy films of topcoat does not give as satisfactory a job, and it is not economically sound because undercoaters are invariably less costly than topcoat finishes. Properties demanded in service, such as water and corrosion resistance, are frequently imparted to an undercoater by inclusion of such raw materials as phenolic resins, china wood or oiticica oil and zinc oxide for water resistance and zinc chromate, red lead and the lead chromate pigments for corrosion resistance. The yellowing properties of phenolic resins, oiticica and china wood oil and the particular color of zinc oxide white, red lead oxide and the yellow and orange lead chromate may prevent their use in the finish coat. Hence an undercoat formulated to include them and to provide the resistance properties required is frequently employed, followed by a finish coat which has a color unaffected by the raw materials which produce water and corrosion resistance.

Principles of formulation have been covered in an earlier chapter. Suffice it to say here that the three types of undercoat primers, primer surfacers and surfacers differ from a formulation standpoint primarily in pigment to binder ratio. *Primers* have the lowest ratio, primer surfacers have a higher one, and surfacers have the highest. Translated into undercoat properties, this means that primers have the poorest filling properties and are hardest to sand, but they produce the greatest bond and hold out the top coat best. They are used non-sanded, scuff-sanded to remove dirt specks, or well sanded, as the only undercoat in a finishing system. They are also used in conjunction with a surfacer in a combination undercoat system, in which case they provide bond between substrate and surfacer. In such cases, corrosion-inhibiting pigments which have the property of making metal passive obviously need only be used in the undercoat which has contact with the metal surface.

Primer surfacers are intermediate in their properties between primers and surfacers. They are used as single undercoats and must be sanded. They provide better sanding than primers at the expense of some desirable adhesion; they also give better adhesion than surfacers at the expense of ease of sanding. They provide economy over the combination undercoat system of primer plus surfacer.

Surfacers have the highest pigment-resin ratio of the three undercoats mentioned. They are used in conjunction with primers as described above, and primarily provide exceptional filling and very easy sanding. These are essential features in preparing unusually bad metal, which is the principle place that the use of a surfacer is indicated. They are frequently poor in "holding out" the topcoat to produce a good full, glossy appearance. They often show the sand scratches badly unless the topcoat receives a polishing such as that given the lacquer finish used on automobiles, or unless a sealer or abnormally heavy film of topcoat is used.

Of the miscellaneous undercoaters, *sealers* are used in conjunction with surfacers or primer surfacers to seal the sand-scratched surface which has been produced by hard sanding of the surfacer or primer surfacer in order to obtain a smooth, uniform paint base over the rough metal. Sealers are products of low pigmentation and poor sanding properties. Their principal function is to provide maximum fullness and gloss in the topcoat more economically than those properties could be obtained by applying topcoat at a film thickness equivalent to that of sealer plus topcoat. Sealers are either baked or flash-dried (air-dried long enough to evaporate the solvent) before receiving the topcoat. If they are flash-dried, sanding is, of course, unnecessary. If baked, they may receive the topcoat either with or without sanding.

Another miscellaneous undercoat is the *ground coat.* This may be any one of the four undercoats previously described. Its distinguishing characteristic is that it has a color which contributes to the color effect observed in the completed finishing system. No other undercoat functions in this way. Its use is indicated in systems where the topcoat does not produce solid hiding. Examples of such systems are to be found in imitation wood grain finishes where for example, a brown graining ink is applied over a red iron oxide ground coat to give the effect of mahogany grain. Another example of such systems is to be found in instances where the topcoat color is such that the amount of pigment required to produce solid hiding either cannot be contained in the formula or else makes the cost of the topcoat prohibitive. In the latter cases it is often more satisfactory to employ a ground coat using much cheaper pigments but having a color close to that of the topcoat. The color of the ground coat, together with that of the topcoat which has incomplete hiding, thus produces the final color effect observed. Using the ground coat with a color close to that of the topcoat color also eliminates variations in final color which may be observed when an undercoat of contrasting color is used.

In preparing wood to receive the topcoat, *stains* are frequently employed. These products are used, as the name implies, to give color to the wood or to highlight contrasting effects already there. There are three types of stains: wiping stains, water stains, and non-grain raising (N.G.R) stains. In addition, shading stains may also be mentioned. *Wiping stains* are pigmented linseed oil with drier and solvent included. They are used for non-porous wood where filling is not required. Such stains are brushed or sprayed onto the wood or they may be thinned out additionally and the wood dipped into the stain. After the stain has dried long enough to impart the desired color the excess is wiped off. In the case of the dip application, most of the stain drains off and it is generally necessary only to wipe the bottom, where surface tension prevents the last of the stain from completely leaving the work.

Water stains and *N.G.R. stains* are dyes dispersed in a solvent. They are used over porous wood followed by a wood filler. In the case of the former type the solvent is water; such stains have the advantage of remaining wet a longer time than N.G.R. stains and thus penetrating deeper into the wood to produce more uniform color. In application, the excess stain may be sponged off, but because of the water vehicle these stains raise the grain of the wood. This must be eliminated by using a wash coat of reduced clear lacquer or white shellac. These act as a size to tie down the raised grain. After they have dried sufficiently (30 minutes or so) they are scuffed with sand paper to eliminate the raised grain and the surface is then ready for the next operation.

N.G.R. stains were introduced as improvements over water stains, at least from the standpoint of ease of use in production finishing schedules. These products use alcohol as a solvent for the dye. Since alcohol evaporates faster and does not wet the wood in the same way that water does, these stains do not raise the grain and thus justify their descriptive name. Because of these properties of the solvent in N.G.R. stains, penetration into the wood is not as deep and uniformity of color is not as good as with water stains. Their use has the advantage of making unnecessary the size coat and subsequent sanding operation.

Shading stains need only a word of description. They are usually colored lacquers applied by spray, preferably next to the wood and before application of sealer. They are used to overcome any non-uniformity of color obtained in the staining operation.

Rot-inhibiting sealers are products having a twofold purpose in the finishing of wood. They have extreme penetrating properties. Their vehicle is either oleoresinous or a long oil length alkyd containing a definite quantity of fungicide, such as copper naphthenate, chlorophenol or phenylmercuric oleate. The drying properties of the oleoresinous or alkyd part of the sealer have some sealing action against penetration of moisture into the wood. The fungicide part of the sealer discourages mildew, rotting and termite activity. These products would be used before wiping stains and after water and N.G.R. stains in those wood-finishing specifications calling for both types of finish.

Wood fillers have the same colors as the wood, stained or natural, over which they are used. They are of two types: those with a bodied oil vehicle which are recommended for overnight dry, but which are sometimes recoated in a high-speed production schedule after drying a minimum of four hours, and those with a very fast-drying nitrocellulose base which can be recoated after 20 minutes dry. These products are used over porous or open grained wood to fill the pores with a product having the same color as the wood itself. This evens off the surface so that the final coat presents a smooth surface rather than the rough one which would be obtained were the filler omitted and the topcoat allowed to follow the natural contour of the wood surface. For successful application fillers may be applied and allowed to dry a short time. The excess is then wiped off with waste or other soft material. Wiping is *across* the grain, as this removes the surface excess, but leaves a maximum in the open grain. Wiping with the grain not only removes the surface excess, but also tends to remove most of that in the open grain as well.

Wood sealers are the final material applied prior to the topcoat. These products may have a lacquer or phenolic varnish base. Their function is to coat closed-grain woods, seal filler in open-grained wood and generally to prepare the surface for the topcoat. After drying they are scuffed with sand paper to remove all dirt and raised grain.

Topcoats are most completely classified by their gloss, making in general three groupings in this manner and having in addition a miscellaneous listing. The three types cover lusterless, semi-gloss and gloss topcoats. Like the three undercoat groups, these topcoat types differ from a formulation standpoint principally in pigment-binder ratio. The undercoats, however, are drab colors, principally red or gray, whereas topcoats cover the entire color range. Lusterless topcoats, like surfacers, have the highest ratio of pigment to binder in order to produce the desired light-absorbing properties. Much of this is low-cost inert or extender pigment, the true coloring pigment being present only in sufficient quantity to impart complete hiding to the coating. Semi-gloss topcoats, like primer surfacers, have intermediate pigment-binder ratios, although in light-reflecting properties they are more like primers. These coatings also cover the entire color range, using only enough color pigment for hiding and supplementing this with sufficient extender pigment to produce the desired gloss. Gloss topcoats cover the complete range of colors, do not use extender pigments in general, and have the lowest pigment-binder ratio of all topcoats, except for light-colored products. In such cases the quantity of pigment required for hiding may result in a pigment-binder ratio higher than that of certain semigloss topcoats, which use a very high hiding color pigment and a very fast flatting extender pigment, and thus have relatively low pigment-binder ratios. Gloss topcoats use only enough pigment to supply complete hiding.

These three classes of topcoats may have vehicles of all three types: oleoresinous, alkyd resin and solvent-type resin. The miscellaneous topcoats have the three vehicle types only in the case of clears. The others are not found in all vehicle types, inasmuch as their special features frequently are derived by utilizing to the utmost characteristics of a particular vehicle type which distinguish it from the others. Topcoats are, of course, the final finish applied and unless transparent or semi-transparent, produce the completed color effect observed by the user.

Lusterless topcoats are light-absorbing finishes used on objects where such properties are necessary or desirable. Examples of items requiring lusterless topcoats are certain photographic equipment and the materiel of war. The need for lusterless black finishes on the interior of cameras is obvious. Camouflaging items of war, that is, making them indistinguishable from their background, is a well known use for these coatings. An interesting variation of this practice was used in World War II. Photography in aerial reconnaissance, so necessary for successful execution of the war, was often prevented by cloud formations between plane and area to be photographed. To overcome this, films sensitive to infrared radiation were used, since cloud formations, though stopping the passage of visible light, are transparent to infrared radiation. Thus it was possible to photograph enemy installations even on cloudy days. When this was accomplished it was observed that lusterless olive drab coatings which had made objects indistinguishable from background foliage when observed with visible light no longer did so when photographed with infrared radiation. The reason for this was that natural foliage reflects a definite percentage of infrared radiation (40 to 50 per cent), thus appearing gray on a photographic film sensitive to it. Lusterless olive drab coatings on the other hand completely absorb such radiation, due to the lamp black or carbon black pigment normally used in producing this color, and thus photograph black with infrared-sensitive film. Thus while false impressions could be created with camouflage paints under normal lighting conditions, pictures taken with infrared radiation readily broke down the disguise. It became necessary therefore to produce lusterless olive drab enamels which maintained the camouflage effect under both conditions of observation. This was accomplished by replacing the black carbon pigment in olive drab finishes with antimony sulfide, the only black pigment having appreciable infrared reflectance. The infrared reflectance of the coating was then adjusted to approximately 45 per cent and once again the material was suitable for camouflaging under both conditions—*i.e.*, it was olive drab color when observed with normal light and gray when photographed with film sensitive to infrared radiation.

Semi-gloss topcoats are combined light-absorbing and light-reflecting finishes used where maximum light absorption is not necessary, and where maximum light reflection is undesirable. For war-time use they represented finishes having better durability and wear-resisting properties than lusterless coatings for those applications where maximum camouflaging was unnecessary. They were used, for example, on such indoor equipment as foot lockers, radar, radio and telephone equipment, etc. For these uses they also offer much better abrasion and wear resistance than lusterless coatings which, because of their extremely low gloss, scratch and mar readily, often showing a lighter color in such areas.

For peace-time use, they provide a finish with a softer, less glaring effect than gloss topcoats for many uses where the latter effect is objectionable. An application of this idea is found in their use on office equipment, venetian blinds, etc. In such applications, the use of gloss enamels would result in disturbing light reflection and glare, whereas semi-gloss enamels give a subdued, more pleasing and restful reflection.

Gloss topcoats are those finishes which reflect the maximum of light. They are used in situations where it is desired to produce the brightest, most eye-arresting appearance possible. These finishes are employed on such familiar manufactured objects as automobiles, refrigerators, washing machines, trucks, busses, etc.

Of the miscellaneous topcoats, the usual *clear finishes* occur in all three vehicle types, and they also have all degrees of gloss, from very glossy to very dull. As the gloss of these finishes decreases, their transparency also decreases, since the ingredients necessary to decrease gloss (metal stearates, extender pigments, etc.), while not normally regarded as adding to the opacity of pigmented coatings when used in them, are nevertheless not completely transparent. Thus as the quantity included in the formula is increased to produce clear coatings of lower sheen, the resulting transparency suffers correspondingly. Clears are used to build up the protective features of the finishing system. Thus in wood and furniture finishing the clear topcoat supplies a film of protective finish for the wood beneath. In artificial graining processes the clear topcoat protects the graining ink and enhances the appearance of the finished article. Clear topcoats in all degrees of gloss are also used either to increase or decrease the gloss of the finished article in circumstances where it is impossible for one reason or another to obtain the desired gloss with the color coating applied beneath the clear.

Aside from the usual type of clear finish there are others for specialized use. Among these are *clear can coatings* and the insulating *wire enamel clears*. Neither carries any extender pigment for gloss control. Can manufacturers have very rigid specifications for the former, and these usually cover composition as well as performance. Such coatings are often varnishes of 15 to 25 gallons in length using china wood or dehydrated castor oils and congo or pure phenolic gums. These are sometimes reinforced with petroleum-type gum like the "Velsicols" for added chemical resistance. Soybean oil-modified alkyd resins (about 40 per cent oil) are also specified for certain uses. Beer cans use a varnish composed of china wood or dehydrated castor oils cooked with a rosin maleic glycerin ester. This is applied as a base coat before forming the can. After forming, a vinyl coating is applied as a topcoat. In curing can coatings, metallic driers are omitted and high heats are used for conversion completely to drive off reaction products of drying, since both these and driers adversely affect flavor. In spite of their greater cost, vinyl compositions for interior can coatings are coming into increased use in the postwar era, due to a scarcity of tin and consequent decrease in the thickness of tin plate used. This has resulted in decreased taste and chemical resistance of the coating beneath the clear, which in turn has created a demand for the greater chemical and taste resistance of the vinyl coatings as compared to the older oleoresinous coatings. Very rigid tests are set up for checking the influence on flavor of coatings used for can interiors.

Wire enameling represents another large use for clear coatings. They are of two types, the conventional and the vinyl.

Conventional wire enamel clears are 15 to 30 gallon oil-modified varnishes in which congo or phenolic resin is the gum. Three to five coats are applied by free-flow dipping, each coat being baked for periods ranging from 3 to 30 seconds and at heats ranging from 600 to 1000°F. The *vinyl wire enamels* contain vinyl formate. Because of their very heavy viscosity, they are not free-flowing and the excess material must be squeegeed off with metal dyes. Six to twelve coats are applied to produce standard film thickness. They are baked for about the same times as conventional clears, but the temperature is around 600°F. Both types are applied in continuous coating machines which pass the wire over a series of guide wheels that conduct it through the clear, the oven, the cooling area and back through the clear. This setup is so arranged as to repeat the operation until sufficient coats have been applied to give the specified film thickness. In application of the vinyl type of coating the dyes for removing the excess are progressively larger to make allowance for the thickness of the coating as it builds up. Advantages of the conventional type are lower cost and added dielectric strength (1100 to 1200 millivolts per 0.001 inch film thickness as against 1000 millivolts per 0.001 inch film of vinyl coating). Advantages of the vinyl type are improved physical and chemical properties, such as flexibility, elongation, scrape resistance, and acid resistance.

One or two other types of clear finishes which are also regarded as pigmented coatings are the *crystal* and *crackle finishes.* These are based on an oleoresinous vehicle containing a drying oil with conjugated double bonds. When these vehicles are prepared in such a way that the oil in them is not gasproofed, the resultant finish produces a characteristic pattern when dried in an oven which is fouled with fumes. Because of the difficulty of controlling the product and the drying, uniformity of results is often lacking and this type of coating has largely been supplanted by wrinkle and hammered effect finishes.

Wrinkle finishes, as the name implies, produce their particular appearance by wrinkling of the coatings. These finishes are possible only with oleoresinous or alkyd resin type vehicles, and only when amine resins are not included, since these resins have the property of completely stopping wrinkling when used in amounts as low as 3 to 5 per cent of the vehicle. Mixtures of oleoresinous and alkyd resin vehicles have been used to obtain control and pattern effects which do not result from either vehicle alone. However, compatibility factors must not be overlooked in these cases. Raw and blown china wood oil and a variety of extenders are also used to control the pattern. Wrinkle effects are not obtained with finishes having solvent resin vehicles. Wrinkle finishes are always baking finishes, since complete and satisfactory wrinkling is not achieved on air drying. They are found in all colors except those delicate shades which cannot be produced because of the considerable yellowing obtained when wrinkle finishes are baked. This yellowing is characteristic of the vehicles of these coatings, since for satisfactory wrinkling it is essential to use unusually high concentrations (0.2 to 1.5 per cent metal based on vehicle solids) of drier (cobalt and manganese soaps) which contribute to yellowing on baking, particularly when used in conjunction with the oils (perilla, oiticica and china wood) that are commonly found in wrinkling vehicles. The most highly regarded wrinkle finishes have very little gloss, although a small percentage have some sheen. These finishes occur in fine and coarse patterns. They are used as a one-coat finishing system, very often on low-cost items, although they are so well liked by some that they are specified on a few costly items of the highest quality. Their original use, however, was in connection with low-cost objects where their pattern (wrinkle design) permitted this single finish to serve the function of an undercoat by disguising metal imperfections and at the same time to serve the purpose of a topcoat by providing a pleasing effect on the finished object. Articles of commerce that use wrinkle finishes are typewriters, time clocks and other small office equipment; articles in and around the home are automobile heaters, home radios, air conditioning units and some of the most modern gas furnaces.

Chemical resisting finishes are a small and very special part of industrial finishes. They are usually semi-gloss finishes used, for example, on chemical laboratory desks and benches where maximum acid and alkali resistance is required. Their vehicles are often the highest quality china wood oil-phenolic resin varnishes available, usually having an oil length in the neighborhood of 12½ to 15 gallons. In their formulation, all pigments not stable to acid and alkali must be omitted. This eliminates aluminum, iron blue, chrome green, zinc oxide, etc. A common green pigment found in such finishes is chromium oxide green. It might be mentioned that some of the newer solvent-type resins may make possible finishes of considerably greater chemical resistance than the type just described, but so far, the newer materials have not appeared attractive economically.

Metal Finishes. The first of these are the aluminum enamels. Such products when applied present the appearance of a solid sheet of aluminum, and are dependent for this effect upon a property of aluminum pigments known as "leafing." This property is augmented by a coating of stearic acid introduced on the pigment during its manufacture. Aluminum pigments occur in numerous particle sizes and in varying degrees of brilliance. Vehicles for these finishes are principally oleoresinous, and ready mixed aluminum paints must employ an oleoresinous vehicle prepared with a neutral and non-reactive varnish gum such as coumarone resin. If this practice is not followed, the non-reactive vehicle destroys the brilliance and leafing properties of the metal flakes and a gray and unsightly finish results. Because of this, aluminum finishes are furnished in compartment containers when it is necessary to use with the metal a vehicle of insufficient neutrality. These containers have two separate compartments which keep metal and vehicle apart until time for use. The compartments have pigment and vehicle in the correct proportions, and when it is desired to use the enamel the two are mixed. Only enough containers are used to furnish paint for a day's run or for finishing a single item, since any additional will be spoiled by standing overnight. Alkyd resin vehicles, although used for aluminum enamels, fall into the reactive category; thus when their use is indicated, they are shipped on compartment packages.

The leafing property of aluminum paints makes them highly desirable for a number of uses. They are used first for the clean bright appearance which they impart to furnaces, spray booths, truck trailer tops and steam radiators. Because of the leafing of the aluminum they provide exceptional resistance to the passage of moisture and are often used in applications where moisture and corrosion resistance are important. Also because of this leafing feature, they have the ability to seal substances in as well as to keep them out. They find application therefore as sealer coatings over finishes which may "bleed" or migrate into a subsequent coat and destroy the desired color. For example, a wooden object may have a bleeding stain in its finishing system. To salvage rejects it may be desirable to paint them with a pigmented topcoat and offer them as second quality merchandise. In such instances, an aluminum paint can be used to seal the bleeding stain in so that it does not discolor the paint finally used.

One other use for aluminum enamels is in stack paints and other heat-resisting applications. Actually, the aluminum does not impart non-combustible properties to the paint. Instead the vehicle is burned away and the aluminum forms a tightly adhering film which is practically a part of the metal itself.

Iridescent finishes are metal coatings widely used in the painting of automobiles and certain smaller objects where a very brilliant effect is desired. These finishes use aluminum which is processed so as to eliminate or minimize leafing—*i.e.*, the non-leafing varieties. In these finishes, it is not desired to produce a solid metal effect. In fact, all tendencies for the powdered metal to go together and produce such an effect must be overcome. This requires fast-setting solvent-type alkyl resin vehicles. It eliminates slow-setting oleoresinous vehicles from consideration, and also necessitates the use of very fast-evaporating thinners, which are responsible for setting the aluminum particles as soon as the coating hits the surface and thus preventing them from coalescing. This is essential, as the desired result is best produced when the particles of metal flake occur at all angles in the coating and reflect the light through the remainder of the film, which preferably is semi-transparent. This produces highlights and changing hues with variations in the contour of the coated object. Other materials used for this effect are pearlessence, an amino product known as guanine and extracted from fish scales, and H-scale which chemically is nacreous mercurous chloride. The former material produces a much more brilliant and attractive effect than aluminum, one similar to that commonly observed on pearlized toilet seats and brush, comb and hand mirror sets which, however, are plastics more frequently than paint coatings. Its use is considerably more costly, and is limited to applications for indoor use since its organic nature makes it inferior to aluminum in exposure characteristics. H-scale also produces more effective finishes than aluminum but is limited in its use because of its corrosive nature. Special precautions must also be observed in the use and application of finishes containing it, particularly to protect workmen from the spray dust.

Hammered effect finishes are metal coatings used to give the appearance of hammered metal. As in iridescent finishes, non-leafing aluminum is required. These products, like wrinkle finishes, are used as one-coat finishing systems, their patterned effect serving both to obscure metal imperfections and at the same time to give a pleasing appearance. They are used on gas furnaces, automobile heaters, vacuum cleaners, electric heaters and similar objects. They are of two types: (1) those which produce the effect of two operations—application of the finish and then splattering with thinner to produce the "hammers"; and (2) those which produce the effect in the single operation of applying the paint. The former have been used with great success for a long time. They are simpler to use, but require more labor. The latter are just being introduced as a labor-saving coating. Their proper use is somewhat more tricky than the two-coat products. These finishes are found with alkyd and oleoresinous vehicles, but seldom with solvent-type resin vehicles; such finishes are possible though not as attractive economically.

Factors Influencing Formulation

Having classified and defined the wide variety of products considered as industrial finishes, the next step is to discuss factors influencing selection of the proper one to be used and causing variations in its formulation from normal. The chief items of consideration are three: (1) cost, (2) conditions of use, and (3) service requirements. Knowledge of these must be available to the formulator because industrial finishes are always applied to a specific product, made to fit a definite manufacturing procedure and based upon a careful consideration of cost. In short, they are a part of the product and are engineered into it.

Cost is the one factor overlying all of the formulator's thinking. Other factors being equal or nearly so, the lowest cost industrial coating will be used for a given purpose. In considering cost, however, the price per gallon of paint is not the only thing to be judged. Conditions of use and service requirements also influence the stiuation, and many instances could be mentioned where a product with a higher cost per gallon may be the most economical in the long run. Wrinkle and hammered-effect enamels are good examples. These products could conceivably have a cost per gallon in excess of the total cost of the gallon of primer plus the gallon of enamel which they are being used to replace. Yet the labor costs involved in applying and baking a single coat of either wrinkle or hammered effect enamels can be so much less than the cost of applying and baking a coat of primer and a coat of enamel, plus possibly even sanding the primer, that they make use of the single-coat materials with the higher gallon cost more attractive from the overall cost picture. Since engineering aspects are important, the industrial paint manufacturer usually works closely with his customers when they are starting operations or when they are contemplating engineering changes, so that economical finishing systems may be employed.

Wide swings in raw material costs can completely change the type of product used for a given purpose. A good example of this was found in the period following the last war. During this time the price of oils increased very greatly in relation to the price of the non-oil constituents of alkyd resins. This resulted in making oleoresinous vehicles more costly than alkyd resin vehicles, whereas prior to the war the reverse had been true. As a consequence, finishes such as dipping enamels for office equipment which had long been successfully based on oleoresinous vehicles were changed over to alkyd resin products. The advantages of one type over the other, for this particular application, are principally economic; and a reversal of the price structure to the situation as it was prewar could conceivably influence a return to oleoresinous base coatings for this particular use.

There are many other factors affecting costs. Some of these will be mentioned as the influence of conditions of use on formulation is taken up next. A complete understanding of costs, however, is apparent only after long experience in the field of industrial coatings.

Conditions of Use. The material under this topic has been divided into three sections which discuss (1) surfaces to which industrial coatings are applied, (2) methods of applications, and (3) drying schedules. Industrial coatings may be applied to wood, ferrous metals, non-ferrous metals and other miscellaneous base materials.

In suggesting a finishing system for *wood*, complete knowledge of the types used by the customer must be available. Inasmuch as woods carry varying percentages of sap and moisture, have open and closed grains, and display many other divergent properties, considerable knowledge of these is necessary in order to offer the most satisfactory finishing system. Reference to the section above on undercoats as they apply to wood finishing will suggest further points which must be known for a successful approach to the problem of natural wood finishing, and of course pigmented undercoats and topcoats must also be considered, although their use over wood in general presents fewer problems than over metal.

In finishing metals, it is essential to know the type the consumer intends to coat. *Ferrous metals* are used in by far the largest tonnages, but in addition there are also to be considered aluminum, magnesium, terne plate, tin plate, galvanized steel, chrome plate, copper and brass, to mention the most common. In discussing coatings for iron and steel, it is *impossible to overemphasize the importance of proper surface preparation.* A subsequent chapter has been devoted to this important subject, but certain aspects of it as they influence formulation and results to be expected are taken up here.

The finest painting system, employing the most costly coatings it is possible to produce, can be rendered completely valueless when applied over steel which has not been properly prepared. As steel comes from the mill, it carries a slushing compound (oil, lanolin and/or other oily materials) which resists corrosion during shipment and brief storage prior to use. This compound should be removed and the surface etched and made passive by one of the many acid-type cleaners available for the purpose. Slushing compounds should be removed, as their oily composition prevents contact between metal and finish, thus preventing anchorage and good adhesion of the film. They are removed with *alkaline cleaners* or vapor degreasers. Where costs are closely watched, one of these methods may be the only cleaning the steel gets. In such cases, thorough rinsing after the alkaline wash is *essential.* Paint systems have been completely destroyed by failure to follow this simple precaution. A film of unremoved alkali on the steel will react with the paint at that point, destroying adhesion and producing embrittlement of the finishing system. To insure thorough rinsing of the alkaline cleaner, pressure washers are preferred. Where this equipment is not available, the washtanks must be kept hot; they must have an overflow and they must supply constant and adequate change in wash water. Alkalinity of the wash water should be checked and kept low.

Vapor degreasers employ trichloroethylene or related materials. These cleaners are vaporized from the bottom of a large tank. The vapor is prevented from escaping by condensation on cooling coils which circle the inside of the degreasing tank. In the central area the heavy vapors hang suspended so that when a batch of the articles to be cleaned is lowered into the degreaser the cold metal causes condensation of the vapors which run down and thus clean the surface. In condensing, the vapor gives up its latent heat of vaporization, which heats the metal so that when the load is removed the hot metal is self-drying. The process is continuous and self-cleaning, since the vapors are not contaminated by material removed from the metal surface even though the liquid is. Occasional redistillation of the degreasing liquid outside the equipment leaves contaminating material in the still and the condensed distillate is returned to the degreaser for further use.

This method eliminates the danger of residual alkali on the metal surface as mentioned above, but in certain instances it presents its own problem in spoiling the finish. This spoilage occurs because it is impossible to completely confine all the vapor within the degreaser. Some necessarily escapes when a load of objects is removed. This vapor creeps across the floor and though completely non-combustible the trichloroethylene is decomposed by open gas flames which are used to heat many industrial ovens. One of the products of this decomposition is hydrochloric acid. This material acts as a catalyst for amine resins, so that if the product being baked in the oven contains one of them the catalytic effect of the acid produces a wrinkled surface and spoils the work. There are certain tricks to overcome this, none of which has so far been completely successful in all cases. Frequently, it is necessary either to remove the amine resin and accept the decreased quality or to move the degreaser to an area where it is impossible for fumes from it to enter the oven. Degreasing is not often followed by an acid wash.

To guarantee that alkali-cleaned metal surfaces contain no residual cleaner a *combination alkali and acid wash system* offers the greatest assurance. In this system an acid treatment follows the rinse from the alkali tank. This serves the dual purpose of neutralizing any alkali not removed previously by rinsing, and in addition the acid etches the steel surface thus providing "tooth" to which the finish may adhere. This etching also leaves the surface passive (less easily corroded or reacted with) by depositing a coating of iron phosphate upon it. The iron phosphate is produced by the acid wash. All acid washes are based on the principle of producing such a coating at the surface of the metal, since such iron phosphate coatings are known to aid in providing improved blister and corrosion resistance. A further advantage of acid-cleaning steel is that incompletely removed acid wash often has no later deleterious effect, as contrasted to the very undesirable conditions resulting from incompletely removed alkaline cleaner.

Another method of surface preparation for ferrous metals is *sand blasting*. This is probably the most costly method, and is not as simple or as clean as others just described. Hence it is used only in situations where its particular attributes are demanded. It is suitable, for example, for the surface treatment of castings and in preparing the surface of sheet metal when exceptionally good adhesion is necessary. Following any type of metal cleaning, the quicker the surface is coated with the first coat of paint the better the results obtained—that is, the better the adhesion and the corrosion and blister resistance. This is especially true in the case of sand blasting where the surface not only has not been made passive by a protective coating of iron phosphate, but is actually in a state more readily reacted upon than it was prior to the sand blasting.

In operations where top quality is not necessary or desired by the customer himself because of the added cost incurred in providing the best cleaning method, it may be difficult to be assured of adequate cleaning. In such situations oleoresinous finishes adjacent to the metal generally provide better adhesion than those based on other types of vehicle.

Of the non-ferrous metals, aluminum is one which has been used in steadily increasing quantities in the past ten years. In addition to aluminum another light metal, *magnesium,* offers such a great advantage from a weight standpoint in airplane construction that satisfactory finishes for these two metals have had to be developed, even though many problems were involved. In this work satisfactory metal cleaning was the key to the problem; it was not until this was worked out that a suitable finishing system was developed for either metal. Much has been written and many specifications cover these processes. For detailed information reference should be made to them and to the chapter on surface preparation in this book. In brief, however, these methods involve a degreasing and an acid-etching operation. Degreasing may be by solvent degreasers or alkaline washes, as described above. Acid-etching in the case of aluminum is accomplished by treatment with chromic or phosphoric acid solutions, and in the case of magnesium by treatment with hydrofluoric acid solution followed by sodium dichromate solution. In the case of aluminum, an electrical method of surface preparation known as anodizing may also be employed. In this method, a protective surface coating is deposited on the metal by using the object as the anode of an electrical cell and passing a current between cathode and anode. Coating the metal quickly after completion of surface preparation is essential; for this purpose a specially designed primer known as zinc chromate primer has proved most suitable.

Terne plate, tin plate, galvanized steel, chrome plate, copper, and *brass* present their own problems from a cleaning and painting standpoint. Use of these metals is too specialized to cover here. Suffice it to say that proper metal cleaning and priming are just as necessary as in the case of metals more completely discussed above.

Other non-wood and non-metal base materials which industrial finishes are used over include *fabric, rubber, plastics, etc.* Each of these presents its own problems. More often than not, however, surface preparation is not considered for these substrates. Finishes used on fabric and rubber must obviously possess great flexibility. Finishes used over rubber and plastic must possess excellent adhering qualities. Accelerators and inhibitors in the rubber being coated may present special problems in developing suitable finishes. Catalysts and plasticizers used in plastics have a similar influence on the development of coatings for plastics, while compounds used for lubricating the molds to prevent sticking of the molding compound and to aid in easy removal of the molded object all introduce problems to be considered.

Having covered a variety of the surfaces considered for coating by the industrial finish formulator, the next step is to mention methods of application of the finish to these surfaces. These include brushing, spraying, dipping, roller coating, and miscellaneous methods. It is not intended to go into detailed explanations of these methods as they are covered elsewhere in this book It is intended instead to discuss briefly the way in which the several methods influence formulation. The principal effect is on the composition of the solvent employed in the coating. Other effects are more or less specific to a particular application method. Intimate knowledge of the manner in which the consumer intends to apply the paint is essential in order to produce one which will most completely satisfy his needs.

Brushing materials generally use slowly evaporating thinners which make the paint stay open or wet long enough to permit brush marks to flow out without at the same time causing sagging. As an aid to prevent sagging, ingredients referred to as flow control agents are commonly employed. These are often soap-like materials which impart a puffiness to the paint that prevents sagging without interfering appreciably with leveling of the brush marks. Viscosity for brushing is heavier than for the usual spray or dip application. This method of application is one of the least used methods for industrial coatings.

Application by spray requires a careful balance of thinners, usually necessitating a combination of quickly and slowly evaporating components. However, final use of the paint may substantially alter the proportions used. For example, small objects on which it is desired to get coverage in one coat require a paint with fast-evaporating thinner that will make a heavy single coat of material hang upon the work without sagging. Wrinkle finishes, hammered effect finishes and automobile wheel enamels applied by mechanical spraying equipment are examples of such finishes. Larger objects may similarly use material with fast-evaporating thinners if orange peel (a pock-like effect resulting from poor atomization and flow out of the sprayed coating) is not objectionable. Refrigerator enamels that produce some orange peel are actually preferred, as the enamel finish then looks more like porcelain. Where good flow is important, slower-evaporating thinners must be used, and complete hiding must be developed by applications of two or more coats within a few minutes of each other. This permits building up a sufficiently heavy coating to supply complete hiding and good flow without being applied so wet as to cause sagging. For heavily pigmented coatings such as surfacers and lusterless enamels the thinner may be primarily slowly evaporating, as the high pigment bulk tends to make the paint spray dry and the slowly evaporating thinners act to offset this feature. Viscosities at which spray men like to apply the paint also have a bearing on the combination of fast and slowly evaporating solvents used to attain the desired results. Spraying viscosities used for non-specialized coatings may range from about 16 seconds to 35 seconds on the No. 4 Ford Cup. Specialized coatings such as wrinkles and hammered effect finishes have their own viscosity requirements for best results.

Two specialized methods of spray application are also in use. These are *electrostatic spray* and *hot spray*. In the former, the paint is atomized into a very slowly moving fog which is given an electrical charge by passing it through an electrostatic field. This charge attracts the fog to the surface to be coated as the surface passes through it on a conveyor. The combination of slowly moving fog and its attraction to the surface results in considerable saving of paint as contrasted to conventional spraying, where the high pressures cause an appreciable percentage to go past the work and be lost through the exhaust stack. In installations where electrostatic spraying equipment is employed the thinner required in the paint is usually much more slowly evaporating than that required by the same paint if it were to be applied by conventional means. This is because paint exists in the atomized fog for a relatively much longer time in electrostatic than in conventional spraying. This being the case, it is necessary to use slower evaporating thinners with materials applied electrostatically, so that they will reach the work with the same degree of wetness and thus produce the same flow-out characteristics. Materials for electrostatic spray are generally reduced more for application at viscosities considerably lower than those used by normal spray methods. Frequently considerable trial and error experimenting is required to establish the correct viscosity for electrostatic spraying, since the range of viscosities giving satisfactory results is narrower by this method than it is by normal methods. This, of course, necessitates closer control by the user of the application viscosity of paint applied electrostatically.

In *hot spraying* of paint, the thinner composition also requires a greater percentage of slowly evaporating components than normal. The reason is different in this instance, however, from the case of electrostatic spraying. Paints having viscosities, at the normal temperature of determination (about 80° F), of 60 to 120 seconds on the No. 4 Ford cup may show viscosities of 18 to 24 seconds on the No. 4 Ford cup when the determination is made at 130°F to 150°F. Equipment for hot spraying is designed to deliver the paint to the spray gun within this temperature range. Thus it is obvious that materials for hot spray may be used unreduced at viscosities (normal temperature) and solids content much higher than customary. Since the solids content is higher, there is correspondingly less thinner present to contribute to good flow; and since the paint cools rapidly to room temperature when it hits the work, it assumes its room temperature viscosity and there is therefore correspondingly less tendency for it to flow. Both these factors contribute to the need for slowly evaporating thinners in hot spray paints in order to produce the desired leveling and freedom from orange peel. Hot spray paints may also need inhibitors such as guaiacol in their formulation to give added stability in paints maintained at temperatures of 130°F to 150°F for extended periods.

Examples of items coated by spraying are automobiles, furniture, refrigerators, washing machines, kitchen cabinets, and all equipment using wrinkle and hammered effect finishes.

The discussion of *dip applications* will also include a reference to related methods since similar factors in all of them cause similarities in formulation. Dipping is of two types: *plunge dipping,* where the article is dropped into the paint and quickly withdrawn either by hand or by mechanical hoist; and *conveyor dipping,* where the object moves into and out of the dip tank on a conveyor at a steady rate. Two related methods are *flow coating* and *tumbling.* In the former, paint is flowed in a steady stream over the work suspended on a conveyor line. Excess paint flows off, is collected and returned to be mixed with fresh paint and reflowed over new pieces. In *tumbling* the pieces to be coated are usually small. A basket of these is tumbled in the paint, the pieces are removed when coating is complete, and the excess drained off. In all these applications it is apparent that the paint flows over the work, that more paint than necessary to cover the work is applied, and that the excess must drain off. This generally requires slowly evaporating thinners, which will permit the paint to flow long enough so that smooth coating results. When too much fast-evaporating thinner is used the paint stops flowing before it is entirely off the piece, and it builds up to produce a rough, uneven surface. The longer the piece being coated the more slowly evaporating is the thinner required. This may also necessitate extra hiding pigment to produce adequate coverage at the top of the piece where the thinnest film of paint occurs; or it may require the addition of agents such as soaps or zinc oxide and other soap-forming materials. When correctly used, these impart a certain puffiness to paints and thus aid in building adequate film thickness at the top of the piece, but still do not too seriously impair flow in the lower section of the piece after adequate film thickness has been built up there. In application of paint by these methods it is often difficult to get the last drops of paint to leave the work because of surface tension effects and because the paint at this point is beginning to get quite dry. Electrostatic detearing (passing the piece over an electrostatic grid) knocks these last drops or tears off and produces a well finished effect. If such equipment is not used, wiping the edge may be employed or in low-cost objects the edge effect may be ignored.

Silking is a common difficulty encountered in dipping applications. It is caused by slight separation of the pigments along the lines of flow that occur as the paint drains from the work. This then causes the line effect with attendant variation in color which is known as silking. Some pigments are worse for this than others and are to be avoided if possible. Certain pigments, wetting agents and other addition agents can be used to help in minimizing this effect. Some vehicles also aid in its elimination, particularly those with the best wetting properties. Good dispersion of the pigment also helps. Inhibitors such as guaiacol and a minimum of driers are also used in dipping paints employing oleoresinous or alkyd resin vehicles. These are used to prevent bodying and even possible gelation that may be brought on by aeration. This is an ever-present factor to be considered, due to reuse of excess paint which flows off the work and to constant mixing of air with the paint as the work is sloshed up and down in the tank.

Accelerated tests for checking dip tank stability are briefly described below under control testing. For more complete details of these procedures reference should be made to A.S.T.M. methods. Results obtained, however, are of value only after being correlated with those obtained in production. Such correlation seldom can be relied upon completely unless other factors such as amount and type of agitation, tank size and rate of addition of fresh paint are also considered.

Examples of articles coated by dipping are bicycle frames, filing cabinets, low cost beds and bed springs, farm machinery and the undercoater used on hoods, and fenders of trucks and automobiles. Flow coating is also used for this last purpose. Tumbling is used to coat many small objects which are then assembled into other articles. Army belt buckles and the metal loops which retain the excess belt are coated in this way.

In *roller coating* the paint, at fairly high viscosity, flows from a reservoir over rolls between which the work passes. Paint is taken up from the rolls by the work and is thus coated. Requirements of paint for roller coat application are that the thinner contain sufficient slowly evaporating component to permit leveling without ridges or other non-uniformity. Generally, this means that very little fast-evaporating thinner is used. Hiding may have to be slightly greater in the case of white or light colors when applied in this way than when applied by spray, but few other precautions need be observed, except that forming of an object sometimes is employed after roller coating and in those cases, the finish must possess adequate adhesion and length to permit this without cracking or peeling.

Roller coating is most suited to coating sheets. Examples of items so coated are wood and metal venetian blind slats, and sheet metal which is later formed into dust pans, waste paper baskets, etc.

Artificial graining is a specialized type of roller coating. In this application, graining ink is applied to a graining plate or graining cylinder (metal plates or cylinders with the grain pattern etched into their surface). Excess ink is then scraped off and a gelatin or soft rubber roll passed over the etched area. This roll picks up the grain pattern and when rerolled over the work deposits the ink, leaving the grain pattern exactly as it was picked up. To permit easy cleaning of the rolls and to prevent their sticking to the plate and the work such inks usually do not require any thinner, but use instead bodied oils or alkyd resins so high in oil length that they approach the properties of bodied oil. These remain wet long enough to permit the entire operation to take place without difficulty from sticking.

Other specialized methods of application include silk screen process and squeegee. Multi-colored designs seen on painted tin cans and on painted sheet metal advertising signs are made by using the silk screen process. In this method a silk screen is stretched across the bottom of a very shallow box-like container. The container is usually the size of the object being coated for easy location of the exact position where it is to be placed. The silk screen holds back paint applied over it except where threads have been removed to produce a design in the silk. A series of these screens, using the several colored paints and having different designs when superimposed upon each other produce the desired multicolored pattern.

Application by squeegee is exemplified by wire coating with vinyl coatings through dyes, as described earlier, and by adaptation of a soft rubber squeegee to roller-coating steel venetian blinds for the purpose of giving a smoother film.

The last subject to be discussed under conditions of use is drying schedules. These include air drying, force drying and baking. Here again in order to properly formulate for the consumer's greatest good an intimate knowledge of the conditions for drying in his plant is essential.

Air drying schedules vary all the way from 3 to 5 minutes to overnight. Such schedules as 3 to 5 minutes do not refer to complete drying, but to evaporation of the thinner with attendant surface drying, so that objects may be handled enough to stack in piles, or so that additional work may go on around the painted objects without fear of marring the finish by light contact. An example of the latter type of finish would be the quick-dry chassis black paints which after 3 minutes are dry enough to permit assembly of other parts without spoiling the chassis finish by contact with the workmen's clothing. Other features of air-dry finishes are the time required to reach the stages of drying referred to as out of dust- and tack-free. These times are associated with air dry paints which dry more slowly than the 3 to 5 minute variety just mentioned. Out of dust is the time required for the paint film to set up sufficiently so that dust will no longer adhere, or so that dust which has dropped onto the surface can be wiped off later when the film is completely dry. This time is reached before the paint is tack-free. Tack-free time is the time required for the film to reach that stage of drying where the film no longer feels tacky under light pressure of the finger and where the finger leaves no print on the film. These periods vary with different paints and certain conditions in the customer's plant may necessitate that these times be shorter in some cases than in others. Air-drying finishes, except for those formulated with solvent-type vehicles, require the greatest amount of drier in their formulation. They generally cannot use amine-type resins as these are heat-converting materials. For this reason phenolic resin-modified vehicles are often included in air-drying finishes for wrinkle resistance and greatest chemical resistance.

Force drying covers drying at temperatures in excess of room temperature and up to about 180°F. *Baking* refers to drying at temperatures in excess of 180°F. In force drying and baking heat may be supplied by any of the common means—steam, gas, or electricity. *Steam heat* is accomplished by convection and requires no other explanation as long as the temperature and the time the object is in the heat are known. *Gas heat* is accomplished by convection and includes indirect- and direct-fired gas. In the former, products of combustion are prevented from coming into contact with the work being baked by the air in the oven picking up heat from the oven walls which confine the products of combustion. In direct-fired gas, which would include Burdette infrared gas ovens, products of combustion are not excluded from the baking chamber. Direct-fired ovens present a problem in that products of combustion may cause gas checking in finishes the vehicle of which contains oiticica, china wood, or dehydrated castor oils.

Electrical heating includes ovens with strip heaters, those using infrared radiation and those where heat is supplied by induction. Heating with strip heaters is accomplished by convection. Heating by infrared radiation is accomplished by converting electrical energy into radiant energy with special electric bulbs. The rays when absorbed by the work are converted into heat which bakes the finish. In induction heating, the heat is produced in steel objects by placing them in an electromagnetic field where this type of energy is converted into heat energy within the object. This is reported to be one of the most satisfactory methods of baking paints because heating is from the metal out rather than from the paint surface inward, the latter often giving skin or surface drying which may result in objectionable wrinkling. Unfortunately induction heating, which overcomes these difficulties, is not economically as desirable as other means and therefore finds only limited use.

In all convection ovens good government of the heated air is essential for efficient transference of heat from air to objects being baked. Adequate fresh air must also be provided so that even in indirect-heated ovens fouling of the oven and consequent gas checking is not caused by the fumes of baking that have not been sufficiently removed. Automatic temperature controllers are provided on all types except infrared and induction ovens. This equipment assures the same bake for all finishes in spite of color. A time-temperature curve can be obtained on such ovens by placing a traveling thermometer on the conveyor line. This instrument plots on a smoked chart the time and temperature relationship as the thermometer travels through the oven.

In infrared ovens, the heat developed is not the same in all cases. This is so because the heat is produced by absorption of the infrared radiation. The greater the absorption the greater the baking temperature, and the greater the reflection the lower the baking temperature. Thus in a given oven time a black paint, because of almost complete absorption of the radiation, will develop a temperature very substantially higher than that developed in a white paint, because of almost complete reflection of the radiation. All other colors fall between these two extremes in the amount of radiation they absorb and thus in the temperature they develop in infrared ovens. Obviously in colors having a high percentage of reflection of the radiation more drier, amine resins, etc., must be used than in colors having a high percentage of absorption of radiation. Thus it becomes clear that two paints of identical formulation except for color may bake satisfactorily in a convection oven, while in an infrared oven one may be satisfactory and the other either too soft or too hard, or one may be too soft and the other too hard. For this same reason traveling thermometers are of no use in determining the temperature developed in infrared ovens. The only satisfactory method is to solder a thermocouple to an object being coated, paint it and send it through the oven. The thermocouple operating through a potentiometer establishes the temperature at any given instant and a time-temperature curve may then be plotted.

Baking introduces several conditions which must be considered by the formulator. These include wrinkling and satisfactory gloss development.

Amine resins, phenolic resins, cold cut gum solutions and zinc naphthenate drier are used with varying degrees of success to overcome wrinkling. Poor gloss often develops as baking temperatures increase. It is more pronounced with some pigments and with some vehicles than with others. Relief may therefore be obtained by a switch in one of these ingredients. Zinc naphthenate is sometimes helpful in bringing up gloss, but the most effective method is to give attention to improved dispersion of the pigment. Haze, developed on baking; is principally due to improper or incomplete wetting of the pigment. This becomes more evident in baking than in air-drying and thus pigment dispersions which produce satisfactory gloss when compounded into an air-drying product may not do so when made into a baking product. The only alternative, if this is the cause of the trouble, is to provide more complete wetting of the pigment when its dispersed base is to be used for baking finishes. It might conceivably be asked at this point if the more completely dispersed pigment base used for haze-free baking finishes might not also be suitable for air-drying finishes, and thus by always dispersing to the ultimate the difficulty just discussed might always be avoided. This would be so were it not for the fact that the cost of dispersing the pigment represents from 75 to 100 per cent of the labor cost involved in producing a gallon of paint, and the more complete the dispersion the greater this cost factor becomes. Hence in the highly competitive field of industrial coatings it becomes necessary to hold dispersion costs to the minimum consistent with attaining the desired results. Thus dispersions for air-dry finishes may not be continued to the point where they could also be used satisfactorily for baking finishes. More of this subject is covered below under manufacturing.

The third and last major factor influencing formulation of industrial coatings has to do with the *requirements placed upon the finish by its use.* Service requirements include (1) exterior durability, (2) chemical resistance, and (3) miscellaneous properties. Laboratory methods of evaluating a paint for these properties will be found in the chapter on Examination of Paints. In this section, the features of the paint which are grouped under each of these three service requirements will be mentioned, together with some reference to the manner in which formulation may be influenced to produce the desired property.

(1) ***Exterior durability*** cannot be ignored for automobile and truck finishes and all others exposed to the weather in use. Properties to be considered are check resistance, chalk and bronze resistance, color permanency, blister resistance, polishing characteristics and corrosion resistance. These are evaluated on the basis of comparisons made on test panels actually exposed to the elements. For most rapid development of these

characteristics, except corrosion resistance, the panels are most often exposed in Florida.

Check resistance refers to the ability of the finish to expand and contract with changes in temperature and moisture content of the atmosphere without opening up with cracks or checks. The factors affecting this property are the three basic ones in formulation: pigment, vehicle and ratio of pigment to non-volatile vehicle. Certain pigments contribute to checking more than others. Organic toners may be mentioned as well as the yellow and orange lead chromate pigments. Oleoresinous vehicles cannot generally be used where exterior durability is a requirement of an industrial coating. Alkyd resin and nitrocellulose vehicles are those most commonly used, although even in such cases sufficient oil modification or plasticizer must be present to produce the desired resistance. Of the amine resins urea formaldehyde generally detracts from, and melamine formaldehyde generally adds to check resistance of exterior baking enamels, although oil length of the alkyd resin used with the amine resin also influences results. Pigment to vehicle ratios may be varied to influence check resistance. Generally less resistance may be expected the lower the ratio, and conversely greater resistance may be expected by increasing this ratio.

Chalk resistance refers to the ability of the finish to resist erosion by the weather and thereby to keep the pigment protected and to prevent its chalking away. *Bronzing* may be considered as a special form of chalking obtained with certain pigments such as carbon black, iron blue, and phthalocyamine blue and green. It may sometimes be controlled by proper choice of pigments. It is felt by some that there is a relationship between chalk resistance and check resistance and that the greater the one the less the other. While there is evidence to support this belief, a definite relationship has never been established, and in spite of its possible existence, a balance can usually be worked out in individual cases to provide adequate resistance for each property. It is perhaps significant of this relationship, however, that chalk resistance, like check resistance, is also influenced by the three basic variables in formulation (pigment, vehicle and pigment non-volatile vehicle ratio) while no other durability property is influenced by all of them. Inorganic pigments except lead chromate yellows generally contribute to chalking much more than organic pigments. Of the inorganic pigments titanium dioxide white, iron oxide yellow and chromium oxide green have shown poor chalk resistance. The development of non-chalking titanium dioxide by the manufacturers of this pigment has helped to overcome its deficiency in this respect. It has thereby made possible the use of lighter and lighter automobile colors introduced during the last few years. Such colors were not previously available because with the older, chalking types of titanium dioxide they required a higher percentage of white pigment than was consistent with adequate chalk resistance. Recent work by industrial coating manufacturers has suggested that incomplete pigment dispersion may have contributed to poor chalk resistance in the case of iron oxide yellow and chromium oxide green. It now appears quite evident that the better the pigment is dispersed the better is its chalk resistance.

Vehicles also affect chalking. Generally speaking, straight oil-modified alkyd resins with or without amine resins provide the greatest chalk resistance and the lowest cost. Nitrocellulose lacquers come next in chalk resistance and very nearly approach the first type when they include high percentages of alkyd resin in their composition. They are usually more costly, however. The presence of phenolic resin in the vehicle decreases chalk resistance.

As far as pigment to non-volatile vehicle ratios are concerned, the higher this ratio the lower the chalk resistance. Consequently this figure is usually fixed at the minimum necessary to provide complete hiding, unless experience has proved that a higher ratio is necessary for adequate check resistance. In those cases some sacrifice in chalk resistance must be accepted, since it is a less objectionable type of film weakness than failure by checking.

Color permanency is primarily a function of pigment, although in the case of white and very pale colors non-yellowing characteristics of the vehicle must be considered. Excluding such cases, color permanency refers to the ability of pigments to resist color change under the influence of the ultraviolet rays of the sun. It is impossible to cover this subject thoroughly here, but certain very general statements can be made even though many exceptions at once suggest themselves. Inorganic pigments on the whole have good color permanency. Lead chromate yellows and oranges are acceptable, although weaker than most others. Color permanency suffers further when these pigments along with chrome greens, which contain lead chromate yellow, are used with white to produce lighter shades. Organic toners are generally weaker in respect to color permanency than inorganic pigments. Of the organic toners considered to have acceptable color permanency, few can be used in combination with inorganic pigments such as white and still maintain it. Even as little as 5 per cent of white has been known to produce unsatisfactory color permanency. Organic toners which do not fall into this classification, but which can be mixed with white and still produce satisfactory permanence, include the phthalocyamine colors (blue and green), indanthrene colors (blue, yellow and maroon) and carbon black, if it may be considered as an organic color. BON (beta-oxynaphthoic) maroons generally permit the use of greater percentages of white than other organic pigments while still maintaining acceptable color permanence.

Blister resistance refers to the ability of the finishing system as a whole to resist the action of atmospheric moisture without raising blisters. The undercoater or coating adjacent to the metal is primarily the one responsible for providing this property. Blistering is known tō occur when pigments containing high concentrations of water-soluble salts are used. One method of obtaining blister resistance therefore is to use only those with low water-soluble salts content. Frequently rust will be found under a blistered area. This suggests that added blister resistance can be obtained by giving attention to improving rust resistance. Surface preparation of the metal is therefore another means of providing added blister resistance. Corrosion-inhibiting zinc chromate pigment may or may not be helpful in providing blister resistance. This is because the corrosion-inhibiting features of zinc chromate are due to a slight solubility of the pigment itself which acts to make the metal passive. In the case of zinc chromate, blister resistance provided by metal passivity may be offset by lack of blister resistance due to the slightly water-soluble nature of the pigment. As far as the vehicle is concerned, ingredients known to give extra water resistance may be used to improve blister resistance. These would include phenolic resins, china wood oil, oiticica oil and dehydrated castor oil.

Polishing properties refer to the ability of a weathered film to regain its original gloss and appearance when polished with a standard type of automobile polish. Failure to polish properly is associated with certain pigments, such as the original rutile titanium dioxide, which resisted chalking well but which, when it did chalk, left the film eroded in such a way that gloss could not be regained by polishing. Pigments which cause excessive chalking also tend to have poor polishing properties. Vehicles also have a bearing on polishing. Better results are generally obtained with alkyd resin coatings than with nitrocellulose lacquer coatings.

Corrosion resistance refers to the ability of the paint system to prevent rusting of the metal substrate. This feature is particularly important to automobile and truck finishing systems in the northern part of the United States where much salt is used on icy streets. Calcium chloride used for settling dust in rural areas is also responsible for rusting. Resistance to corrosion is provided by proper metal treatment and by inclusion in the paint, used next to the metal, of a corrosion-inhibiting pigment. These include zinc chromate, lead chromate, lead oxide (red lead) and basic blue lead sulfate. The lead pigments cannot be used in sanding undercoaters because of the hazard of lead poisoning. Anything which adds to water resistance of the system also adds to the corrosion resistance. Outdoor exposure panels (except tidewater exposures) do not give information on what may be expected from the standpoint of this property; instead salt spray cabinets are used. Information on these may be found in the chapter on Examination of Paints.

(2) **Chemical resistance** is the second subject to be considered under service requirements of the paint system. These characteristics refer primarily to paints used indoors, but none the less exposed to unusually severe conditions. The properties to be considered are water or moisture resistance, acid resistance, alkali resistance, oil and grease resistance, gasoline resistance and toxicity. Most of these are properties required by refrigerator, washing machine and chemical laboratory bench finishes, as well as others.

Water or moisture resistance is very similar to blister resistance described above and the same factors aid in providing it, namely good metal preparation, use of pigments with low water-soluble salts content and use of vehicles which add to this property. The primary difference between the term as used here and that used above is in the method and duration of testing for this property. For blister resistance, panels exposed in Florida are generally relied upon. When accelerated water soak tests are used to evaluate this property, a four-day test at room temperature is considered adequate by many, although there are more severe tests. In the case of refrigerator finishes, however, tests are often continued for twelve weeks (2000 hours). Humidity cabinets are also used. Their severity as compared to water soak tests is dependent upon temperatures of operation. Humidity tests conducted at 95 to 100°F are generally more severe than water soak tests at room temperature, whereas a watersoak test conducted at the same temperature as a humidity test is more severe. Aeration of water soak tanks also increases the severity of the test.

Acid resistance refers to the ability of the paint system to withstand the action of acids. This feature is necessary in finishes used on chemical laboratory benches and desks to resist the action of acids which may be spilled. It is also necessary in refrigerator finishes to resist the action of fruit juices, vinegar, the lactic acid of sour milk, etc. It is necessary in washing-machine finishes to resist the action of "Clorox" and other bleaches. Pigments, such as aluminum, affected by acid, are to be avoided in coatings requiring acid resistance, while vehicles containing phenolic or amine resins are used to increase this property. Tests for acid resistance are set up on the basis of soaking panels in acid solutions of definite concentration, or by filling a wax ring on a test panel with the fruit juice or acid solution in question. Panels are rated for their resistance on a comparative basis after definite periods of exposure.

Alkali resistance refers to the ability of the paint system to withstand the action of alkaline materials. This feature is necessary in the same situations where acid resistance is required in order to prevent attack by alkaline solutions spilled in chemical laboratories and to resist attack by ammonia, soap and other alkaline materials which may be used in cleaning refrigerators or which must be used in and around washing machines. Pigments such as aluminum, iron blue, etc., which are sensitive to alkali must be avoided. Phenolic and amine resin vehicles are used to provide this property, but the most alkaline-resistant vehicles are those that do not include ingredients which are esters, *i.e.*, saponifiable materials. This means that greatest alkali resistance cannot be obtained with oleoresinous or alkyd resin vehicles and is obtained in the case of solvent-resin type vehicles chiefly when the ester type constituent is held to a minimum. In spite of this extra alkali resistance of certain solvent resin finishes, cost considerations often prevent their use and force the acceptance of the decreased alkali resistance of oleoresinous or alkyd resin products. Tests for alkali resistance are made in the same way as those for acid resistance, substituting standard alkali solutions, soap solutions, ammonia, etc., for the solutions used in the tests for acid resistance.

Oil and grease resistance refers to the ability of the paint system to withstand softening and deterioration in the presence of oil and/or grease. This property is a requirement of finishes used on lubricating equipment for gasoline stations, of refrigerator finishes to resist the action of butter and lard, and of finishes used on transformers and other electrical equipment where oil is used for cooling and insulation. This requirement in general does not limit the use of pigments. As far as vehicles are concerned, those with shorter oil lengths are to be preferred, preferably when modified with amine resins. High-temperature baking also improves grease resistance. Products with solvent-type vehicles are usually eliminated from consideration because of cost, although they are frequently excellent in their resistance to these agents. Tests for oil and grease resistance may be made by hot or cold immersion tests or by wax ring tests, as described above under acid resistance. Inasmuch as failure in use due to poor grease resistance is often caused by softening of the film and consequent scuffing off of the paint, grease resistance tests are often accompanied by an abrasion test. In such tests a pad constantly kept wet with the test material by means of an adjustable oil or grease cup is placed in contact with the test panel. A fixed weight is applied and the pad is made to oscillate along the length of the panel. Severity of the test can be influenced by changing the weight or by varying the abrasiveness of the pad.

Gasoline resistance refers to the ability of a paint system to withstand attack by gasoline. This property is a requirement of paints used around gasoline stations as well as those used for certain materiel of war, such as the inside of gasoline cans and on landing field mats where resistance to high-octane gasoline which may be spilled is a necessity. This property does not limit pigmentation. For vehicles short oil products and high baking temperatures are employed. Amine resins further increase this property. Evaluation is on the basis of immersion panels. Severity of the test may be varied by changing the composition of the liquid in which the panels are immersed. Benzol, toluol, alcohol, esters and other solvents may be used in conjunction with the gasoline for this purpose.

Toxicity does not refer to a resistance feature of the film but rather to poisonous effects which may be obtained in use. This feature is important in connection with all coatings used on food containers. It must also be considered in connection with coatings used on baby's and children's toys where the finish may be chewed off and swallowed. It is also important in finishes which are sanded. Lead-containing pigments and lead driers must all be avoided in such uses. Pigment suppliers will furnish information on the toxicity of their pigments for uses such as those listed above. In general properly converted vehicles give no trouble from this standpoint.

(3) *Miscellaneous service requirements* are the last group to be considered. These include light reflection and absorption, abrasion resistance, heat resistance and fire and flame resistance.

Light reflection and absorption may refer to the gloss of the film, the daylight reflection or the infrared reflection. Equipment for evaluating these properties and for the determination of film thickness which is necessary for this evaluation is described in Chapter 24. The influence of gloss on formulation has been covered earlier in this chapter under the discussion on topcoats. It remains only to mention that its evaluation is either by visual comparison or by gloss and sheen meters. In preparing panels for such ratings film thickness has a distinct bearing on the value obtained and careful control of this feature must be maintained.

Daylight reflectance cannot be evaluated visually, but must be done with the aid of equipment such as the Hunter Multipurpose Reflectometer. Daylight reflectance requirements are established for white finishes used on such objects as the inside of the reflectors for fluorescent lighting fixtures. The National Association of Lighting Fixture Manufacturers has established, for example, that daylight reflectance on such coating shall be 80 per cent minimum. At the same time consumers require that blue white paints be supplied to them. Since many of the light-fast pigments used to offset the yellow and provide the blue tone to white paints have practically no daylight reflectance these requirements may have one of two effects: either they limit the depth of blue white which can be produced or they force the use of those blue pigments which have some daylight reflectance and thus will not reduce it to below 80 per cent when used in white paint to produce a desired depth of color.

Infrared reflectance has been discussed earlier under lusterless camouflage coatings. This property of a paint may be measured by the Hunter Multipurpose Reflectometer and other equipment described elsewhere.

Abrasion resistance is well described by its name and is a requirement of finishes where extreme wear and tear is encountered. An example of a coating requiring such resistance is the one used on the window moldings of automobiles where excessive rubbing with sweaty arms in summer and with heavy overcoats in winter requires that it have exceptional abrasion resistance. Another example of such a coating is the one used on the hard rubber steering wheels of automobiles where constant contact with warm, sweaty hands also requires excellent abrasion resistance. This property is considered to be of such importance that a special machine has been designed to evaluate it. As a result of the information obtained, the abrasion resistance of coatings used on automobile window moldings has been increased from failure in 30 minutes to still satisfactory at the end of 100 hours. The Taber Abraser and falling sand or silicon carbide are other methods of evaluating this property (see Chapter 24), while still another method of evaluating abrasion resistance is described above under the section on oil and grease resistance.

Heat resistance is a requirement of finishes used on articles which produce heat, among which may be listed toasters, electric heaters, grilles, and roasters, coal oil and gas stoves, and similar items. Resistance to heat means the ability of a finish to withstand discoloration and loss of gloss at elevated temperatures. Pigments which provide this property to any appreciable extent must be inorganic, particularly those which are calcined in their manufacture. Moderate heat resistance can be obtained with alkyd resins modified with non-drying oils, such alkyds to be used alone or in combination with amine resins. For the extreme heat resistance which would be required by a modern gas range no oil-modified organic coating can be used; in fact at present no organic coating of any sort is used, such finishes being vitreous enamels instead. However, silicone resins have exceptional heat-resisting properties, so that more and lower cost production of these products may eventually lead to a truly heat-resistant paint material based on them. This property is evaluated by comparing color and gloss of panels held at room temperature to similar panels held at elevated temperatures for extended periods of time. The time and temperature of test are established by those which the finish will have to withstand in use.

Fire and flame resistance refers to the ability of the coating to retard the propagation of flame. This was a requirement of coatings for tent fabrics during World War II and is necessary in ship paints, etc. Specifications for such paints often call for antimony oxide white pigment, and for the vehicles of such materials the inclusion of chlorinated products such as chlorinated paraffin is often specified. Tests for this property are made by timing the progress of a flame under standardized conditions of burning.

Manufacturing Methods for Industrial Finishes

The production of industrial finishes depends just as much on manufacturing technique and control as on formulation and proper choice of raw materials. Oleoresinous varnishes and alkyl resins are cooked in small batches (up to 250 to 300 gallons) in copper or Monel metal open-type kettles heated over coke or gas fires. Larger batches with better color and providing better uniformity are processed in stationary closed reaction vessels of aluminum or stainless steel. These are directly heated with electric strip heaters or indirectly heated with oil bath or Dowtherm (diphenyl oxide) which are heated in electric, gas or coal boiler systems. These kettles are also equipped with variable-speed agitators, reflux condensers, inlet for inert gas and suitable means of discharge by gravity into reducing kettles.

Each batch of oleoresinous varnish or alkyl resin is tested for color, solids, acid number viscosity, and specific gravity. Air-drying and baking properties and film characteristics are also checked.

In the manufacture of pigmented materials the steel ball or pebble mill is perhaps the most widespread method of dispersion. Essentially these mills consist of a cylinder mounted so that it is caused to revolve by means of a gear drive. The interior is lined with buhrstone, or specially hardened steel. The mills are charged with hardened steel balls, or in the case of a pebble mill with flint pebbles or specially processed pebbles. These mills are water-jacketed for cooling. In this type of mill, mixing and grinding are carried out in the same unit, and after it is loaded very little manual attention is needed. Because it is completely enclosed there is very little loss of volatile matter, which is the case in open types of equipment. The mill is usually charged half full of pebbles or in the case of a ball mill approximately one-third full of steel balls.

The material charge (pigment, vehicle and volatile) is very important in relation to size of batch produced, ease of dispersion, fineness of grind and manufacturing cost per gallon of material.

Each different type of pigment and each combination of pigments along with different types of alkyds presents its own individual method of charging to obtain the maximum efficiency from each mill. Ball mills range in size from the laboratory 1 gallon mill to 2000-gallon production mills.

The type of pigments used and the fineness of grind specified will determine the number of hours required to disperse the batch.

Roller mills are equipped with hardened steel rolls which are hollow in order that the roll may be internally water-cooled. The common mills have either three or five rolls; the three-roller is generally horizontal while the five-roller may be vertical or angular. The rolls are mounted in the framework of the machine so that they may be adjusted for different grinds. A hopper is mounted on the feeding side of the mill over the first and second rolls. The paste is scraped from the last roll by means of a scraper knife, running across the entire length of the roll and placed at an angle so that the paste drops into the kettle. The first roll revolves at the slowest speed and each succeeding roll revolves at approximately twice that of the preceding roll.

Roller mills require the constant attention of an operator to adjust and feed materials to the mill, but they are easily cleaned and various colors can be run on the mill in succession without too much contamination from the preceding batch.

Stone mills are practically obsolete because of their small production rate. They are essentially two buhrstones surfaces, the top one being stationary and having a circular opening in the center through which the paste is fed into the mill.·The bottom stone revolves and the paste is dispersed between the two grinding surfaces; centrifugal action carries the paste out of the mill.

The Baker-Perkins mill is similar to a dough mixer in that two blades or mixer arms revolve in opposite directions. Very heavy pastes are used in this type of equipment. The Baker-Perkins is mainly used for white enamels.

North Standard Fineness Gauges have been used for several years by the paint industry to check and control the grinding operation. They are made of hardened steel ½″ thick, 2½″ wide and 7″ overall length. They contain on the top surface two paths 5¼″ long and ½″ wide. On the 4-mil gauge the paths are graduated uniformly from 0.004″ to 0.000″ deep and are calibrated from 0 to 8. A few drops of enamel or paint are dropped in the wells at the 0.004″ end, and by means of a scraper a film is drawn the entire length of the instrument. Viewing the film at about a 15° angle permits ready observation of undispersed particles of pigments. At the point where these are just visible, the fineness of grind is read.

The following is a rough guide for fineness of grinds for different types of paints and enamels:

House paints: No. 1½–2
Flat wall paints: No. 4
Industrial primers: No. 5–6
Industrial Enamels
    Semi-Gloss: No. 6–7
    Gloss : No. 7–8
High-grade industrial enamels
    (Refrigerator and Automotive enamels): No. 8

From the above illustration it is evident that primers, enamels and all pigmented goods do not receive the same amount of dispersion.

Grinding a primer until fine would destroy the filling properties and adhesion. Conversely, an enamel that is not dispersed completely will be lacking in gloss, will not develop the ultimate strength of the dry colors, will have excessive settling and may have an exceedingly seedy appearance.

After the pigment has been dispersed on any of the above-mentioned equipment and the mill base checked for fineness of grind, thinning and tinting are the next operations. The mill base is usually dropped by gravity into a tank equipped with agitators. Here the remaining vehicle, volatile and drier are added and thoroughly mixed. Care must be taken in reducing and thinning the paste that no separation occurs. An alkyd resin product having limited petroleum thinner tolerance, for example, should be reduced slowly. This permits the batch to take up the thinner gradually, so that excessive amounts of it which have not as yet been taken up by the batch will not kick it out of solution. After the batch is completely reduced it must be shaded to the proper color. As a rule, primers are ground out fairly close for color and may only need a touch of black; however, all enamels must be tinted to the desired color. The shading colors used for tinting must be ground in a vehicle which is completely compatible with the batch of enamel being shaded. The formulator generally specifies what type of shading pigments should be used. A batch of acid- and alkali-resisting green enamel can be ruined by using chrome green shading colors for tinting; therefore, proper selection of shading colors—not only the vehicles but also the pigments—is an important factor in industrial finishes.

The control and testing of industrial finishes is also very important as each batch of material is made for a special purpose and to fit into the customers' individual production set-up. Each product should be tested in the same manner that the customer will use it. If the customer bakes his enamel, it should be tested by baking for the same time and temperature, since these have a decided bearing on color, gloss, toughness and other qualities of the finished product.

The package properties of industrial finishes are highly important. Even though agitator drums are used in shipping industrial finishes they must remain in suspension over extended periods and must not skin. Properly balanced extenders and correct fineness of grind are the two most important factors in controlling suspension. In the case of light-colored enamels that are not properly dispersed, a slight color drift may take place in the package, especially if it has stood for a long period of time. This is due to wetting out of pigment not developed to its ultimate strength initially. Tests that should be made on each batch include:

Viscosity. Each batch of material should be adjusted to a predetermined standard viscosity, as the customer will expect to reduce each shipment in the same manner, and a variation in original viscosity will alter the reduced viscosity and hence the spraying properties he obtains. The Ford Cup or Stormer Viscometer are two well known instruments for controlling viscosity. When the batch of paint is ready for viscosity adjustment, special care must be taken to use the proper volatiles as spraying properties, leveling and flow will be impaired by the wrong choice.

Solids. Many customers specify a minimum and a maximum limit on total solids. This is an important factor, as a batch of paint that is high in solids can be reduced to the proper solids, with an increase in yield of the final batch which will materially lower the cost.

Color. In industrial finishes color is very important, as the customer may finish part of his work with one batch of enamel and part with another batch, and when all parts are assembled on a production line they must match. Standard color panels and wet samples must be maintained, as a slight variation in color from batch to batch will eventually end up with material that will be sveral shades from the original standard. Color is usually judged visually.

Gloss and Sheen. The usual practice is to compare the batch with a standard; however, the Hunter 60° Glossmeter and the Hunter Reflectometer are gradually being adopted.

Hiding Power. The Pfund Cryptometer or Checker-Board Method may be used. The Cryptometer consists primarily of two plates of glass whose optically flat surfaces are separated by a fixed angle in which a wedge-shaped film of paint is formed. By sliding the top plate back and forward a sharp line of demarcation (showing the point of complete hiding) alternately appears and disappears. This point is read on a millimeter scale etched on the bottom plate which by referring to a table the number of square feet of area hidden by one gallon of paint is at once determined.

Determinations are made by the checker-board method by applying paint on a smooth, impervious area composed of alternate black and white areas, with a checker-board effect, until the checker-board effect is completely obscured. Calculations are then made by a predetermined formula. Hiding power is of extreme value to the customer for calculating the mileage or number of square feet of area he can expect to cover with a given enamel.

Hardness. The Sward Hardness Rocker is a well known method of test for hardness. This device consists of two 4-inch metal rings spaced 1 inch apart, a circular level at the bottom, to level the instrument, and two tube-style levels in the lower half for indicating the beginning and end of the test. The harder the film, the more oscillations the rocker will make after being set in motion. The standard is 100 complete oscillations on polished plate glass.

Adhesion. The use of the "thumb-nail" and spatula as a means of testing adhesion is still the main method of test. However, the impact test is gradually becoming more and more important. This test is performed by allowing a known mass of metal (usually spherical in shape) to fall a certain distance by gravity upon a coated steel panel. The point of extrusion is examined for adhesion of the film to the metal.

Bleeding. Some customers specify non-bleeding enamels, especially red, as a striping or decorative white lacquer will be applied over the baked red enamel. It is very essential that each batch be tested for this phenomenon. Para, toluidine and some lithol reds will bleed or become soluble in the lacquer thinner and will discolor the white lacquer causing it to be pink instead of white. A very small percentage of bleeding red pigment will contaminate the entire batch, and even though the enamel is formulated with non-bleeding pigments, a mill or tank that is not free of bleeding reds may render the batch useless as a non-bleeding red enamel.

Dip Tank Stability. Many consumers of industrial finishes apply the coating by dipping. Dip tanks will range in volume from 100 gallons to 4000 gallons depending upon the size of the object to be coated. Even though the tanks are agitated and new material is constantly being added, it is essential that the material be stable for long periods. Mechanical means to simulate large-scale operations are used for testing. A disc or paddle revolving through a small tank containing 8 to 12 ounces of enamel under test is usually used. A constant supply of volatile is added to compensate for loss due to evaporation.

Resistance Properties. Industrial finishes may be required to withstand water, acid, solvents, alkali and other chemicals. The customer generally specifies the method of test and concentration of solutions to be used. An important factor in performing these tests is panel preparation and film thickness.

Film Thickness. Film thickness may be determined with a micrometer, or the General Electric Thickness Gauge which operates on an electromagnetic principle. The Magne-Gage is a very rapid method of measurement. This instrument consists essentially of a small, permanent bar magnet, freely suspended from a horizontal lever arm. The latter is actuated by a spiral spring which is coiled by turning a graduated dial. The attractive force between the magnet and the specimen is indicated on the graduated dial, and the readings are converted to thicknesses by reference to a chart. Control of thickness of a paint film is very essential, as results obtained in the above described tests are directly affected by the thickness of film. All specifications definitely state at what film thickness tests are to be made, and the approval or rejection of a paint film may be dependent upon use of the correct thickness of film.

Exterior Exposure. Exposure tests have been accepted for a number of years as a prerequisite for intelligent paint formulation for exterior coatings. Experience has indicated that the more rapid or accelerated tests are not always reliable. Every pigment and combination of pigments in different vehicles should be given outdoor exposure as proof of durability. This is especially true of automotive finishes. Color fading is perhaps the first thought in exterior exposure, but attention should be paid to such paint film changes as dirt collection, loss of gloss, chalking, checking, cracking, erosion, and general appearance.

The above are only a few general tests. However, it must be kept in mind that each item of industrial finish is specified for a particular use or purpose and must be formulated and manufactured for practical usage.

(Acknowledgment is hereby given to Mr. S. W. Farrell and Mr. C. Leopold of the laboratories of the Ferbert-Schorndorfer Company for their assistance in organizing material for this chapter.)

Chapter 21

Trade Sales Paints

EXTERIOR

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Paint products stocked by dealers for sale to retail customers are known generally as "trade sales" items. These include such products as exterior house paint, shingle stain, spar varnish, exterior enamels, asbestos shingle paints, caulking compounds and coal-tar products. (Porch and floor enamels are also in this category but are not covered in this discussion.)

The exterior performance of paints is affected by (1) quality of the coating material, (2) conditions under which it is applied and type of base surface on which the coating is used, and (3) film thickness.

Paint consists of pigment and organic binder. Each is equally important to good paint. Carbon black is one of the most durable pigments, and quality paints made with it will easily last from 8 to 10 years. The best white paints, on the other hand, usually endure for about 5 years. So it is evident that the pigment used has considerable bearing on the durability of paint. Unsatisfactory pigment can cause a paint film to begin to deteriorate within a few weeks after application, regardless of the quality of vehicle.

Likewise, if the vehicle is unsuitable, the paint will be of poor quality irrespective of the pigment used. The vehicle itself must be able to withstand oxidation, ultraviolet light, moisture, change in temperature, etc. Excellent films can be prepared from many types of drying vegetable oils, the most common being linseed oil. Also, since 1925 phenolic and other synthetic resins have been available; when used alone these are inherently more durable than the drying oils.

Conditions of painting are extremely important to the longevity of the coating. For example, paint should not be applied when the temperature is too low, or the humidity excessively high; nor should paint be applied to a surface with frost on it (such as frosty steel). Condensation of moisture under a coating prevents adhesion of the coating to the base surface.

Of the various surfaces on which paint is used, bonderized steel is a good example of a high-grade surface ready to receive paint. Steel that is galvanized and bonderized is even better. Wood, in general, is quite satisfactory, though the several grades of wood vary with respect to their suitability for paint. Alkaline surfaces such as concrete, cement block, and cement asbestos board are more difficult to coat. In each instance precautions must be taken properly to prepare the surface for painting.

Since thickness of the film also influences durability, care must be exercised to avoid making the film too heavy or too thin. A heavy film prevents thorough drying and too thin a film will not provide proper protection to the surface.

With these general points in mind, let us consider the various trade sales items individually.

House Paints

The most important factors in house painting are:

(1) Film thickness
(2) Quality of pigment and vehicle forming film
(3) Surface
(4) Painter

In order to secure the desired film thickness, 4 to 5 mils, two or three coats should be applied; however, it is not necessary to apply as much paint to the north side of a house as to the most exposed sides. Two coats on the exposed side and one coat on the north side are generally satisfactory, especially if the house is washed clean before painting. A good paint fails by gradually washing away.

There is a real advantage in applying paint in two or three coats rather than in one extra-heavy coat. Let us consider an area of average siding close to a nail head. One extra-heavy coat would tend to be lost in this area due to seepage in the fibers, whereas a multiple coat application has the advantage that the first coat will act as a sealer, holding out the succeeding coats. This results in a much more uniform final thickness and protection.

In order to obtain a total of 4 to 5 mil film thickness, paint cannot be spread more than 400 to 500 square feet per gallon. One coat of typical house paint brushed out so as to cover 700 square feet per gallon would use less paint but would give an insufficient film thickness. Since the cost of spreading paint ranges from four to twenty times the cost of the paint itself, paint should always be applied in the proper manner.

A typical two-coat system today consists of an undercoater followed by a glossier finish coat. A typical undercoater is formulated so as to have about 36 per cent pigment volume concentration and is reasonably low in gloss, so that the next coat will not tend to creep and crawl. Many undercoaters today carry a small percentage of resin in case zinc oxide is not used in the pigmentation. In general, either zinc oxide is part of the pigment or a resin is part of the vehicle. An undercoater should have good filling power and in this way control penetration of the vehicle. A typical prewar top coat had a 32 per cent pigment volume concentration and was pigmented with 50 per cent leaded zinc and 50 per cent titanium magnesium pigment. Others would carry small percentages of lead carbonate and lesser quantities of titanium magnesium.

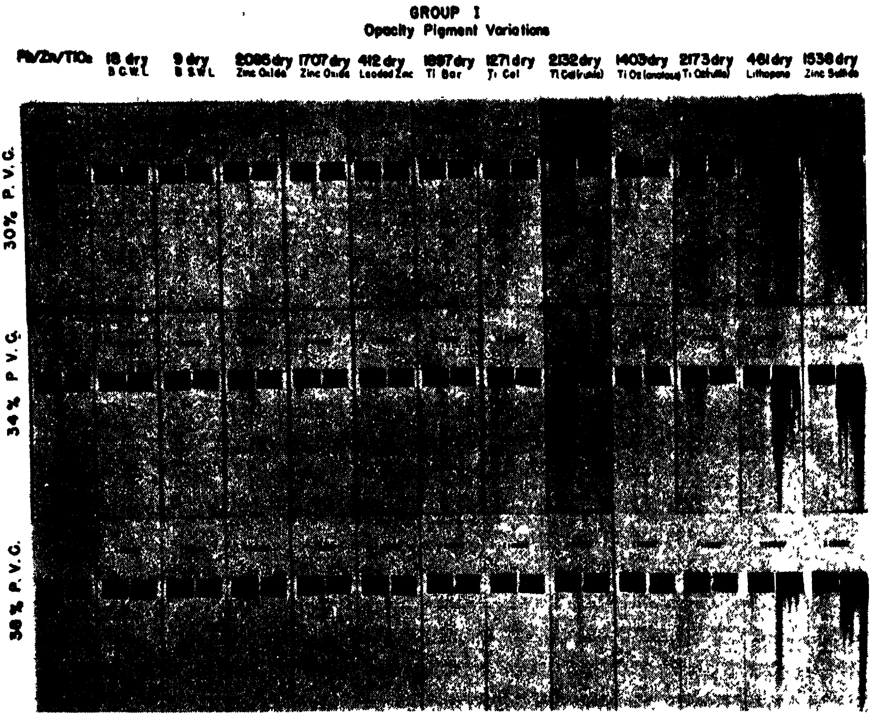


FIGURE 90. Iron and copper stain test. 3 months exposure—Florida, 45°, south.

High-grade paints of this nature are reasonably "self-cleansing." Those containing lead carbonate generally have less erosion after 4 years' exposure. Before the war a typical vehicle would have run about 88 per cent linseed oil containing a small percentage of polymerized oil. During the war, due to vegetable oil shortages, a higher percentage of polymerized oil was used, together with more thinner, at the expense of the total oil content. The vehicle contained approximately 65 to 70 per cent oil solids and the pigment volume concentration was raised to about 36 per cent. Due to the type of oil used, the top coat still had high gloss and was very satisfactory.

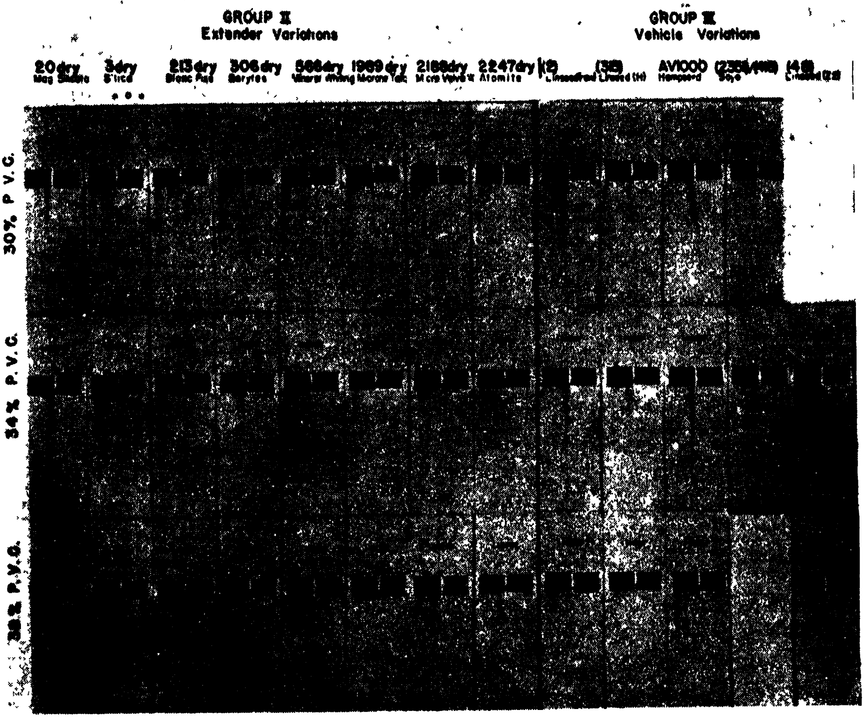
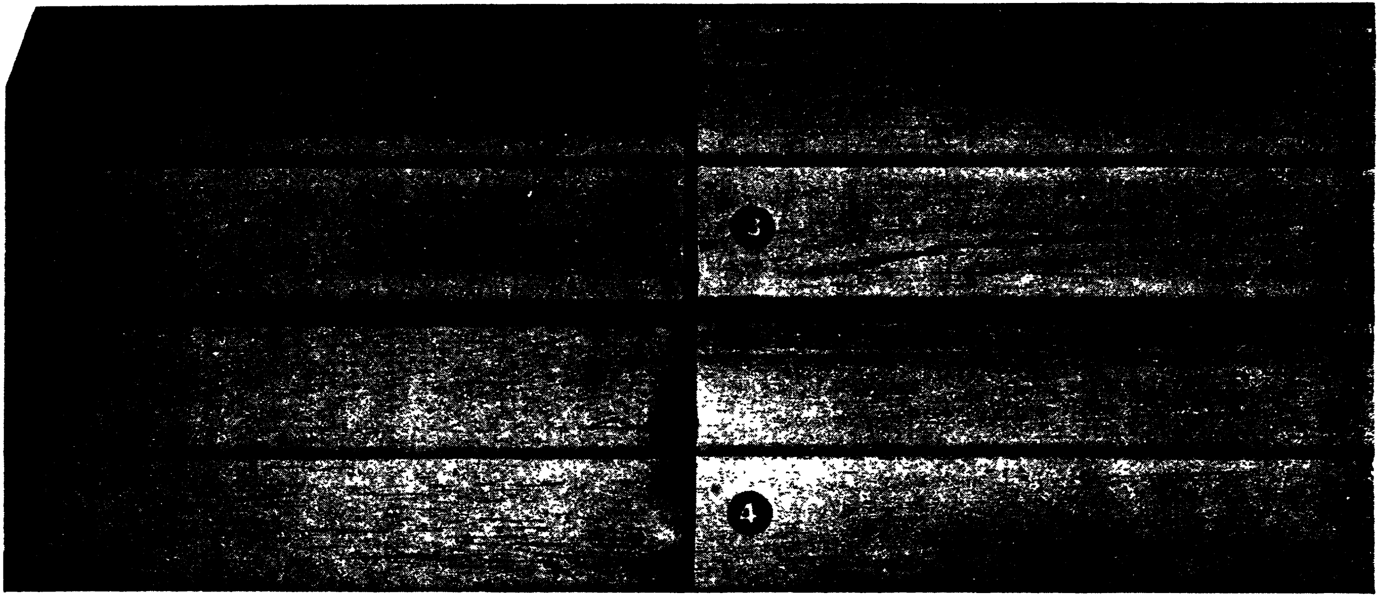


FIGURE 91. Iron and copper test. 3 months exposure, Florida, 45°, south.

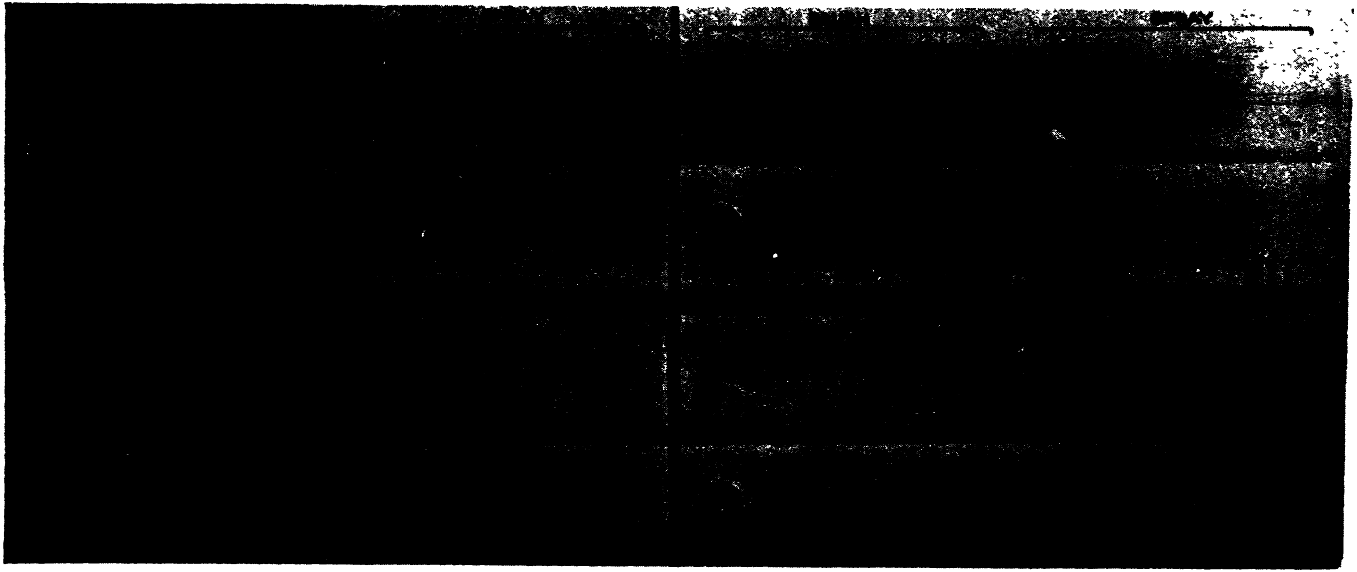
Experience has shown that this formulation is even better than the prewar raw linseed oil type in most respects. This type of formulation is characterized by better drying and less wrinkling and will undoubtedly be the standard of the industry for some time to come.

In Figures 90 and 91 are given a series of iron and copper stain tests. In the panel picture the opacity pigments, extenders and vehicles were varied as shown. Zinc oxide gives good control of mildewing but it causes staining under copper gutters and screens. Varnishing screens will stop the stain. The use of synthetic plastic screens will do away with the trouble altogether.



(*Courtesy Allied Research Laboratories*)

Figure 92. Brush versus spray application of Rex 471 over various weathered surfaces, *before painting*. 1. No film breaks. 2. Deep cracks. 3. Eroded to wood. 4. Bad checking and cracking.



(Courtesy Allied Research Laboratories)

FIGURE 93. Brush versus spray application of Rex 471 over various weathered surfaces, *after painting*. 1. No film breaks. 2. Deep cracks. 3. Eroded to wood. 4. Bad checking and cracking.

Figures 92 and 93 show the advantage of brushing over spraying, especially in areas having deep cracks.

Since the peeling of house paint sometimes is one of the serious failures, this should be considered briefly. Peeling is invariably due to moisture and generally, any serious peeling is due to moisture vapors coming from the inside of the building. The less serious type of peeling occurs around faulty flashings or other openings in the exterior surface of the house that allow exterior water to get into the fibers of the wood in localized areas. This type of failure is usually corrected by applying caulking compound, puttying joints, etc.

To avoid difficulty from interior vapor in new construction, barriers should be installed. The barrier itself should be aluminum foil, asphalt-impregnated paper, or some other mechanical barrier that stops moisture. Installation of barriers after a house is built is very expensive. Vapor barriers should be on the warm side of the house, that is, on the inside of any insulation. The humidity comes from the inside of the house and tries to get out, and this causes blistering.

Blistering is never observed on an unheated open building, such as a barn or a garage. Builders in general today understand that vapor barriers must be on the inside of the house, but a few years ago they frequently put them on the cold side of the house right under the sheeting or siding.

In general, house painting in the late fall or early winter should be avoided, since much moisture will be trapped within the wall and insulation in these seasons, and this may cause serious peeling and blistering before spring.

If a home has been built without the proper precautions for avoiding blistering, one of several things might help cut down the amount of blistering. A coat of aluminum paint over the plastered walls in the home will slow down the rate of vapor migration and in this way reduce blistering. A glossy oil paint also assists in this respect. Still another method of reducing the effect on the outside paint is to ventilate the outside wall; this precaution can be carried out by prying up siding boards at regular intervals and keeping them up by inserting thin wood slats (or match sticks). In this way the moisture will be removed directly to the outside atmosphere and will not penetrate through the wood siding.

All loose paint should be removed by scraping before repainting.

A formula for a white house paint is given below.

***Exterior House Paint* (White) Federal Specification TT-P-40**
Output, 100 gallons

153#	**Titanium dioxide**
445	**White lead (Basic Carbonate & Basic Sulfate White Lead)**
312	**Zinc oxide**
158	**Magnesium silicate**
170	**Raw linseed oil**

185	Bodied linseed oil—Body $Z_2.Z_3$; Acid Value 8–10
182	Mineral spirits
18	Liquid drier
	Pigment Volume 36.7%
	Vehicle Solids 66 %

Shingle Stain

The conventional high-quality shingle stain uses a drying oil as the binder. The vehicle would contain about ¾ volatile and ¼ vehicle solids. Raw oil, polymerized oil or air-blown oil is generally used. The stain will carry a minimum of pigment. This is a difference between stain and paint. A thick film is not desirable on shingles. A ridge of coating at any one point on the joint of the shingle would act as a dam to collect water that would settle and rot the wood. This difficulty is avoided by keeping the pigment content to about ¼ that of normal paint. Stain often carries a preservative such as creosote or other chemical to control fungi. In general, cedar shingles are no longer popular for top work since fire insurance rates are higher with wood shingles than with other types.

Spar Varnish

Spar varnishes were considered in some detail in Chapter 19 and therefore will be mentioned only briefly here. Spar varnishes such as those commonly used in trade sales have undergone radical changes in the last 35 years. About 1905 Wood Oil was introduced as a varnish ingredient, resulting in a significant improvement in spar varnishes. Until then few spar varnishes had good drying qualities. A typical earlier spar varnish containing 100-gallon length linseed oil and a hard natural resin required 1½ to 2 days to dry. An early China Wood Oil spar varnish would be a 40-gallon length ester gum resin. In about 1925 phenolic resin was brought into use and for the first time durability came from resin as well as from oil. A formulator today might choose to use dehydrated castor oil or other oils with resins in making spar varnish. This was common practice during the war when China Wood Oil was scarce. Phenolic resins with modern oil combinations make excellent varnishes, such as those which are used on station wagons. In Florida durability ranges up to fifty weeks, which might be equal to 2½ to 3 years in Ohio. Alkyd varnishes do not yellow so much on exposure nor are they as mildew-resistant as the phenolic type.

A high-grade trade sales spar varnish today would very likely be made with pure phenolic resin. Unfortunately, the term "spar" is much misused in the trade in that it is frequently applied to many varnishes that are not of the highest quality.

A spar varnish formulated for use on surfaces that are to be immersed in water for longer periods of time are usually made with shorter oil lengths. In the past the Navy, for instance, has specified oil lengths such as 12½, 25, and 33 gallon.

A spar varnish formulation is given below.

Spar Varnish (Army-Navy Specification AN-V-26)
33 Gallon Oil Length

Non-Volatile	60%	
Resin*	28	* 100% Phenolic
Tung oil	60	
Castor oil	10	
Linseed oil	2	
	100%	
Volatile	40%	
n-Butanol	5	
Turpentine	10	
Mineral spirits	75	
Petroleum naphtha	10	
	100%	
Weight per gallon	7.58	

Exterior Enamels

In order to fabricate good exterior enamel, the best vehicle possible must be used. It is pigmented to get the color and opacity required. Typical general-purpose exterior enamel vehicle contains about 25 to 35 per cent phthalic anhydride. A typical white formulation would carry ⅓ pigment, ⅓ vehicle solids, and ⅓ thinner by weight. Volume analysis of this product would be, roughly, 8 per cent pigment, 37 per cent vehicle solids, and 55 per cent volatile. It would contain approximately 3 pounds of titanium dioxide to the gallon. Soya or linseed alkyd could be used and, in certain instances, zinc oxide may be used as the pigment, in which case the alkyd used must be non-reactive. Long-oil enamels are very satisfactory, especially for wood, but they have the general disadvantage of requiring longer drying periods. A formula for an exterior white enamel is given.

Exterior Enamel White (Ordnance Specification 3–175 A)
Output, 100 gallons

326#	Titanium dioxide
564	Alkyd varnish (linseed-soybean oils, phthalic anhydride 34%)
10	Liquid drier
108	Mineral spirits
	Vehicle solids 40%

Caulking Compounds

The vehicle of a caulking compound should remain elastic over long periods of time and yet it should surface-dry so as not to collect dirt. A satisfactory vehicle has been made by taking the residue from fish oil of a low iodine number and blowing it with air. Soya bean oil bases have also been used. Pigmentation usually contains asbestos fiber, a pigment for opacity, other pigment filler, drier and the thinner.

Asphalt and Coal-tar Paint

These materials are generally low in cost. Coal-tar materials are especially durable and long-lasting in spite of the fact that they may "alligator" and check on exposure. Under certain conditions, such as around sewage plants, these products frequently out-perform other paints which are made from expensive synthetic type polymers.

Petroleum-base materials are generally cheaper than coal-tar products and are sometimes combined with vegetable oil to improve their performance. Under-frame chassis blacks used by the automobile industry are a good example of the petroleum asphalt type of formulation.

INTERIOR

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In Chapter 18 on "Principles of Paint Formulation," the subject of pigment-vehicle relations was discussed, and many of the other important properties of the various pigments and vehicles were mentioned. This section will cover more in detail the formulation of finishes used for the interiors of homes, schools, hotels, offices and factories.

Finishes, both interior and exterior, are applied for one of two reasons and more often for both, (1) their decorative value, and (2) as a means of protecting surfaces from wear, moisture, dirt, frequent washing, or perhaps from some chemical encountered in and around an industrial plant.

Our ideas on decorative value have been broadened somewhat by studies made on better lighting. Tests have proved that greater efficiency in the school, office and factory may be obtained by better lighting and proper selection of decorative colors, better lighting being secured in part by means of painting and the proper selection of colors. The accident rate of men working around machinery has been decreased by the use of correct color schemes. This increased use of color in industry has necessitated the formulation of many new products which will resist severe chemical conditions.

In formulating a finish, it is most desirable that the resulting product be practical. No finish is practical unless it is easy to apply, dries satisfactorily and fulfills the other requirements of performance called for. A reasonable cost is also an important factor. In a highly competitive market, the cost may become of primary importance, and a careful selection of raw materials is imperative. It is, therefore, suggested that formulators not only know the relative physical properties of available raw materials but also the relative costs of these materials.

Paints and enamels may be regarded as materials having pigments and vehicles as the two major components. The pigment portion may be classified into prime or hiding materials and extenders. The vehicle portion may consist of a combination of resins, oils, thinners and driers. A varnish may be defined in a like manner.

Interior finishes may be classified into the following general groups according to use:

(1) Wall primers and sealers
(2) Wall finish coats. These are produced in four sheens: flat, eggshell, semi-gloss and gloss.
(3) Enamel undercoaters
(4) Enamel finish coats. These are produced in four sheens: flat, eggshell, semi-gloss and gloss.
(5) Varnishes
(6) Floor paints and enamels
(7) Miscellaneous products

The differences between the various pigment-vehicle systems may best be explained by a study of the principles of formulation and their relation to the physical properties of these systems.

It was pointed out in Chapter 18 that the ratio of pigment to non-volatile vehicle by volume is a very important factor in determining the gloss or sheen of a given system. In any given system, increasing the pigment to non-volatile vehicle will decrease the sheen. A number of the other physical properties of the product and the dried film are dependent on the P/B ratio.

A very important property in trade sales formulation is package stability, *i.e.*, after six months to three years, will the material in a tightly sealed can be in the same workable condition as it was when first made and will the color and drying properties be the same? Most trade sales items will move to the consumer and be used within six months to two years after manufacturing, but there are instances when retailers may overstock on slower-moving items, with the result that these products may remain on the dealer's shelves three years or more. Often the consumer overpurchases and has material in his home or paint shop for a year or so before use.

The amount and type of settling, is of prime importance. Most pigmented products show some settling, but it is only objectional when the settled portion forms in a very hard, dry layer on the bottom of the container and can only be reincorporated with difficulty.[1]

Croll[2] discusses settling with reference to the effect of particle size, degree of grinding, wetting properties and viscosity of the vehicle. Better wetting liquids are likely to accelerate settling. Improved fineness of grind or degree of dispersion is usually an aid to non-settling. Initial body or viscosity of a given system is dependent to a certain extent upon the degree of dispersion and viscosity of the vehicle. The settling is likely to decrease as the viscosity of the system increases.

Non-settling properties may be improved by use of such pigments as asbestine, diatomaceous silicas and calcium carbonates. Use of agents such as metallic soaps, lecithin and certain metallic naphthenates may prevent settling in a given system.

The consistency or viscosity is an important property because of its effect on other properties, such as brushing, leveling, non-settling, and hiding. In general, increasing the consistency adversely affects the brushing and leveling properties of a given system. It is therefore most desirable that the consistency remain constant during ageing in the package. This may be accomplished in part by the proper selection of pigments and vehicles. Basic pigments, such as zinc oxide, carbonate of lead and chrome oranges are likely to be reactive with highly acid vehicles, and in such cases they tend to thicken. The vehicle itself may be unstable, bodying or even gelling taking place on aging. Such a vehicle is likely to cause livering of a paint or enamel in the package. The brushing and leveling may be affected to such an extent that the product is not usable.

A pigmented system is normally considered as having good brushing or working properties when it shows a minimum resistance to application with a brush, and is of such a nature that a desirable thickness of film is produced. In actual practice, the brushing properties include the consideration of the spreading rate and lap time. In general, easy brushing is indicative of high spreading rate, while the opposite holds true of poor brushing products.

Lap time is not a definite time, but is the lapse of time between the completion of the painting of one section, and the start of painting an adjacent section. It is necessary that the paint on the new section work into the first section easily and in such a manner that when dry no line of demarcation is visible. Lap time is dependent upon the evaporation rate of the solvents from the film and upon the nature of the vehicle solids.

Troutman[3] states that the flow and leveling characteristics of paint systems are definitely influenced by the state of pigment structure.

Highly flocculated systems have a tendency to retard flow and leveling properties, whereas deflocculated systems will flow more freely. Thus the degree of wetting and the dispersion attained in a given system have a direct bearing on this property. Good flow is desirable for the elimination of brush marks, but it should not be such that sagging is encountered on vertical surfaces.

Leveling is also dependent upon the rate of drying and the nature of the vehicle solids. Adjustments in the flow of a system may be made by choice of thinners of different evaporation rates. Slower evaporation aids the leveling.

The hiding or opacity of a paint is the property or ability of the paint to obscure the surface over which it is applied. The hiding power of a paint is often expressed as the area which can be obscured by one gallon. In Chapter 18, it was pointed out that pigments differ considerably in their hiding properties and that their individual hiding values vary to a certain degree depending on the paint system in which they are used. The obscuring power of any given system varies with the thickness of film applied.

A number of methods for the measurement of the hiding power of paints and pigments are used, some of them based on wet films and others on dry films. G. S. Haslam[4] has pointed out the advantages and shortcomings of the cryptometer as a control instrument. Haslam states that that hiding power is composed of two factors; one, referred to as the "brightening" index, is the increase in brightness over a black background with increasing film thickness. The other factor is known as the "contrast obliterating" index and is the film thickness necessary to obliterate a given contrast. He points out that the cryptometer measures only the latter of these two factors, and that in comparing paints of different brightness, the results may be misleading.

R. A. Morrison[5] shows the results of hiding power tests comparing data obtained using the Pfund Cryptometer and wet hiding brush outs made over a black and white checker board. The author points out that hiding power determinations on a mixture of white pigments do not check with the theoretical value calculated from the hiding of the individual pigments.

The New York Production Club[6] has endeavored to find an absolute method for determining dry hiding that would be reproducible in different laboratories. Films were applied to Morest Sheets by various methods and contrast ratios then determined by means of a photometer. An outline of a suggested method for determining the dry hiding power of a paint is offered as the result of this work.

The color and color permanency of paint systems are dependent upon the type of pigment used, pigment concentration and vehicle characteristics.

Most pigments have good color stability in the package. Prussian Blue or Iron Blue has been one of the worst offenders in times past. Blue paints and enamels and similar products which carried lead chromate greens were subject to change of color on ageing. It was pointed out in Chapter 6 that iron blue is ferri-ferrocyanide and that lead chromate greens are a mixture of lead chromate and iron blue. Some of the earlier iron blues would undergo chemical reduction to the ferrous state in the package and would lose their intense blue color. Many have had the experience of opening a can of blue enamel and instead of finding a nice blue color, as expected from the color card, have found a much lighter color. Sometimes this enamel, when brushed out, will darken to the original color due to the oxidation of the ferrous ferrocyanide back to the ferri-ferrocyanide, but often the color will not come back to the original. With a green enamel, as the blue faded out, the color would approach that of the yellow lead chromate portion of the pigment. Phthalocyanine blues and greens do not show this tendency and are recommended where cost permits.

Iron blues are more or less sensitive to alkali. Some formulators have been in the habit of adding small portions of soap solutions or dilute alkali solution to obtain certain body characteristics. It is also possible that these alkaline materials may enter by contamination in the plant during manufacture. Alkalies cause the blue color to fade out permanently in the package. Pigment manufacturers have learned to protect their iron blues considerably against the effect of slight traces of alkali. It must be remembered, however, that iron blue and chrome green pigments, as a class, have poor alkali resistance and should not be used where an alkali-resistant finish is required. Pigments such as phthalocyanine blue, green and chromium oxides should be considered where alkali resistance is required. Free lime and other alkaline salts in plaster may cause fading of iron blue in the dry films.

Retention of drying properties on ageing in the package is also a very important point to consider. Certain pigments tend to absorb driers or cause them to lose their efficiency, with the result that a four-hour drying enamel on aging may show bad tackiness even 24 hours after application. The greatest offenders in this respect are carbon black, lamp blacks, iron blues, chrome greens and certain organic reds. Certain vehicles may also show tendencies to lose drying properties on aging. This may be overcome by the proper selection of driers and the use of a material such as Nuactl. This subject was covered in Chapter 16.

As mentioned previously, interior finishes are judged on their performance and cost. From the economic standpoint, it is therefore important to achieve the desired finished job with as few coats as possible, especially in view of the rising labor cost of application. It should also be kept in mind that pigments are purchased by the pound but sold by the gallon in the finished product. Therefore, the bulking value of a pigment should be considered as well as the cost per pound and the area of hiding per pound. In Chapter 18 tables were given which showed these figures for the commonly used white pigments. It is common practice for the manufacturer to place information on the package label regarding the proper preparation of the surface. Where more than one coat is to be applied, the recommended schedule of finishing is given. In many states a detailed chemical analysis is required to be shown on the label. It is suggested that the formulator keep label directions as clear and concise as possible.

Wall Primers and Sealers

Wall primers and sealers may vary widely in their composition depending on where they are to be used. Most wall primers and sealers are intended for use on plaster, wall board, tile, brick or concrete. The pigment-binder ratio will fall between that of a semi-gloss and gloss enamel, or from 1/.9 to 1/2.5. The pigments used are lithopone, titanium calcium or titanium oxide, together with such extenders as the silicates and carbonates. Degree of opacity of the primer depends more or less on the type and quantity of prime pigments used. The vehicles vary in quality, the common types being made from long oil-rosin or ester gum varnishes in combination with blown or other specially treated oils.

A satisfactory wall primer and sealer should have good brushing properties. It should especially seal and stop the varying "suction" of porous plaster with one coat and thus prevent absorption of the succeeding coats. In this way a finished job is possible with two or three coats at the most. It should dry hard enough in eighteen hours to allow recoating the second day. It should seal in any free lime which might be present in the plaster or other masonry. On new plaster or concrete however, it is advisable to recommend washing the surface with a solution of zinc sulphate before applying the primer unless the primer recommended has outstanding alkali resistance.

Improved alkali-resisting primers may be obtained by using short to medium-length tung oil varnishes, plasticized with methyl abietate and certain percentage of coumarone resin. The chlorinated rubber-base paints and the S-5 "Pliolite" resin paints may be used where a high degree of alkali resistance is needed. Where bad moisture conditions exist, as in breweries, dairies, textile mill and many underground buildings, special so-called wet wall primers are required. In such cases the primer must have excellent water resistance and adhesion to the surface. These properties are to some extent dependent upon the vehicle used, although careful selection of pigments is necessary.

A typical formula of a Wall Primer and Sealer for use on plaster and wall board with no special requirements is shown herewith.

	Pounds	Gallons
Lithopone	400.00	11.20
Rutile titanium dioxide	100.00	2.85
Magnesium silicate	80.00	3.37
Aluminum stearate	1.00	——
50 Gallons Ester Gum—Wood Oil		
Linseed oil varnish 50% solids	192.50	26.25
Blown linseed oil	143.50	17.50
Ester gum solution 62%	138.20	17.50
Mineral spirits	131.15	20.01
6% Lead naphthenate	9.06	1.25
6% Cobalt naphthenate	.59	.07
	1196.00	100.00

Pounds per gallon	11.96
Viscosity	90 K. U.
P/B ratio	1/2.2

Wall Finish Coats

Flat wall paints are so formulated as to produce dry films with low angular sheen, varying from a dead flat to an eggshell sheen. Flat paints are usually produced in a line of light colors, white and black. The selection of pigment and vehicle is limited only by performance requirements and cost. Pigmentation may consist of either lithopone, titanium oxide, titanium calcium, zinc oxide or mixtures thereof, together with such extenders as calcium carbonates, silica, silicates and barium sulphates. The non-volatile portions of the vehicles may vary from ten gallons in length to straight oil.

The pigment to binder ratio is very important in that it exerts a very definite influence upon such properties as sheen, consistency, brushing, leveling, hiding, enamel hold out, and washability. The pigment to binder ratio is not only dependent upon the oil absorption of the individual pigment used but also upon the properties desired of the paint.

Flat paints as a general class have a P/B ratio of 1/.4 to 1/.9. The consistency may vary depending whether the paint is to be sold as a ready-to-use product or as a flat to be reduced by the painter. The viscosity and type of body may be controlled by a number of methods.

The consistency of a flat paint may be increased (a) by the selection of high oil absorption prime pigments and extenders; (b) by increasing the vehicle solids or increasing the viscosity of the oils or varnishes used;

(c) by increasing total pigment concentration; (d) by incorporating metallic soaps; (e) through chemical reaction; and (f) by the addition of various bodying agents.

Pigment manufacturers offer a number of prime pigments in several grades based on oil absorption values. Extenders such as magnesium silicate and diatomaceous silica have higher oil absorptions than calcium carbonate and yield higher viscosities. However, calcium carbonates vary in oil absorption and alkalinity. The alkali present, being of a soluble type, reacts readily with any free acids which may be present in the vehicle to form soaps. These soaps may increase the consistency in some systems, but in others have the adverse effect by breaking existing gel structures. Aluminum stearate is the metallic soap most commonly used to obtain increased consistency. The gel structure produced in a given system will depend on how the soap was introduced into the system, what type of mill was used, and the temperature during grinding.

If chemical reaction is used as a means of increasing viscosity, care must be taken that the reaction is completed within a short time and does not result in excessive after-bodying on aging. Highly acidic vehicles may react with basic pigments to cause gelation of the paint. The speed of this reaction may vary dependent upon the particular ingredients. Troutman[7] states that neutral vehicles usually lack the desired wetting action, while vehicles of excessive acidity may cause an extensive puffing action upon water additions, especially if the pigments used show affinity for water. The type of organic acids present may also influence the degree and type of viscosity obtained. The effect of some of the more common organic acids is shown in the following table.

	Control	Tung Oil Acids	Stearic Acid	Naphthenic Acid	Linseed Acid	Perilla Acids	Soya Acids	Rosin Acids
Consistency (No water)	83	78	78	76	74	74	75	82
Consistency (1% water)	122	123	142	132	132	132	134	140
Puff condition (with water)	None	Definite	V. Def.	V. Sl.	Def.	Def.	Def.	V. Def.

The consistency is expressed in Krebs Stormer units and the puffy nature is based on an arbitrary grading. Troutman does not indicate the quantity of the acids added to the paints. The above data show that all the acids except naphthenic caused a definite increase in rigidity or puff. The tung oil acids showed little effect on the consistency, while the other acids caused increased consistency.

As previously stated, prime pigments and extenders vary in non-settling properties. Pigments of higher density or bulking are more likely to settle than pigments of low density. For example, titanium magnesium pigments show less tendency to settle than titanium barium pigments. The magnesium silicates and diatomaceous silicas generally have better suspension properties than calcium carbonates. The calcium carbonates are superior to barium sulphate and the coarser silicas. Surface-treated prime pigments and extenders are available which show excellent non-settling properties.

Vehicles have certain effects on the non-settling. The factors involved are rather complex, depending in part upon the wetting properties of the vehicle. Viscosity is important in that for a given paint system, the tendency to settle increases as the viscosity decreases. It is advisable that the vehicle contain at least 32 per cent of non-volatile materials.

The sheen may be controlled (a) by varying the pigment-to-binder ratio, (b) by selection of prime pigments and extenders, (c) by the use of flatting agents, and (d) by the degree of dispersion or grinding.

High pigment-to-binder ratio will produce a low sheen; increasing the binder will increase the sheen. Fine prime pigments will give higher sheen than the coarser pigments. Greater differences are found among the extenders. Magnesium silicates and silica are better for flatting than the carbonates. The precipitated carbonates even show a difference from the natural carbonates. The diatomaceous silicas are very effective in lowering the sheen. The addition of metallic soaps such as aluminum stearate also tends to lower the sheen.

The degree of dispersion or grinding should not be forgotten because it is the variable factor independent of the selection of pigments and vehicle. The sheen generally increases as the degree of dispersion increases. If a fine grind is required to produce a smooth finish, the flatting must be obtained by increased P/B ratio or by the use of flatting agents.

Ease of brushing may be controlled by (a) vehicle composition (b) consistency control (c) introduction of pigment flocculation and (d) use of metallic soaps such as aluminum stearate.

Ease of brushing will vary in a manner inversely proportional to the viscosities of the oils and varnishes used. Heavy bodied oils produce hard brushing. Long-oil varnishes are better brushing than short-oil varnishes. The use of at least a portion of slowly evaporating thinner such as kerosene is desirable to insure the proper lap time. The brushing will vary inversely with the percentage of non-volatile vehicle.

Flocculation of the system in most desirable. This may be accomplished by using a relatively poor wetting vehicle or by the addition of a small amount of water in the form of a soap solution.

Leveling is controlled by (a) proper selection of oil and varnishes,

(b) acidity, (c) proper selection of extenders, (d) evaporation rate of the thinners.

Bodied oils show better leveling than thin oils, and most blown oils than kettle-bodied oils. Blown soya oils possess better leveling properties than blown linseed oils. Varnishes vary depending on the nature of their composition and method of cooking.

Highly acidic vehicles are likely to cause poor leveling. This is more apparent if there are reactive pigments present.

The silicate type of extenders show poorer leveling than the calcium carbonates. Again the use of a portion of slowly evaporating solvent may correct poor leveling properties. The use of stearates tends to reduce leveling.

The semi-gloss and gloss wall paints are formulated along the same principles as the flat paints except that the ratio of binder to pigment is increased to give the desired sheen. The vehicles employed usually vary from 20 to 40 gallons in length, although there are exceptions.

The quality of vehicles of all wall paints varies with the selling price to be met or with some particular property requirement. The cheaper vehicles consist of mixtures of gloss oil (limed rosin solution) and bodied oils. The medium-priced vehicles consist of oleoresinous varnishes blended with oils to give the desired properties. The resins used in these varnishes may be rosin, ester gums, maleic type resin or mixtures thereof. In formulating white wall finishes, it is desirable that the films have reasonably good non-yellowing properties. Of the oils, soya oil and dehydrated castor oil have the least tendency to yellow. The resins also vary in their after-yellowing properties.

The higher-priced vehicles are composed of alkyd resins or mixtures of alkyds with oils and oleoresinous varnishes. The alkyd resins of the soya-modified type have excellent non-yellowing properties.

Washability of a wall finish is another property that is important, not only to the home owner but even more so to the maintenance engineer of hotels, office buildings and schools. This property depends somewhat on the pigment-binder ratio, and also upon the water and alkali resistance of the vehicle used.

For certain architectural and industrial uses, where whites of maximum fumeproofness and non-yellowing properties are required, damar varnishes are used. The straight damar finishes are not very elastic and are subject to chipping and cracking, especially around window frames. This may be overcome by plasticizing them with oils, but this is done at the sacrifice of reduced fume resistance and non-yellowing. The addition of a small percentage of zinc oxide has been found to minimize yellowing tendency.

Where resistance to acid fumes is a factor, it is necessary to use pigments which are inert to acids. For special acid- and alkali-resisting properties resins such as "Parlon," "Pliolite" and "Vinylite" are recommended.

Typical formulas for wall finishes are shown below.

Flat Wall Paint

	Pound	Gallons
Rutile titanium calcium pigment	276.00	10.20
Lithopone	414.00	11.62
Calcium carbonate	138.00	6.11
Magnesium silicate	69.00	2.91
Aluminum stearate gel	56.50	8.65
Bleached linseed oil	16.80	2.16
Blown linseed oil	44.20	5.40
Kettle-bodied linseed (Body X)	43.10	5.40
25 gal. ester gum—castor oil varnish 45% solids	173.50	23.70
Kerosene	162.00	23.70
24% Lead naphthenate	0.97	0.10
6% Cobalt naphthenate	0.40	0.05
	1194.47	100.00
Lbs. per gallon		11.94
Viscosity		90 K. U.
P/B ratio		1/.73

Semi-Gloss Wall Paint

Rutile titanium calcium pigment	585.00	21.60
Aluminum stearate gel	63.80	9.75
Kettle-bodied oil (Bodied X)	58.50	7.30
Refined linseed oil	38.00	4.87
25 gal. "Pentalyn A" castor oil Varnish 50% solids	320.00	44.10
Kerosene	99.06	12.26
24% Lead naphthenate	0.77	0.08
6% Cobalt naphthenate	0.32	0.04
	1163.45	100.00
Lbs. per gallon		11.63
Viscosity		85 K. U.
P/B ratio		1/1.1

Gloss Wall Paint

Lithopone	344.00	9.65
Rutile titanium calcium pigment	243.00	8.98
Kettle bodied linseed oil (Body X-Y)	122.00	15.20
Ester gum solution 65% solids	41.50	5.06
25 gal. wood oil varnish (43% solids)	369.00	50.60
Mineral spirits	66.40	10.20
24% Lead naphthenate	2.00	.21
6% Cobalt naphthenate	.80	.10
	1188.70	100.00
Lbs. per gallon		11.88
Viscosity		80 K. U.
P/B ratio		1/2.0

Enamel Undercoaters

Enamel undercoaters should have P/B ratios falling between those of flat and semi-gloss paints. They are intended mainly for use over wood, but should also be satisfactory for use over metal, "Masonite" or masonry. The desirable properties are (a) ease of application, (b) good leveling, (c) good sealing or enamel hold-out, (d) good overnight dry and (e) easy sanding.

The film should dry tough and hard, but also have good adhesion to the wood or to the surface to which it is applied. It should not be so high in gloss or so hard that the succeeding coats of enamel will not adhere. The film should be such that it can be easily sanded without clogging or gumming the sandpaper.

Since enamel undercoaters are used on woodwork and furniture, good leveling with a minumum of brush marks is desired. There should be no sagging or running. This is especially of importance in painting paneled woodwork and sharp edges.

The amount of hiding pigment needed is determined more or less by the selling price of the product. However, it is usually desired that solid hiding be obtained with one coat of the enamel undercoater and one coat of enamel.

The drying hardness and toughness are obtained by the proper selection of vehicle, which may vary from 15 to 30 gallons in oil length.

Certain precipitated calcium carbonates are highly recommended for use in enamel undercoaters to give improved enamel holdout. A typical formula suggested by the manufacturer of such a pigment follows.

Enamel Undercoater

	Pounds	Gallons
Rutile titanium dioxide	55.00	1.57
Rutile titanium calcium pigment	218.00	8.05
Magnesium silicate	98.00	4.12
"Surfex" (calcium carbonate)	357.00	16.18
Aluminum stearate	2.00	
50 gal. castor—linseed varnish 50% N. V.	236.00	32.33
Ester gum solution	40.00	5.12
Mineral spirits	129.60	19.93
1% Soap solution	16.60	2.00
Pine oil	7.27	.94
Kerosene	59.00	9.08
24% Lead naphthenate	2.18	0.23
6% Cobalt naphthenate	3.64	0.45
	1224.00	100.00
Lbs. per gallon	12.24	
Viscosity	80 K. U.	
Pigment to Binder	1/.55	

Enamel Finish Coats

Enamel finish coats are usually produced in a range of varying sheens. As with the wall finishes, the gloss may be controlled by the P/B ratio. Gloss enamels generally dry harder and have higher gloss than the ordinary gloss wall finish. This is accomplished by use of harder-drying varnishes of shorter oil length, or of synthetic vehicles such as the alkyds. Enamels, as a general rule, are not quite as easy-brushing as wall finishes because of the lower oil content, but they still should apply easily with a two or three-inch brush. Enamels should dry in four to six hours and should be hard enough overnight to recoat. The enamel should produce a good hiding, full coat appearance. It should level and flow well on flat surfaces and show no brush marks. It should not flow away from sharp edges or sag or run in corners. It is desirable that white enamels be so formulated that they may be tinted with ordinary oil colors without losing their inherent properties.

As with wall finishes, the selling price will determine the amount of hiding and the quality of the vehicles used. Low-grade enamels are often very short and brittle and chip easily when used on furniture and woodwork. They often show poor gloss retention and poor washability. These low-grade enamels are frequently made from mixtures of gloss oil and bodied or blown oils. The quality may be improved by use of properly cooked varnishes using wood oil and the harder resins such as ester gums, "Pentalyn" ester resins, phenolics and maleics. The higher-priced enamels are formulated with alkyd varnishes. Such enamels dry quickly with excellent hardness, gloss and fullness. The gloss retention is outstanding. The washability is excellent. The white and light tints show very little after-yellowing.

Varnishes

Interior varnishes are still used in large quantities, but not to the extent that they were 25 years ago. Varnish finishes on cabinets and wood trim have been replaced by enamel finishes. It is not to be inferred that the use of varnish is rapidly disappearing. Many people still prefer clear finishes, especially where beautifully grained woods are available. If enamel finishes are desired, cheaper types of wood may be used. The resins and oils in a varnish determine to a large extent the characteristics and use of a varnish. Varnish formulation has been covered in Chapter 19.

As wood finishing is an extensive subject, this discussion will be limited to the products more generally sold for the home and their method of application. Wood floors may be finished in a number of ways depending on whether they are hard or soft wood. Many users and floor finishers prefer white shellac on their floors. The advantages of shellac are quick dry, easy cleaning and easy sanding to refinish. Shellac does not have the tendency to yellow as much as varnish on ageing. The disadvantage of shellac is the brittleness and poor water resistance. The use of varnish is more desirable because of the greater wear resistance and washability. Fuller coats of varnish may be applied which bring out the grain of the wood as well as giving greater protection.

The most serious error made in finishing floor surfaces is improper sealing of the surface with shellac, a liquid wood filler or a substitute shellac. These should not be used because they have no affinity for the succeeding coats of varnish. Floor surfaces should be built up with varnish from the bare wood, thinning the first coat with turpentine and following with one or two full flowing coats of the full-bodied varnish. Open-grained wood such as oak should be filled with paste wood filler. Excess filler should be removed from the surface before applying varnish. The close-grained woods, such as maple, birch and yellow pine, do not require filling. If desired the wood may be stained before varnishing. Soft wood floors are seldom encountered except in older homes. Sometimes it is advisable to finish these with a floor paint. Another method is to apply a system consisting of ground coat, graining compound and color varnish. Still another system is the use of a penetrating floor finish usually applied in two coats, with buffing after each coat to wipe off the excess material. The surface is then waxed and polished.

In finishing woodwork, cabinets and furniture, preparation of the wood is essential to bring out the natural beauty of the grain. It should be sanded very carefully to a smooth surface. It is common practice to sponge the wood surface to raise all particles of fiber in the wood so that they can be cut away during the sanding operation. After the wood has been properly sanded and has dried, one coat of wood stain of the color selected is applied. Next a thin coat of shellac is put on. After it has thoroughly dried, the surface is sanded to a smooth finish. Some finishers prefer to apply a second coat of shellac. Then on open-grain woods such as oak, chestnut, walnut, etc., one coat of paste wood filler of the proper color is applied, allowing it to set twenty minutes before wiping off what remains on the surface. Wiping is always done across the grain rather than with the grain. The paste wood filler should be allowed to dry at least overnight and should then be sanded to remove all filler remaining after the wiping operation. As many coats of varnish as necessary should then be applied.

If a rubbed finish is desired, allow at least 72 hours for the varnish coat to become perfectly hard and then rub the surface with pumice stone and water or pumice stone and oil. Pumice stone and water give a dull finish, while pumice stone and oil produce an eggshell finish. Varnishes used for furniture must be tough and hard, and should not turn white from hot dishes, alcohol, water or fruit juices. They should retain their hardness without becoming tacky or soft when subjected to the heat of the body. Floor varnishes should dry to tough, hard films which will withstand abrasion and frequent washing without turning white. They should withstand boiling water, alcohol and fruit juices.

Floor Paints and Enamels

Floor enamels have a P/B ratio similar to that of other gloss enamels. This will vary with the type of pigment used, such as lithopone and titanium pigments or a mixture of these plus some extender. The vehicles will vary depending upon the qualities and properties desired. The better qualities of floor enamels are made from medium oil alkyds and modified phenolic-alkyd vehicles. Next in order would be vehicles of modified phenolic varnish (25 to 35 gallons in oil length), pentaerythritol ester varnishes (35 gallons in oil length), maleic ester varnishes (25 gallons in oil length), and congo varnishes (25 gallons in oil length). These enamels should dry to hard, tough films, which will withstand abrasion and frequent washing. They should have good gloss retention. Floor enamels are applied to both wood and concrete. Some difficulty may be encountered if applied to sub-surface concrete such as basement floors. Moisture and alkali in the concrete will cause softening of the more common oleoresinous floor enamels due to saponification of the oils and resins. Floor enamels made from rubber-base vehicles are recommended for this type of floor.

Miscellaneous

There are a number of other trade sales items sold for special purposes. Colors in oil are individual pigments such as lamp black or chrome green ground in oil, and are made so as to have a semi-paste consistency. The composition will vary depending on the individual properties of the pigments. It is desirable that the pigments be well ground and that the consistency be such that the oil color will mix easily with the paint or enamel to be tinted. Glazing liquids are products of low to high pigmentation used for obtaining Tiffany wall finishes. They consist essentially of extender pigments ground in varnish and are more or less transparent. The finisher quite often adds a small amount of color in oil to glazing liquid to give the desired color. Paste wood fillers are primarily short to medium oil varnishes pigmented with extender. Their use was mentioned in the paragraph on wood finishing.

The subject of water-thinned paint and resin emulsion paints will be discussed in Chapter 22.

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Chapter 22

Water and Emulsion Paints

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The use of water paints goes back to antiquity. The Egyptians and the Greeks used sour milk plus freshly burned lime to make a whitewash that had as its binder a calcium caseinate gel which was the reaction product of lime and the casein in the milk. Artists in the Middle Ages used tempera colors for painting portraits, scenery and decorations. The binder used in these paints was white of egg. Water paints underwent a renascence around 1900. Powder paints containing glue, whiting and chalk first made their appearance. We know such paints today as kalsomines, and they are still widely used as ceiling finishes in certain localities. The major objection to this type of finish is its lack of washability.

Casein powder paints were introduced about the same time. As their name implies, casein is used as the binder. A powder paint consists of powdered casein, hydrated lime, a preservative, inert and hiding power pigments, with lime-proof colors for tinting. Upon the addition of water, a reaction begins to take place between the casein and the lime and a calcium caseinate gel is formed which serves as the paint's binder. The user of this type of paint was plagued with two troubles. The first was that after mixing, the paint had to stand long enough to allow the formation of the calcium caseinate gel; the second was that the paint had to be used before the caseinate gel solidified.

In its early stages this paint was too dependent upon the idiosyncrasies of colloid chemistry to become a potential threat to interior oil-base wall finishes. However, today casein powder paint is still sold in large volume, and its stability after reduction has been increased by the use of alkalies which inhibit the solidification of the calcium caseinate gel.

The British made the next advance in the water-paint field with distempers which were forerunners of the present paste emulsion paints. Glue was used as the protective colloid in the aqueous phase and bodied oil as the oil phase. The pigments used were clay, silica and lithopone. Distempers did not make much progress in this country, and it was not until the early twenties that the next advance in water paints took place.

To overcome the objections to powder casein paints, a paste type of casein paint was introduced. An alkaline casein dispersion was used as the binder, and the pigments consisted of clay, silica, and lithopone. The early casein paste paints were far from satisfactory. The casein was of a poor type and it was extremely difficult to protect from the action of bacteria and enzymes. Carbon dioxide, a by-product of the reaction between casein and bacteria, caused the paint containers to blow up, and the odors of putrefaction caused customer complaints. In addition to these troubles the films lacked washability, and the unplasticized casein caused peeling troubles. But the paints made progress due to their hiding and application characteristics; and the progress was at the expense of conventional oil-base wall finishes, as well as of casein powder paints. The casein powder paint group fought casein paste paints with rather pointed remarks concerning the price of water when bought in the form of a paste paint, and the paint industry deprecated the use of water in paints.

As the knowledge of how to handle casein increased, the original faults in these paints began to disappear; glycerin became popular as a plasticizer; phenol, substituted phenols and chlorinated phenols were used as preservatives, together with alkaline fluorides. To improve the washability characteristics small amounts of vegetable oils, such as linseed or china wood oil, were added to the paints. Today the average casein paint contains approximately one pound of casein and up to two-tenths pound of vegetable oil per gallon—a form of emulsion paint in which the protein component represents approximately 85 per cent of the binder.

Casein paste paints reached their zenith at the Chicago World's Fair. By the time of the New York World's Fair and the San Francisco Exposition of Progress, emulsion paints in which an emulsion of alkyd and protein was used as binder were showing signs of some day becoming competitive with casein and conventional oil-base paints as finishes for interior walls.

Webster defines an emulsion as a suspension of fine particles or globules of a liquid in a liquid. In an emulsion-type flat paint the oil phase is usually the dispersed phase, and the aqueous phase is the continuous phase. Another way of putting it is that most emulsion-type flat paints are of the oil-in-water type.

Why an oil-in-water emulsion paint? The viscosity of the paint decreases with each addition of water. It is also possible to clean up brushes, containers, and spills with soap and water. The application characteristics of the paint are excellent. The paint film drys rapidly due to its semi-porous structure, and this type of structure enhances the hiding power of both the hiding pigments and inert pigments when contrasted with a comparable oil-base finish containing the same pigmentation. Finally, there is the absence of paint odor, due to the ability of the protein component of the aqueous phase to tie up the oxidation products of the oil phase.

After deciding what position the water should assume in an emulsion paint, came the problem of package stability, and that is an exceedingly important problem when a paint is distributed on a national basis. By keeping the paste viscosity high in an emulsion paint, settling troubles which are inherent in oil-base paints can be avoided. High viscosity will keep the paint in excellent condition during exposure to the summer heat and the winter cold. And there is also the Barnum-like appeal of buying a gallon of paint at the store, bringing it home, and after a little work, and some water from the faucet, finding that instead of a gallon there is now a gallon and a half.

Now a word or two about emulsion stability. Emulsion stability is a high-sounding phrase used to cover up the lack of knowledge regarding the behavior of the aqueous and oil phase components—in other words, how they get along at their interface. The emulsion stability factor is present from the time the paint is manufactured, until it is safely on the wall and the furniture is back in place. The package stability of the paint; how it reduces with soft, hard, acid or alkaline water; how it brushes; how it cleans out of the brush with water, or soap and water; and how the film appears when dry: all these properties can come under the all-inclusive phrase "emulsion stability."

Pigments have not been previously mentioned, but they are part and parcel of the aqueous phase until the paint is on the wall, and the emulsion commences to break through dehydration. Where they go after that is still a source of argument. Wherever they go, they do an excellent hiding job, due not only to the difference in indices of refraction which exists between the binder and the pigment, but also to the presence of a pigment-air interface brought about by the porosity of the film, which is a function of the protein component of the aqueous phase. Pigments used in emulsion paints must be free from soluble or partially soluble calcium compounds, such as the oxide or sulfate, or reactive zinc compounds, such as the oxide. Soluble calcium or zinc compounds react with the protein component of the aqueous phase, and calcium and zinc protein complexes result. If they are present in sufficient quantity the emulsion will break on reduction, or equally serious, they will cause the paint to roll up under the brush. The brush becomes gummy, as the emulsion has inverted, and instead of using soap and water to wash the brush, thinner has to be used. As a result, emulsion paints go down a step or two in the user's opinion.

Pigments have now been identified as part of the aqueous phase. Water, protein, protein solvents, thickening agents, preservatives, mildew inhibitor, anti-foaming compounds and emulsifying agents make up the remainder of the phase. It is this phase that has received the major share of attention, not only because it is the least understood, but also because it is the origin of an emulsion paint's success or failure. The oil phase may be either of the alkyd oleoresinous or the bodied-oil type.

The emulsion flat paint was officially recognized by Federal Specification TTP-88, Paint, Resin Base Emulsion, Interior, Paste White and Tints issued December 27, 1940, and its revision TTB-88A dated May 26, 1945. The revised specification has strengthened the performance requirements of emulsion flat paints, which indicates the progress which has been made in their formulation in the few years that they have been in existence. It is interesting to note in passing that it was unusual during the war years to increase the performance requirements of a paint; usually the interim specifications took cognizance of raw material availability. However, such was not the case with the emulsion paints.

The accumulation of formulative experience which included work on water-reducible paints to meet the war-time T-1279 specification, as well as the development of many new emulsifying agents which were chemically designed for emulsion paint usage, has made possible the production of water-thinned paints having varying degrees of gloss, whose performance characteristics should approximate those of high-grade synthetic wall enamels.

Like the flat emulsion paints we have considered, the gloss emulsion paints are also of the oil-in-water type. In other words, the paints reduce with water for application.

Ease of application and many of the other advantages of emulsion flat paints are enjoyed by the gloss emulsion paints. Easy clean-up with soap and water is one of the most desirable properties of the water-thinned enamel. Without this advantage the emulsion paint would perhaps lose much of its customer appeal.

In the formulation of gloss emulsion paints, it is desirable for the pigment to be present in the oil phase, in contrast to the flat emulsion paint in which the pigment is in the aqueous phase, both in the package and during application. In emulsion flat paints, some of the pigments which make up the pigment component function as protective colloids, and in so doing contribute to the stability of the paint. In gloss emulsion paints the pigment should be in the oil phase, and the formulative problem is a more complex one due to the fact that the pigment may not be used as a protective colloid. In other words, in this type the pigment only complicates the problem of emulsification.

As previously mentioned, a gloss emulsion paint contains a water and an oil phase. In the formulation of the paint the pigment may be dispersed in the aqueous or oil phases, or into an emulsion of the two phases. Migration of the pigment from the water to the oil phase is controlled by treated pigments, or by surface-active agents in the oil or water phase which force the pigment into the oil phase by preferential wetting. Typical of these agents are the rosin soaps.

The aqueous phase contains protective colloids, thickening agents, preservatives, mildew inhibitors, anti-foaming compounds and emulsifying agents. The oil phase consists of the pigment dispersed in a suitable resin or vehicle which may be of the oleoresinous, alkyd, or newer types of synthetic resins, which are now popularly called elastomers.

Emulsion copolymers or latices have shown some promise in water-paint formulations. While not strictly a product of the war, the development of emulsion-type copolymers was greatly accelerated by the sudden curtailment of the natural rubber supply, and the emulsion paint chemist, after riding successfully on one of the end products of copolymerization during the war years, decided to work with them as paint raw materials.

The emulsion copolymers, after polymerization has taken place, have a high solids content, and yet for all practical purposes they have a fluidity equal to that of water. For purposes of comparison, the same film-forming solids in organic solvent solutions contain only one-third to one-half the amount of resin that the emulsion copolymers can carry. This high solids content is of interest in most emulsion type finishes.

The emulsion paint formulator has directed his effort not only toward the production of interior finishes, but for such exteriors as for concrete, brick, and stucco surfaces; and the future market for such finishes is only now limited by the availability of raw materials.

The use of water in paint is centuries old, and the new water paint model, the resin emulsion paint, while still in its infancy, is gaining in popularity each year as the public becomes better acquainted with the merits offered only by this type of finish.

Chapter 23

Solvent-Type Finishes

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By solvent-type finishes are meant solutions of film-forming agents and their modifiers that dry by evaporation of solvent with subsequent deposition of the film in usable form without further oxidation or polymerization. Since suitable film strength demands high molecular weight, these finishes presuppose that the film-forming substance is already polymerized to a high degree, but is still soluble to a usable extent in available solvents. A wide range of such materials exists, and in Chapter 13 the vinyloid group, which includes styrene, acrylic resins vinyl and vinylidene chloride and acetate copolymers, etc., were considered. In this chapter the soluble derivatives of the most widely available natural polymer, cellulose, will be used in discussing the solvent-type finishes.

Cellulose is the basic structural element of plant life, where by a complicated photosynthetic process the carbon dioxide and water of the air and soil are condensed to a highly polymerized rigid, tough material. Cotton and wood are the two major sources of cellulose for industrial purposes. Chemically, cellulose is a long-chain polymer characterized by recurrent anhydro-glucose residues and three replaceable hydroxyl radicals per unit. In itself cellulose is considered insoluble, although its combination with alkali and carbon disulfide to form viscose, and from this rayon, is of great industrial significance. Similarly, cellulose can be dispersed in ammoniacal copper solutions, in concentrated thiocyanates, particularly calcium thiocyanate and in some other reagents. These are not strictly film-forming solutions, since the cellulose itself is regenerated as rayon or cellophane by chemical precipitation from the dispersion.

The three replaceable hydroxyls, however, afford opportunity to alter the molecule to secure more favorable results. The nitration of cellulose is an old art, and by adjusting time, temperature and concentration factors fairly predetermined percentages of nitration can be secured. Similarly, the hydroxyls can be etherified by alkyl or aryl chlorides in alkaline environment to give a wide range of useful products, or they may be acetylated to give varying percentages of the acetate. All of these products have better solvency in organic solvents and from them are made the finishes to be discussed in this chapter.

Of all the cellulose derivatives, the nitrates are by far the most important as film-formers. They are the basis of the whole pyroxylin lacquer industry, which in tonnage far exceeds the other derivatives of cellulose. The chief property of value is the fact that a solution of cellulose nitrate, in a wide range of organic solvents, rapidly deposits a tough, clear, hard film by evaporation. This characteristic has been known for over 80 years, since the chance discovery that a mixture of 3 parts of ethyl ether and 1 part of ethyl alcohol would dissolve nitrated cotton and redeposit it as a smooth, tough film. This product, called collodion, found early use in photography and medicine and is still an article of commerce. However, large-scale use of nitrate solutions did not come until the 1880 period, when solutions in amyl acetate and other solvents, softened with castor oil, became in demand for the coating of fabrics to make artificial leather as well as to give finish to natural leather. At approximately the same period considerable attention was given to the first synthetic plastic, a combination of nitrated cellulose and camphor known as "Celluloid." Scraps from the manufacture of toys, billiard balls, collars, etc., could be dissolved in such solvents as acetone, ethyl and amyl acetates, etc., and these were found to have merit as coatings for brass and silver articles and other specialized but small-scale uses.

The big impetus to the development of these finishes started with World War I. Airplanes were first used in this war, and these were fabric-winged. Nitrocellulose dopes were used in large quantities to tauten these fabric surfaces, and also as quick-drying identification colors on shells and other munitions. Simultaneously other developments were occurring. To meet the inordinate demand for acetone to make cordite powder, many projects were undertaken. One, developed in England, produced acetone and *n*-butyl alcohol from grain by a special fermentation process; and since no use existed for the butanol this product accumulated while the acetone was used. [Another project, in California, secured acetone from kelp seaweed, leaving as by-product considerable calcium propionate.] With the end of the war, there were millions of pounds of surplus smokeless powder available at very low cost. There was also the need on the part of the rapidly growing automobile industry for a finish that was faster than the color coat and varnish system which was then employed. This system necessitated over two weeks to finish a car, an incredibly strangling bottle-neck to the desired high production.

This need, plus the available materials, plus the development of a process of reducing the viscosity of the nitrocellulose, led to the development of present-day nitrocellulose lacquers, and in 1923 to the first production finishing of automobiles with these materials. In a few years practically every car made was lacquered and the manufacture of these products had shifted in great measure from the old-established lacquer specialty makers to the paint and varnish trade in general. With improvement in quality increasing rapidly, more and more products took advantage of the rapid drying and hard, tough, resistant surface, and these finishes soon took over most of the furniture and radio business, the toy and novelty trades, and hundreds of varied products.

The advent, first of alkyd air-drying and baking enamels, and later of the urea- and melamine-modified alkyds, together with the rapid drying available by infrared baking, eliminated many of these uses, but there has been a constant increase in the output, indicating that new uses are replacing the old.

Nitrocellulose lacquers differ greatly today from their early formulations but are still essentially an assembly of varied ingredients, classified broadly as cellulose nitrate, solvents, resins, plasticisers, pigments and sometimes other agents, such as stabilizers, fungicides, fire retardants, crystallizing materials, etc. Often there will be 20 or more ingredients in a single formula, each chosen for economy or utility. By proper choice in formulation, materials can be made.that are hard or soft; drying almost instantaneously or so slowly that they can be brushed; clear or colored with any desired shade of pigment or dye; of high gloss or dead flat sheen; of quite low viscosity to give a thick single spray coat or of heavy viscosity to permit gasket dipping. There is no other finishing material that permits as much manipulation of the desired result, and this is probably the reason for the constant increase in use even as large segments of its former realm are taken over by other finishes.

We shall now take up briefly the materials of which these are composed, which comprise practically all the products used in the finishing industry. Lacquers have been made using as ingredients most of the natural and synthetic resins, most of the known oils and plasticizers, most of the pigments and practically all the solvents. However, the major fields are more limited and the ingredients of importance substantially less in number.

The prime ingredient, of course, is the nitrocellulose itself. This is made, as mentioned before, by nitrating with mixtures of nitric and sulfuric acid the pure cellulose from cotton linters or purified wood-pulp. After nitration the material is thoroughly washed to remove traces of acid and degradation products and the residual water is replaced by alcohol.

Dry cellulose nitrate is a dangerous material and cannot be shipped; at present it is received wet down with 35 per cent by weight of alcohol. In appearance it resembles moist cotton, with a slightly harsher feel. The product is described in accordance with its type and viscosity, *e.g.*, RS 20 second or SS 5–6 second. The first implies solubility in esters and ketones with a viscosity of 20 seconds by the Hercules falling-ball test; the second a spirit-soluble material requiring little active solvent but a high percentage of alcohol, of a viscosity of 5 to 6 seconds by the above test. The determination of viscosity is carried out in many ways—the falling-ball method to be described, by efflux methods such as the Ford or duPont cup, by torsion viscosimeters such as the MacMichael or the familiar Stormer, or by comparison methods such as the Gardner Holdt. The Hercules method employs a 14 inch tube marked off 2 inches from each end, and of 1 inch diameter. The lower end is plugged, and the solution to be measured is brought to 25°C and poured into it. A steel ball of 5⁄16 inch diameter and weighing 2.043 grams is moistened with solvent and dropped into the tube. Time is taken on a stopwatch for its traverse down the 10 inches between the marks. This is the recorded viscosity. To keep solvent and concentration constant is of course essential; the standard solution is composed of 12.2 parts of the nitrocellulose, 22 parts of 190-proof alcohol, 48.3 parts of benzene and 17.5 parts of ethyl acetate.

Uniformity of viscosity is of prime importance in lacquer manufacture and the makers of nitrocellulose find it necessary to blend batches to be able to send out uniform products. Commercial viscosities run from 600 to ¼ seconds, although material has been made as high as 3000 seconds and as low as 18 centipoises, which is considerably less than ¼ second, possibly 1⁄16. The material is not fully nitrated, as the completely nitrated product is very difficultly soluble and is of inordinately high viscosity. Against the theoretical 14 per cent nitrogen of this product, commercial soluble nitrocellulose runs from less than 11 to 12.5 per cent nitrogen.

We now have considered the basic film-former. For use, it must first be dissolved. Since the formulation of the "Volatiles" in lacquers was considered in detail in Chapter 15, only a brief mention of the solvents will be given here. There are literally hundreds of organic compounds that dissolve nitrocellulose, but when considerations of price, availability, toxicity and evaporative range are taken into account, the number shrinks rapidly into a comparatively few esters and ketones, with occasional newcomers such as the nitroparaffins, the glycol ethers, etc. For practical purposes the esters are the acetates of ethyl, isopropyl, *n*-and *sec*-butyl alcohols, amyl alcohols, methylamyl alcohol and a few higher members of the series; the propionates of butyl and amyl alcohol; the lactates of ethyl and butyl alcohol, and the acetate of glycol ether, usually called "Cellosolve" acetate. Of the ketones, acetone, methyl ethyl ketone, methylisobutyl ketone mesityl oxide, diacetone alcohol, cyclohexanone and isophorone are widely used. Furfural, nitrobenzene, nitromethane, nitroethane and nitropropane, diethyl carbonate and a few other materials have found occasional use. In addition we must consider the first solvent mixture, ether and alcohol, although neither material is a solvent in itself.

There is an unscientific but widely used truism that "like dissolves like." As cellulose nitrate is an ester, it is to be expected that esters would dissolve it. It has an anhydro-glucose oxygen atom that might be considered kin to the ketone carbonyl, so ketones are also logical solvents. The nitrate radical requires some pushing and hauling to render it chemically similar to the nitrohydrocarbons mentioned above, but they do dissolve it, even though nitrocellulose is a misnomer for the compound from the standpoint of science. The glycol ethers are compounds in which the ether and alcohol components of collodion are combined in a single molecule, and they are good solvents. The theory of solution is richly documented; it is full of data and of contradictions, and is outside the sphere of this discussion. It must be mentioned, however, that solutions of this type are vastly different from inorganic solutions, where solubilities are accurate and definite. Here we have a vague dispersion, ranging from almost solid gels to thin liquids with no definite limitations. In comparing solvents the one that at a definite concentration of cellulose nitrate at fixed temperature gives the lowest viscosity is somewhat arbitrarily classified as being the best; from this standpoint ethyl acetate and acetone are good. For all but special purposes, however, these are inferior, from a practical standpoint, to many other solvents such as butyl acetate and methylisobutyl ketone. For we really demand more from a solvent than mere solvency; it must permit practical application to the work. Acetone and ethyl acetate are too volatile for most applications, although in the specialized case of knife-spread coatings for fabrics they have worked well. What is required for the general type of industrial coating is a good solvent, with an evaporation rate that will permit rapid spraying, without bubbling or dusting, and that will dry in a reasonable number of minutes to a clear, unblemished film.

There are other requirements for solvents, such as compatibility with other solvents and diluents, with resins and plasticizers used in the formula, toxicity and cost. It is seldom possible to combine all the requirements in any single material. Therefore the actual lacquer solvent is a mixture, sometimes a very complex mixture, of active solvents, of latent solvents such as the alcohols, of hydrocarbon diluents, and of plasticizers which are essentially very high-boiling, slowly evaporating solvents and exert some influence on the properties of the solution as well as on the dry film. We might have a simple mixture, such as butyl acetate and toluene, that would serve our purpose, or half a dozen ingredients such as ethyl acetate, diacetone, butyl alcohol, methyl isopropyl ketone, toluene and xylene. The number of possible and usable combinations would run to an astronomical figure, each formulator has his favorite mixture and is probably justified in his affection for it. Conditions such as we have had in recent years, with war and boom making solvents difficult to obtain, have forced the use of many weird concoctions, and the wonder is that so many peculiar combinations did so well.

The derivation of these solvents may be mentioned briefly. Originally butyl alcohol as well as ethyl and amyl alcohols were derived from fermentation. And much is still so made, but under economic handicaps due to high farm prices for corn, molasses, etc. A large share of the output now is derived by strictly synthetic processes from gases—natural gas and those resulting from petroleum refining. Ethyl alcohol is derived simply from ethylene, combined with sulfuric acid and then hydrolyzed. Butyl alcohol requires a more complex operation. Here acetaldehyde is condensed to aldol, dehydrated to crotonaldehyde, hydrogenated to butyl aldehyde and then to butyl alcohol. A variety of amyl alcohol far purer than the product derived from fermentation fusel oil is made by chlorinating pentane and then hydrolyzing with lime. Isopropyl alcohol can be made by hydrogenating acetone, and conversely can be dehydrogenated back to acetone if economic reasons demand. All these alcohols can be acetated, to make up one of the most important groups of solvents.

The ketones can also be obtained from gases by synthetic methods. Acetone is made from propylene, as well as by the fermentation process mentioned earlier. It is condensible to diacetone alcohol, which in turn can be dehydrated to mesityl oxide. By hydrogenating mesityl oxide, methylisobutyl ketone is formed, which on further hydrogenation gives methyl isobutyl carbinol, or methylamyl alcohol, which in turn yields methylamyl acetate. It is notable that all these compounds are used in lacquers to some degree, and their production and use are increasing. Similarly *sec*-butyl and *sec*-amyl alcohols are derived from butylenes and amylenes.

The glycol ethers are derived by the reaction of ethylene oxide with alcohols. The ethyl and *n*-butyl ethers are widely used in lacquers, giving mild solvents with suitable evaporation rates, good tolerance of hydrocarbons and pleasant odor. The remaining alcohol group can be acetylated to yield a solvent of slower evaporation rate. Their compatibility with some resins is limited and must be considered when these solvents are used.

The nitroparaffins are made by vapor-phase reaction of paraffinic gases (methane, ethane and propane) with nitrogen oxides. They also give mild-odored solvents with excellent dissolving characteristics, stability and miscibility.

As can be observed from this hasty survey, a large and growing list of organic active solvents, made in high purity on a large scale, is available to the formulator of solvent coatings. The choice depends on a combination of many factors, the most important of which in recent years has been availability. Another important criterion has been dilution ratio—a measure of tolerance of the solvent with the cheaper diluents, such as toluene, xylene and naphtha which actually compose the greater portion of most lacquer-solvent mixtures. To determine this, a known volume of a definite concentration of cellulose nitrate in the given solvent is titrated with toluene to the point of precipitation. Several trials are made adjusting concentrations so that at the end point there will be approximately 8 per cent nitrocellulose, since too high and too low concentrations introduce extra error into what is none too accurate an analysis. The dilution ratio is usually expressed as the number of volumes of non-solvent that can be used to dilute 1 volume of the solvent under these conditions without precipitating the solute. For instance, the dilution ratio of butyl acetate may be expressed as 2.7 volumes of toluene, or 1.45 volumes of lacquer diluent naphtha per volume of butyl acetate. That of methyl isobutyl ketone is 3.4 with toluene, 1.0 with naphtha.

It must be stressed that good lacquer formulation does not attempt to use the limit of this tolerance, but leaves a safety margin for diminished solvency due to resins and other ingredients and to allow for some leeway in application. However, when choosing a solvent, dilution ratio is of importance. For instance, we have two solvents offered, A at $1.50 per gallon, B at $1.25 per gallon. If A has a dilution ratio of 2 with toluene at 25¢ per gallon, the cost of the mixture is 67¢ per gallon. If B has a ratio of only 1, the mixed cost will be 75¢ per gallon. Obviously the net cost is not necessarily in line with the quoted price of the solvent. There may be other factors, such as pleasant odor, mild action on undercoats or others that will justfy the more expensive mix, but that is another story. It should also be remembered that most lacquer solvents are bought by the pound and the product sold by the gallon, so it is logical, everything else being equal, that the product of lower specific gravity would be more profitable.

It was noted above that diluents comprise a large share of the formula. They are used both as economical replacements and also as solvents for resins and plasticizers in their own rights. Toluene and xylene are the outstanding products, although some close-cut high solvency petroleum naphthas are used in some formulae to achieve better odor and milder bite. Toluene and xylene are obtained both from coal-tar light-oil fractionation and from petroleum, which contributed the greater portion of the toluene for nitration to TNT during the war. For some special purposes turpentine, pine oil, dipentene and other solvents of this type have been used, as have the higher-boiling coal-tar fractions.

At this point we have a solution of nitrocellulose in a mixture of organic solvents. In itself this is of value in very few cases, since it is low in solids content, in adhesion, in luster and in flexibility. Such solutions have been used as tautening dopes for fabric airplane sections and for millinery, and as conveyors for phosphors for fluorescent lighting tubes. In general, considerable further modification is needed. For flexibility plasticizers are required, and these, as mentioned before, are essentially very slowly evaporating solvents. The use of castor oil is old, but still extensive, particularly in the formulation of dopes for coating paper and textiles. Camphor, a solid ketone, is the plasticizer used in "Celluloid," but it is too fugitive, odorous and lacking in elongation value for the thin films used as coatings. Most of the useful plasticizers are esters, those of phthalic, phosphoric and sebacic acids being most generally employed. Tricresyl phosphate, tributyl phosphate, dibutyl phthalate and dibutyl sebacate are widely used. A condensation product of glycol and sebacic acid has found many uses, and orthonitro biphenyl has been found valuable as a low-cost, although highly colored, plasticizer. Plasticizers are employed in percentages usually running from 5 per cent to over 100 per cent of the cellulose nitrate content, depending on what type of lacquer is desired. The choice of a plasticizer, like that of a solvent, is made after considering several factors in which availability, price, color, toxicity, elongation, evaporation rate at the temperature of use, and tensile strength should be included.

With the plasticized solutions we begin to arrive at the first true lacquers. Although these products are still lacking in luster and hardness, and are not as durable under exposure or as good in adhesion as those containing resins in addition, they serve well for coating flexible articles, such as imitation leather-coated papers, including the so-called lacquer decalcomanias, artificial flowers, cable lacquers, decorative packaging and many other industrial products. By proper choice of resins to be added to the above mixtures, many other desirable properties are introduced and the field of use vastly widened.

The resins originally used in the manufacture of lacquers were of natural origin. They included shellac, usually bleached and dewaxed, mastic, sandarac, elemi and dammar, both the Singapore and Batavia varieties. Dammar required de-waxing, generally accomplished by dissolving the whole resin in aromatic hydrocarbon and then precipitating with an alcohol. The resultant sludge of alcohol-insoluble wax was removed, and the remaining solution made a very excellent lacquer resin. Practically all these resins were cut off in 1941, since they originated in the area overrun by Japan, and supplies have only recently begun to trickle in. They now meet strongly entrenched synthetic resins of great and increasing merit, and can hardly be expected to regain their earlier position in the field, although they will undoubtedly recover some portion of it.

The first artificial resin to be used was glycerated rosin, commonly called ester gum. This is compatible with cellulose nitrate, although the lime- and zinc-treated rosins used in varnishes are not compatible. Ester gum afforded an increase in gloss and hardness, but its toughness, exterior durability and color are inferior and restrict its value to a limited number of interior uses, such as gasket lacquers for pencils, broomhandles, etc. A great improvement in ester gum was made by the addition of maleic anhydride; these maleic ester gums have a very wide and growing use in the industry, particularly in lacquers for wood. They have excellent compatibility, very fast solvent release, increased hardness and improved toughness, together with good gloss and cold-checking resistance when properly plasticized. Their resistance to weathering, to continued heat, and to discoloration is not good enough for use in the best grades of lacquers, but a wide variety of alkyd resins have been developed that afford great improvements in these directions.

Both drying and non-drying alkyds are used. The non-drying types usually employ the fatty acids of coconut, castor and cottonseed oils; the drying types use linseed and soya in short or medium lengths. The non-drying oils give resins of superior color and freedom from lifting—the phenomenon that occurs when one coat of a lacquer bites into a semi-cured undercoat and develops wrinkling and blistering. On the other hand, drying-type alkyds usually improve adhesion and moisture resistance. With proper formulation, lacquers can be made to give many years of exterior durability; in fact the largest maker of automobiles still uses lacquer on all its models.

A question of definition may arise here. Is a finish that is predominately an alkyd a lacquer or a so-called synthetic finish? Since even a minor percentage of cellulose nitrate requires a complete change in the solvent system, such finishes should be considered as nitrocellulose lacquers, even though the percentage of modifiers is far greater than that of the cellulose nitrate. On the other hand, the use of ethyl cellulose in minor percentages is in a different category, since here no great change in solvents is needed and the ethyl cellulose may be considered as a drier.

In the bulging formularies of the lacquer manufacturers many other resins have found use. Urea and melamine resins have been employed on some special jobs where high resistance to heat and discoloration are important. Many of the vinyloid resins, film-forming agents in their own right, have also found useful auxiliary employment in conjunction with cellulose nitrate. These include several of the methacrylate polymers, a polymerized vinyl acetate, a limited area of the vinyl acetate-vinyl chloride copolymers, some of the condensation products of cyclopentadiene and maleic anhydride known as "carbic" resins, and many others. Since many lacquer formulas are tailor-made to meet some special combination of conditions it is often necessary to get off the main road into the by-ways, and some very peculiar combinations have been strikingly successful. For broad, large-scale uses it can be assumed that the maleic-modified ester gums and the lacquer-type alkyds are the important resin modifiers. A few modified and polymerized oils have also appeared; these act as part resin and part plasticizer, giving some excellent results within their sphere, as do the methyl esters of rosin and hydrogenated rosin.

The ingredients of clear lacquers have been discussed above. By proper choice we can make a thin protective coat for silver or brass, a high-solids gloss wood lacquer for kitchen tables or pianos, a tough protective coat for linoleum or bowling pins, and many other industrial products. It remains to mention the materials that provide color and modify sheen. The latter is of prime importance in the wood-lacquer field, where it is often not desired to rub a finish to satin or dull effects; the use of proper transparent pigments accomplishes this objective. There are two types of these: metal soaps, such as aluminum stearate and palmitate, and silica alcogels. The latter give a harder and tougher film and are freer from haze or clouding; as a result, they are rapidly encroaching on the metal soaps which for many years had the field to themselves. With these modifiers a gloss lacquer can be tempered to any sheen desired—semi-gloss, satin, or dull.

Color can be imparted by dye or pigment. The dyes used are both spirit-soluble and oil-soluble types, which give beautiful transparent effects with very little light-fastness. Greater durability is obtained by using the phosphotungstic and phosphomolybdic acid lakes of the dyes. These retain most of the brilliance and transparency of color, but are appreciably more resistant to light-fading, bronzing and bleeding.

The pigments which produce solid, opaque colors are essentially those used also for oleoresinous and alkyd enamels. For black, carbon black is by far the most effective, although lamp and bone blacks are sometimes used for tinting; graphite, for certain special effects; and the greyish black antimony sulfide, stibnite, for colors with high infrared reflectance. As for white pigments, zinc oxide was at first practically the only one available. Pure zinc sulfide later came to the fore because of its much higher opacity; and today the titanium dioxides are by far the most important white pigments. It may be well to emphasize here that in solvent-type finishes, where the vehicle solid percentage is comparatively low, it is imperative to use pigments of maximum hiding power. As only a fraction of the total weight of pigment per gallon compared to those used in house paints, for instance, is permissible in these finishes, those used must be of maximum strength. Zinc sulfide is preferable to the weaker lithopone; pure titanium dioxide to the let-down calcium and barium derivatives; pure chrome colors to recovered or otherwise let-down varieties; and so on. Except in special surfacers and other rare cases there is no room for inerts in a lacquer formula. It is also of passing interest that white lead, one of the outstanding paint pigments, is practically never used in lacquers.

For blue, ultramarine, iron and phthalocyanine blues have all been employed. Chrome greens, hydrated chromium oxide greens, and phthalocyanine greens find their place on the lacquer palette, while the chrome yellows and oranges, including the molybdated varieties, together with occasional uses of the hansa organic toners and the cadmium sulfide yellows, give a variety of choice to this part of the spectrum. Here too the earth colors—ochre and sienna, and raw and burnt umber—which were once of prime importance have been gradually supplanted by synthetic iron oxides, which are now obtainable in a wide range from yellow through reds and browns to almost black.

For reds, toluidine, para and the various lithol-type toners are most widely employed, with indanthrene reds and maroons and the cadmium sulfoselenides rising in importance. The bleeding tendency of reds and maroons is most marked in lacquers, whose powerful solvents are almost certain to cause bleeding of organic reds. Recently an organic red was developed that will not bleed under white lacquer. This is a metallic derivative of β-oxynaphthoic acid and it is now in production. Formerly, when red was required, inorganic reds such as the cadmium selenides were almost mandatory.

One of the earliest uses of lacquers was as a vehicle for bronze powders. These important pigments are finely divided aluminum, or alloys of aluminum and copper, giving attractive metal effects when dispersed in suitable vehicles. Bronzing lacquers of the best qualities use selected batches of nitrocellulose to minimize greening and gelling. This is also combatted by the use of such organic acids as citric, maleic, and tartaric, and by various proprietary products. It is still preferred to mix the vehicle and bronze just before using, in such quantities as to have only a minimum amount left over for the next day. This is especially true of the gold and copper finishes containing copper-zinc alloys. These have a strong tendency to gel to irreversible masses and must be handled carefully.

From what has been said, the make-up of a lacquer formula begins to take shape. Let us take one example—a red automotive lacquer for a fire engine. A full glossy finish is desired, rapidly drying, of maximum resistance to bronzing and fading, capable of withstanding frequent washing with the usual detergents, flexible enough not to shatter if struck a blow, yet hard enough not to mar easily when polished. The prescription indicated would include, at spray consistency, 10 to 12 per cent of ½-second nitrocellulose, 12 to 15 per cent of lacquer alkyds, 4 to 6 per cent of plasticizer and about 6 to 8 per cent of toluidine red toner. The remainder would be solvent, let us say a mixture of 35 per cent of butyl acetate, 10 per cent of butyl alcohol, and 55 per cent of toluene. For most pigmented lacquers, it has been found advantageous to supply the material in a concentrated form, requiring the use of a thinner, or reducer, to bring the material to the desired viscosity; accordingly, the above percentages would be revised in proportion to the reduction desired. The chief gain from this concentration would be to diminish the settling tendency of the pigment. Since, according to Stokes law, this is inversely proportional to the viscosity, the settling is less in the more concentrated and hence more viscous solutions.

The technique of incorporating the various ingredients varies with the opinions of lacquer technicians. Some charge a pebble or ball mill with nitrocellulose, resin, plasticizer, solvent and pigment, as purchased, and combine dissolving and grinding in one operation. Others make stock solution of the nitrocellulose and resins, stock pastes of the pigments in plasticizer or in nitrocellulose, and mix the desired formula from these. Where large regular runs of stock items are standard, the first method has the better production possibilities; but if a large number of small volume specialty items comprises most of the output, the second seems preferable.

The enclosed ball or pebble mill has been the favorite grinding medium, although roller mill grinds in castor oil and other plasticizers still are extensively used. So are pastes made from dispersions of nitrocellulose, plasticizer and pigment on rolls such as are used in the rubber industry. Here the sheet of dispersed pigment is cut into chips and either sold as such or dissolved to a heavy paste and used as a stock solution. This method gives a superior dispersion, but the process is hazardous and the equipment expensive. Several companies specialize in making such dispersions, which they sell to lacquer makers.

The purpose of most finishing products is two-fold—to protect the surface and to beautify it. Insofar as protection is concerned solvent-type lacquers may fall short of the maximum qualities developed by other finishes, particularly the baked alkyd-amines and vinyloids, not to mention the still newer and more resistant silicones. However, they do give a very considerable degree of protection in ordinary environments, and this is obtained with great ease and flexibility of operation, without the need of baking equipment. In addition, lacquers lend themselves to an almost unlimited variety of decorative effects. As mentioned previously, practically all colors both transparent and opaque, are available, in all degrees of luster. The lacquer-type decalcomania makes possible the reproduction of any wood, marble or other photographable effect on any surface. Etching lacquers turn out millions of nameplates, emblems and similar articles in remarkably attractive and economical fashion. Crackle lacquers are still used to give interesting two-toned effects easily and cheaply. These are over-pigmented, underplasticized lacquers. When applied to a lacquer undercoat and dried, they split apart to irregular areas, resembling alligator leather, showing the undercoat color in the cracks.

Pearl lacquers have outstanding beauty for some objects, and merit a little discussion. The base of this material is the iridescent film on the horny scale of certain fish, chiefly the herring. This is rubbed off the scales by brushes into a water slurry; the water is poured off and replaced by alcohol, and the alcohol then replaced by amyl acetate. In this nitrocellulose is dissolved and the resulting paste is called pearl essence. A few ounces of this paste in a gallon of suitable clear lacquer gives a beautiful pearly effect, and when applied to glass beads provides the artificial pearls of commerce. Other uses are for fish bait, cosmetic containers and many other decorative articles. In brief, with proper choice of lacquers and their accessory materials metal is made to look like wood, wood like metal and both like porcelain, giving the designer and sales manager a valuable arsenal in his battle for consumer favor.

The other cellulosic-base solvent finishes are as yet of comparatively minor importance. Cellulose acetate has not found large use other than as a plastic, while the acetobutyrate has attained stature recently as a base for fire-retardant airplane fabric finishes. Here its tautening effect is adequate, while it is far superior to the nitrate in resistance to fire.

A recent adaptation of the cellulose acetobutyrate lacquers consists in forming a stiff gel, rather than a solution, in a mixture of isopropyl alcohol and xylene. When heated to 150°F this melts to a fluid into which articles may be dipped. When withdrawn, the coating sets instantly on cooling and dries to a very thick, tough film. Airplane steering wheels and toilet seats are among the objects so finished.

Ethyl cellulose is gradually increasing in favor as a coating material. Its virtues are low-cost solvents, low specific gravity (a pound covers more square feet than a pound of the nitrate), diminished inflammability, and better heat and light resistance. Defects are sensitivity to a wide range of solvents, fats, etc., limited compatibility with most of the preferred resins, and an inherent softness in comparison with the nitrate and acetate types. In one of the most widely used war-time lacquer specifications cellulose nitrate and ethyl cellulose were used conjointly—a practice that is becoming more widespread. Ethyl cellulose lacquers, as well as the acetobutyrate types, are increasing in use, but are still far from reaching the scale of nitrate production. The alcohol-soluble ethyl cellulose types have recently come into vogue as bases for such specialized finishes as linoleum lacquers, wall-paper lacquers, and coatings for asphalt-containing compositions where hydrocarbon solvents would result in bleeding of the asphalt. With the increased production and availability of ethyl cellulose, and its definite advantages in some respects, it would seem that the development of specialized resins for use with ethyl cellulose would give needed impetus to its much wider adoption as a solvent finish. As a molding plastic it has won definite position, and its use during the war as a hot-melt peelable coating for packaging metal parts will probably continue in peace time.

Another carbohydrate ether, at present only a laboratory product, may soon be of importance in industry. This is the allyl ether of starch, which possesses both the characteristics of a solvent-release finish and, by virtue of the unsaturated allyl group, additional oxidation and polymerization possibilities. Allyl alcohol and chloride are now reasonably priced industrial chemicals and their derivatives will be heard from in no uncertain terms in the future.

The methods of application of these finishes are widely varied. Brushing is the least important, although it is occasionally employed. Spraying is by far the most important method, and the essentials of this procedure are common knowledge. Dipping takes various forms and warrants a brief discussion. Many articles, *e.g.*, dustpans, toy scooters, axe handles etc., are free-dipped in a thin lacquer or lacquer enamel so formulated as to allow free drainage and a smooth flow. Automatic dipping of such objects as paintbrush handles, fish baits and kitchen-utensil handles usually requires a heavy lacquer, the rate of withdrawal of the article being calculated to match the rate of descent of the film. In a modification of this, the rack of articles to be dipped remains stationary while the lacquer is gradually drawn off. A third type of dipping, used for articles of uniform cross-section, such as broom handles, lead pencils, etc., is the gasket or squeegee lacquer. Here the lacquer is of maximum solids and high viscosity, and the article is dipped into it through a hole in a rubber gasket of smaller diameter than that of the object. On withdrawal, the excess coating is smoothly wiped off by the gasket and a uniform quick-drying and attractive film is applied at minimum cost of material and labor. For coating cable a variant of this procedure is used, coupled with a drying tower to permit winding the coated cable without sticking.

Paper fabrics can be coated either in web or sheet. Most of the coated fabric is finished by knife application; the heavy lacquer is poured in back of the accurately beveled, micrometer-adjusted knife-blade under which the moving web passes. A short oven evaporates the fast solvents used and allows quick rewinding and recoating. Other lacquers are applied by roller methods, such as the standard Chambers varnishing machine; this is especially applicable to paper or foil sheets.

Applications by means of centrifugal whirling, by silk-screen printing, and other means again indicate the versatility of this type of finish, which can be adapted to meet almost any specification of properties and applicability.

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Chapter 24

The Examination of Paints

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The testing of paints is performed for four reasons: (1) to obtain uniformity of factory output; (2) to assure compliance with the purchaser's specifications; (3) to guide research in new products and formulations; and (4) to ascertain what competitors are doing. Each of these categories has its own requirements, and test methods used for one are not necessarily adapted for another. For example, a test which works well when run by the same man, using the same technique, on products of known formulation, may be totally unsatisfactory in the hands of another operator, or when applied to a different product.

Testing is becoming more of a science with the passage of time, but there is still a great deal of art in it, and the only way to learn is to do it, not once, but many times. Instrumental methods are becoming increasingly important, for obvious reasons, but it must be remembered that the use of an instrument in a test method does not abolish all the troubles that may have been experienced. Problems such as sampling, preparation for reading, calibration of the instrument, and interpretation of the results, remain with us, even though a photoelectric cell or some other mechanical gadget does the actual measuring.

To go into detail on all of the possible test methods for paints, varnishes, lacquers, printing inks, and related products, would be too lengthy by a factor of several hundred. Dr. H. A. Gardner has written a book of some 640 good-sized pages, covering this one subject, and more developments are occurring all the time. Therefore, raw material tests and chemical methods of analysis are omitted from this chapter. The test methods which are applicable to the liquid material, as manufactured, will be discussed first, followed by tests which are applied to the dried film.

The density, or weight per gallon, is probably the simplest of the tests. The obvious method is to weigh a known volume of the material. Since water weighs 8.33 pounds per gallon at 25°C, it simplifies the arithmetic if we take a container holding some multiple of this figure. A cup, holding 83.3 grams of water is the one most commonly used. Its weight in grams, divided by ten, is then the weight per gallon. The only precautions necessary are to be sure that a representative sample of the paint is obtained, that there is reasonably close temperature control, and that the cup is completely filled with paint and contains no air bubbles.

The consistency of most unpigmented products is very simple, at least in theory. Most of them are Newtonian liquids, which means that their viscosity is independent of the rate of shear, as long as the rate is not so great that turbulent flow is obtained. The Gardner-Holdt tubes are most commonly used, although various efflux instruments are occasionally specified, especially if the purchaser's laboratory is more accustomed to testing petroleum products, where higher precision is usually demanded. One of several falling-ball instruments is sometimes used for lacquers, and a number of others will be met with occasionally. Several of these will be described in connection with pigmented products. Most of them work well, and will give satisfactory results. They are more trouble to use and to clean, and the additional precision which they give is rarely required. The pronounced effect of temperature on viscosity requires careful control, if accurate results are to be obtained.

The problem of consistency is much less simple when we come to pigmented products. In general, these are plastic rather than viscous, although there are exceptions, and the results obtained are dependent upon the method used. For plant control, efflux instruments such as the Ford and A. S. T. M. cups, are adequate for many products; but their use in specifications is to be deplored, unless some control is exercised over the materials used, and even then trouble may arise. The theory of consistency, applied to materials such as paints, is beyond the scope of this chapter, but it must be borne in mind that two materials may give identical rates of flow under one set of conditions, such as with a cup, and still differ widely under other conditions. At least two, and sometimes more, different forces must be used to be certain that two products have the same consistency characteristics.

Two commonly used instruments which provide an easy means of changing the driving force are the Krebs modification of the Stormer Viscometer, and the Gardner Mobilometer. Both of these use a driving weight which may be changed to suit the requirements of the problem and measure time required for a certain travel distance. The choice between these instruments is dictated partly by personal preference and partly by the characteristics of the particular material being studied. The Krebs instrument is much more easily cleaned, and, since measurements may be made in the original container, it permits more products to be measured in a given time. The Gardner Mobilometer covers a wider range of consistencies, and may be used for fairly heavy pastes. The most useful information is usually obtained by calculating the reciprocal of the time, or the rate of travel, for either instrument, and plotting this against the driving force. For many products this will be a straight line, defining the consistency properties of the materials completely, except for thixotropy.

Many other consistometers have been developed, usually for some specific problem, but none has been widely used by the paint industry. Certain penetrometers have occasionally been suggested, especially for putties and caulking compounds.

The hiding power, or opacity, of a paint film is tested by the logical expedient of painting it out and seeing what it will hide. There are two methods, in general, of doing this. Complete hiding is obtained by brushing out the paint until no more background can be seen and weighing the amount of paint used. From this and the weight per gallon, the hiding power in square feet per gallon may be calculated. Many paints, however, change their hiding power as they dry; in general, it is the hiding power of the dry paint with which we are concerned. One method of approaching this is to spread out a number of samples at increasing spreading rates, and determine the hiding power by inspection when they are dry. Partial hiding is determined by spreading the paint at some predetermined rate, usually about what would be used in practice, and determining the ratio of the brightness of the dark and light portions, usually by a photoelectric instrument. This "contrast ratio" is a measure of the hiding power.

In general, contrasting black and white backgrounds are used, but objection is sometimes made that paint is rarely called on to hide a black and white checkerboard. Various other combinations of white and gray and black and gray have been suggested. One idea that might have merit is to use a background presenting various contrasts. The paint is spread on at a standard rate, and the most pronounced contrast which is completely obscured is reported.

Fineness of grind is determined with an instrument known variously as the Hegman Gage, or the Sherwin-Williams Gage. The paint is drawn down channels of decreasing depth and the point at which particles break through the surface is recorded as the fineness. This is largely a measure of the degree of dispersion obtained, and is affected only slightly by coarse particles in the pigments used. Dispersed air bubbles and solvents which evaporate rapidly will give trouble unless care is taken.

The color of liquid paint materials is a problem only with the clear varnishes and lacquers. It is nearly always dealt with by comparison with material standards, either solutions of inorganic salts, or suitable chosen glasses. As long as the liquid does not differ too much in hue from the standard, no trouble is experienced, and the measurement is simple. When the sample is too red or too green to make a satisfactory match, the method fails entirely. The problem should be susceptible to the same processes that have worked for reflection colors, but no one in the paint industry has yet done so, although the American Oil Chemists' Society, and others, are seriously concerned with it.

Such other properties of the liquid as odor are usually tested subjectively and the result is left to the judgment of the analyst.

The measurement of drying time may be regarded as intermediate between the liquid and the solid coating material. It is, of course, one of the fundamental properties of a protective coating, and since it is the one property above all others on which the paint industry is based, we should know a great deal about it and be able to measure it with great precision. Unfortunately, we know very little about the mechanics of the process, especially the oxidation-polymerization form, and the measurement is grossly inaccurate. Probably more trouble is caused by differences of opinion about the drying time of coatings than any other single subject with which we deal.

In the first place, drying is essentially a change in consistency. As mentioned, the phenomenon of consistency is a vast one, and one about which much remains to be learned. That branch of it dealing with materials of high consistency in extremely thin films is almost totally unexplored. Secondly, the process is extremely sensitive to many variables, including temperature, film thickness, air circulation, humidity, and probably others about which we know little. As if this were not enough, we have an end point which is essentially a matter of personal opinion, since the critical question is whether the coating is dry enough, in a certain time, for some specific purpose which is frequently not known to the technologist engaged in testing it.

The result of this chaotic condition is that, although many machines have been invented which purport to measure drying time, and several of them have been extensively used, the simple process of poking at the film with the educated finger remains the standard method by which this test is conducted. Even here, confusion is worse confounded by a lack of agreement on nomenclature. In general, we agree that "set-to-touch" is the point where no paint adheres to the finger when the paint is touched lightly, but even here opinion is by no means unanimous, and when we get to terms such as "dry hard," "dry through," "tack-free," and "print-free," we have about as many opinions as we have technologists. Some time ago, the results of a cooperative test on a series of varnishes were examined where the "dry-hard" times on the same varnish ranged from 7½ to 96 hours, depending upon the laboratory reporting.

The general unsatisfactoriness of the measurement of drying time has stimulated the inventiveness of a number of people, with the result that a wide variety of machines are described in the literature. Most of these share the common factor of applying a force to the coating at intervals, and searching for some end point which is detected rather easily. The Drying Time Recorder marks the film with a gear which rolls slowly across it. Several end points may be detected by examination of the dried film. The Sanderson Drying Time Meter drops a stream of sand in a spiral pattern on the rotating film. The end point here is the place where all the sand may be removed from the film with a light brush. These two instruments are the only automatic ones that have had any wide acceptance, although devices which drop tissue paper, flock, etc., on the film, press canton flannel against it, or mark it in various places have been proposed. All these devices are attractive in that they do not require continuous attention and yield numerical results which are not dependent upon personal opinion or individual definitions of sensations. However, they all share two draw-backs. The end points, in general, do not agree with any known sensory impression, most of them giving an end point somewhere in between the "set-to-touch" and "dry-hard" times. Also, the rate of drying of a film is markedly affected by the circulation of air over its surface, and these machines all operate to interfere, often unpredictably, with this circulation. Unless this factor is carefully controlled, duplication of results by different laboratories cannot be expected.

Another set of proposals to the periodic application of some mechanical test to the film are the various print tests, the rolling-ball tester, the flock machine recently proposed by the New York Paint and Varnish Production Club, various suggested methods for measuring tack-free time, and several others. None of these has received much acceptance, although each has considerable merit. They share the advantage that the panel may be kept under the proper conditions for drying in between tests, but the continuous attention necessary to make the test at suitable intervals is burdensome, especially if fairly high precision is required, so that the tests must be made frequently. As specification and control tests they are useful, since only one operation, at the expiration of the established time, is necessary. Another drawback to their use for research purposes is that large panels are usually required, since the test cannot often be repeated on the same portion of the film.

A variation of the drying-time problem consists of tests wherein the film is dried under adverse conditions. Here the appearance of defects, rather than the drying time, is the criterion by which the coating is judged. The most common of these are the gas and draft tests applied to varnishes. Some varnishes, on drying in foul air, will wrinkle and otherwise become defective, while others are likely to wrinkle in a strong draft of air. Conditions for testing these properties have been set up. The report is usually either "yes" or "no," with no attempt to grade the materials.

Other special tests occasionally used involve drying under other unusual conditions, such as cold, high humidity, etc., or on unusual substrates. These are not common, and unless otherwise specified drying tests are performed at 25°C and at approximately 50 per cent relative humidity.

When we consider tests applied to the dry film, we have two general classes; those which attempt to measure some physical property of the film, and those which attempt to evaluate its merit for some particular service. There is, naturally, some overlapping between the two.

Since one of the primary purposes of many coatings is decoration, naturally the appearance characteristics—color and gloss—are extremely important. By far the most common and for many purposes the most satisfactory method of evaluating color is by visual comparison with standards. The human eye is the most convenient and one of the most accurate color-measuring devices we have, and it rarely gets out of adjustment. Devices have been developed for making the matches under standardized conditions of illumination and view, and for bringing the sample and standard together so that the judgment may be made readily. These have been used less than they deserve, as undoubtedly a great deal of the trouble experienced arises from variations in the conditions under which the judgment is made. A number of sets of color standards have been produced, so that a numerical value may be assigned to a color, if desired. These include the Munsell and Ostwald systems, and the Maerz and Paul Dictionary of Color.

With all its advantages, the eye has difficulties which have led to the adoption of photoelectric devices for some color-measuring purposes. It is difficult for an observer to give a numerical rating to color differences, so that marginal cases of color matching, fading, yellowing, etc., depend upon personal opinion as to whether the difference is greater than permissible. The result is frequent controversy. Further, the eye cannot remember, with any precision, what a color looked like some time in the past, so that unless a sample of the original material can be preserved—which is sometimes difficult to do without change in color—it is impossible to evaluate such changes as fading and yellowing with any precision. Difference in texture or gloss between sample and standard are sometimes difficult to allow for, and the preservation and distribution of color standards are also drawbacks to visual measurements.

The spectrophotometer, an instrument which evaluates the light reflection of a sample for each wave length of the visible spectrum, is the fundamental machine for the measurement of color. The Hardy Recording Instrument, made by the General Electric Company, is rather widely used, although there are only a few in the paint industry. It records the information in the form of a curve, plotting the amount of light reflected against the wave length of light used. The interpretation of this information is a complex exercise in mathematics, which is beyond the scope of this discussion; but very precise information on color may be obtained. The operation of the instrument is complex, requiring considerable skill, and the interpretation of the data is arduous. It is the only instrument available, however, by which certain color problems can be solved.

The Hunter Multipurpose Reflectometer is the most widely used color measuring instrument in the paint industry. By the use of three filters, three numbers are obtained. One of these, obtained with the green filter, is the diffuse reflectance, or brightness, of the sample, and is useful, by itself, for the determination of hiding power and for calculations involving illumination. It is also a useful measure of dirt collection on exposure and of fading of gray paints. The other two numbers, together with the green filter reading, may be used to calculate a second set of three numbers, which may be regarded as the coordinates of the point representing the color in a three-dimensional space. If the space is properly chosen, equal distances between points will correspond to equal perceptual color differences, and by calculating the distance between two points, a numerical value for the color difference may be obtained. The uses of such a numerical value in problems of color matching, fading, and yellowing are obvious. Unfortunately, results of fairly high precision are necessary; although the method has appeared in a few specifications, we do not have much information on what kind of agreement may be expected between different laboratories. A few other spectrophotometers and colorimeters have been used to some extent, but little information is available on their behavior.

The reflection of ultraviolet and infrared radiations is not, properly speaking, a color problem, but it is attacked with the same instruments, by a proper choice of illuminant, filter, and photocell. Ultraviolet reflection is of some theoretical interest in connection with the question of exterior durability, and it also is required for paints which are used in connection with ultraviolet lamps for therapeutic and other purposes. Infrared reflectance assumed great importance during the war in connection with camouflage paints; but it also has considerable significance in paints for storage tanks or other places where heat reflectance is desirable, as well as being useful in predicting the behavior of paints to be dried by infrared radiation. Unfortunately most of the photocells available at present do not cover the greater part of the range of wave lengths which carry heat radiations.

The other important appearance characteristic of coatings, namely, gloss, depends fundamentally on the directional distribution of the light reflected from the surface. This distribution may be measured with an instrument called a goniophotometer, of which there are only a few in existence. The complete results are expressed as a family of curves, and the interpretation is very difficult. A number of instruments have been designed which measure the amount of light reflected, usually in the mirror direction, under certain specified conditions of illumination. In the most frequently used one, the 60° Glossmeter, the amount of light striking the surface at 60° from the vertical is reflected at 60° in the opposite direction. In the interests of getting enough light to measure accurately, not only the light reflected at 60° but also that for several degrees on each side is collected and measured. This works very well for flat and eggshell surfaces, as long as the instrument is properly adjusted, but fails when higher-gloss surfaces are encountered. Proposals have been made to reduce the aperture size for higher gloss finishes. Some successful work has been reported with the Aminco-Scott instrument, with which the direction of illumination and view, and the size of the receptor aperture may be changed. There is not, as yet, any agreement as to the most suitable size aperture for various gloss ranges, and more work will have to be done before we can expect a standard method. There is also some evidence that 45° gives results correlating better with visual judgments for high-gloss surfaces than does 60°. A number of other suggestions have been made, dealing with ratios between specularly reflected light and light reflected at some other direction, usually either vertical or just off the specular direction, the first for low-gloss surfaces and the other for surfaces having a tendency to exhibit "bloom." No generally acceptable procedure has been worked out, however.

A special case, applicable to flat paints, is sheen, which is gloss at a grazing angle of illumination and view. An instrument which permits the measurement of this property has been developed, but it appears that there is no great demand for numerical ratings, and that visual judgment of its presence or absence is sufficient for most purposes.

Another special case of the directional distribution of reflected light is the night visibility of traffic paints. Here the illumination is at near grazing and the view is of the light returned in essentially the same direction. An A. S. T. M. subcommittee is struggling with this problem, but the best they have been able to do is to construct an apparatus which permits the visual comparison of sample and standard under these conditions.

The principal difficulty that most gloss measurements encounter is that a person's subjective impression of the gloss of a surface is a synthesis of a large number of different factors. It is frequently difficult to separate out one of these impressions, measure it, and then have it correspond to a judgment which is influenced by a number of other factors. For this reason, most tests for gloss, especially of high-gloss products, are made visually. The Detroit Paint and Varnish Production Club described a method of making these under uniform conditions and in comparison with a set of standards, which seems to work very well.

The other appearance property of paints, such as brush marks, orange peel, blushing, and large particles are usually determined by visual inspection.

Hardness, adhesion, and abrasion resistance are three tests which are frequently thought of as service tests. As they are generally run, however, they are physical properties of the film, and have little relation to the service expected.

Hardness is an elusive concept, and its measurement is complicated because it rarely means the same thing to different people. To some it means impact resistance, to others resilience, elasticity, abrasion resistance, or mar resistance. The Sward Rocker, for example, seems to measure some form of elasticity, rather than hardness in the classic sense. However, it seems to follow the "hardening" of a number of baking enamels very well, and is extremely useful in developing the proper curing schedule for heat-convertible finishes. Impact resistance is related to adhesion, and, to a considerable extent to flexibility. The tests used involve dropping weights under controlled conditions on the panel, which is usually metal. Visual evaluation appears to be the only satisfactory method of examination. The Hart Impact Tester drops a hammer under standard conditions of height and weight, while a number of specifications call for dropping of balls of various weights from various heights. Which side of the panel should be struck and whether the panel should be supported or not are questions that are by no means settled.

Abrasion resistance is most commonly measured by use of the Taber Abraser, although other methods have their advocates. Falling sand or quartz, rotating the panel in sand, and blowing sand against the surface have been used; recently a method using a strip of sandpaper, with sandpaper and panel both moving, though at different speeds, was described. The type of abrasive, rate of abrasion, and duration of the test, or choice of end point are all matters which vary with the user. The recovery time allowed the panel between one abrasion and another is frequently important, since with dry abrasion, tests frequently generate a good deal of heat, which must be allowed to dissipate, especially if the material tested is thermoplastic.

Special cases of abrasion resistance are the wet abrasion resistance, or "washability," test for flat wall paints, in which soap, or some other cleaning compound may be used, if desired. This type of abrasion test has been developed for traffic paints, where a machine drives a rubber tire over the sample. In this case, some impact is provided, since many traffic paints fail by loss of adhesion and chipping away, rather than by wear alone.

In this test, as in all other adhesion tests, the substrate is an integral part of the test, and its nature and surface preparation must be carefully reproduced, if the test results are to be worth the trouble of making them. Adhesion is most commonly evaluated by scraping with a knife, and this test can be very useful in the hands of one skilled in the art. Various devices which hold the cutting edge in a standard position and apply a standard, or in some cases an increasing weight to the knife have been used to some extent. A test using a tensile strength machine, which measures the force required to pull the coating loose from the substrate, has been described by the New York Paint and Varnish Production Club. Adhesion may also be judged visually in connection with impact and flexibility measurements.

Flexibility, in some cases, such as metal decorating enamels, is a service test, and is tested by putting the coated metal through the same drawing, stamping, or shaping operation that it is expected to undergo in practice; in most cases, however it is simply as a measure of inherent property of the coating. By bending a panel over a mandrel, the extension of the film before cracking may be determined. By use of the conical mandrel various extensions are obtained on the same panel, and the handle makes control of the rate of bending, which is important, a good deal easier. The Rumpometer, which deforms the panel by pressure from the reverse side, gives similar results, although the calculation of the extension is more complex. Careful control of panel thickness, film thickness, drying of the film and temperature are also necessary to obtain reproducible results.

Immersion tests are generally tests of a fundamental property of the coating, although here again they may be service tests in special cases, such as interior coatings for containers. Immersion may be in hot or cold water, alkali, salt, acids, or organic solvents. Hot and cold water and alkali are the most common. Metal panels are commonly used for water tests, and the outside of test tubes for alkali tests. Temperature control is important, especially in the alkali test, and film thickness and conditions of drying probably need more attention than they usually get. The films from water immersion are usually given two hours to recover from any temporary whitening. Films from the alkali immersion are usually regarded as acceptable if they are not seriously disintegrated.

Essentially the same results as from water immersion are obtained if a cooled panel is suspended in a humid atmosphere, bearing in mind that the effective temperature is somewhere between that of the atmosphere and that of the panel.

Accelerated durability tests have received a great deal of attention in recent years; within their limitations, they have been accepted as extremely useful tools for the formulator. The number of variables which need control are so great that their use in specifications has produced a good deal of grief and recrimination. The work of the Cleveland Paint and Varnish Production Club has explained the reason for some of these discrepancies, and it may be that in the future better agreement may be expected.

Attempts to use other light sources, particularly mercury vapor arcs, for this purpose have been made, but their characteristics differ so markedly from those of sunlight that the usefulness of the results is questionable, or else the acceleration obtained is so slight that little good is accomplished.

Most panel exposure tests are accelerated to some extent, as those locations are chosen which will give the full effects of exposure. In addition, we frequently expose panels at an angle of 45° facing South, which accelerates the sun's effects substantially. Florida exposures accelerate the exposure even more.

A large number of accelerated corrosion tests are also available, the salt spray test being by far the most popular. As the New Jersey Zinc Company has shown, the absorption of salt solutions by paint films is substantially slower than is the absorption of distilled water; hence a test such as salt spray is essentially a test of the integrity of the film, which means in part of the efficiency of the finishing system used, and of the ability of the anticorrosive pigments used to prevent the spread of corrosion of bare spots. The test is much more useful for the inspection of finished products than for the formulation of new and improved products, since many products may give excellent results in the salt spray and still fail rapidly in service.

The evaluation of exposure results requires skill and practice in observation. A numerical guide, such as the Federation Standards, is extremely useful in recording the stages of panel deterioration, and record sheets such as are issued by the Federation insure that all the pertinent information is recorded. The use of the standard scale adopted by the Federation where 10 is perfect condition and zero is complete failure should be suggested. The temptation to use 0 for no change and increasing numbers for increasing failure is frequently present, but its introduction only adds more confusion to a field that already has enough. The use of a scale of 100 is also tempting, but leads to fictitious precisions. Ten steps, or at most 20, produced by the use of one-half step units, are ample for most of these visual judgments. Of course, changes such as fading, loss of gloss, and collection of dirt are subject to instrumental determination, and in these cases the actual results should be reported.

Other accelerated tests, for settling, by heat and agitation; for yellowing, by heat; for embrittlement, by heat; and others have been proposed, but none has been adopted to any great degree.

The field of service tests is the most important phase of the examination of paints, since it is the court of last resort. If a finish is satisfactory in use, no more needs to be said, and if it does not deliver the service expected of it, all the favorable test results in the world are of no avail. Paradoxically, only brief mention of this field will be made, in spite of its acknowledged importance. This is partly because the subject is so diverse that it cannot be covered in detail, and little purpose would be served by discussing a few fragments of it. Another consideration is that most of the procedures for conducting service tests are obvious, and do not need much emphasis. A few generalities only will be given.

Obviously, in conducting service tests, the coating should be exposed to the conditions it will meet in service, on the substrate, and in the thickness that will be used. In order to speed up the answer and to provide some factor of safety, we usually attempt to expose a finish to the most arduous set of conditions possible. To test traffic paints, a road with a lot of traffic is chosen; to test mildew resistance, a place with lots of mildew. However, care must be taken not to overdo this. In attempting to accelerate things too much the forces may be thrown out of balance. In the case of traffic paints, a road with abnormally high traffic loads gives undue weight to abrasion resistance, and since all the paints wear out rapidly, weathering gets no chance to operate.

The importance of using the same substrate and surface preparation as will be used in service is well known, but there is a tendency to forget the importance of the use of the same finishing cycle. We know it is important in industrial work, but the tendency to forget it in other fields sometimes leads to grief. A lot of work was wasted in the study of mildewcides because the panels were painted in the laboratory, shipped to the exposure site and exposed. All the materials tested looked good, until it was realized that dry paint does not infect easily. When the panels were painted in place on the test fence, much greater differences were obtained.

The same sort of error may arise by testing paints applied by skilled professionals in the laboratory when they are intended for use by amateurs in their homes. Traffic paints may be applied to roads and, because the test is designed to compare a lot of samples, the first ones have several hours to dry before being placed in service, while the last one has only fifteen minutes. Other obvious examples will come to mind.

Another important generalization in service tests is that repetition is essential. The variability of test results is nowhere greater than in this field. Definite conclusions can be drawn only when the test is repeated a number of times. We are all familiar with the occasional paint job that has performed far above all rational expectations, and even more familiar, because everyone calls our attention to it, with the occasional job that, for some obscure reason, falls way below what was expected of it. If our test happens to hit one of these, our results are worse than worthless. Fifty tests of ten samples, each repeated five times, are much more valuable than fifty tests of fifty individual formulations.

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Chapter 25

Surface Preparation

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In the previous chapters it has been emphasized that paint finishes are primarily used to give maximum protection to the surfaces to which they are applied. However, this goal can only be attained by proper surface preparation. Everyone has at some time or other tried to paint a piece of bare wood. This usually gives poor results, because most people are not aware of the need for proper surface preparation. Experts know that because of the nature of wood, certain pre-paint preparations must be made before applying the surface coat; the pores must be sealed and the resin thoroughly covered with suitable materials. When painting metal surfaces one is faced with similar, although not identical problems. Metal surfaces too are made up of many pores and these are usually filled with all types of soil. It is the removal of these soils that constitutes the major problem in the pre-paint preparation of metals. By soil the trade refers to dirt, oils, greases, rolling compound residues, chemical residues, oxides, scale, rusting agents, etc.—in other words, any material which is present on the surface of the metal and is foreign to its pure condition is classified as soil. These materials must be removed if a satisfactory surface for proper paint adhesion is obtained.

STEEL

Steel is probably the most widely used metal. Since it can readily be formed into many shapes by various means of manufacturing, its surface is likely to contain practically all types of soil—oil, chemicals, rust and scale—of these soils, rust and scale constitute the major part. Therefore, to simplify the first part of this chapter, the discussion will be limited to steel and to the application of the various methods of surface preparation in this field. These methods can be applied to other metals with suitable modifications.

As everyone is well aware, paint will adhere to any surface upon which it is deposited. Therefore, if the soils are not removed from the surface, the paint will adhere to them. Since most soils as a rule are not firmly attached to the metal surface, pulling away of the paint, or peeling, soon occurs. This constitutes rapid paint failure.

Rust and chemical salts of iron are the type of soils that become component parts of the metal surface. These soils will ultimately cause paint failure; with them, however, the failure or rupture of the paint film requires a much longer period of time before revealing itself. At the time the surface is painted the presence of these "rusting agents" is often not visibly apparent and therefore no evident ill effects can be seen. It is known in the field, however, that since paint films are porous moisture soon penetrates and activates these "rusting agents," promoting the formation of rust under the paint film. Rust is itself hygroscopic and therefore draws more moisture to itself and produces more rust. Ultimately, the rust will flake away from the lower strata and take with it the paint film covering it. This may be classed as slow paint failure. It is evident that to have a durable paint film, both types of soil must be completely removed or neutralized.

It must be realized that "maximum paint adhesion" is a relative term depending largely on the paint adhesion required by the manufacturer. Each manufacturer has his own definite surface-preparation problems and end result requirements. Therefore, answers to these surface preparation problems can be evaluated only by the individual manufacturer, who knows the ultimate end results desired and the condition of the metal surfaces to be painted.

The field of metal-surface preparation covers a wide and diversified range. Basically, it can be divided into two specific groups, depending on the means employed for soil removal. These are the mechanical and chemical means of surface preparation, under which are many sub-classifications. A tabulation of the methods would be as follows:

A. Mechanical
    (1) Abrasion cleaning
        (a) Manual methods
        (b) Mechanical methods
    (2) Flame cleaning
    (3) Sandblasting

B. Chemical
    (1) Solvent cleaning
    (2) Alkali cleaning
    (3) Emulsion cleaning
    (4) Pickling
    (5) Acid metal cleaning
    (6) Phosphate coatings
        (a) Crystalline
        (b) Amorphous

It will be shown in the subsequent discussion that paint adhesion and durability improve as one progresses downward through the above tabulation. However, it should be pointed out here that in many cases no one pre-paint process alone will produce the desired paint film durability. A combination of surface preparation systems is usually a requisite to ultimate durability. Some of the more common methods of application will be outlined. An idea of the surface condition after treatment and the general durability of a paint finish on such a surface will also be presented.

Abrasion cleaning involves the use of either sandpaper, emery cloth or wire brushes to remove the soil. This type of cleaning is readily adaptable to both manual and machine-type application. Where rust is scuffed off prior to refinishing, as in small garages, the former is usual. In industry where the localized heavy rust scale must be removed from a surface prior to chemical treatment, the machine methods are often used. This type of treatment does not produce a good bonding surface, since only the solid types of soil are removed. The liquid types, such as oils and greases, remain and no passivation of the surfaces has taken place. If no liquid soils are present, the scuffed surface produced by abrasion gives good initial paint adhesion. However, in a short time the rusting agents left under the paint will cause failure.

Flame cleaning is primarily the method of applying several small intense flames to the surface of steel, usually structural steel. As a result of this intense heat the scale literally "pops off." This is caused by the different temperatures of expansion of the scale and the steel. This method will also "burn off" any liquid soils that may be present on the surface of the steel. Paint adhesion on these surfaces has been found to be fair. However, the rusting agents have not been removed and since the surface has not been passivated it is but a matter of time until paint failure occurs.

Sandblasting finds considerable application on plate steel where it is desirable to remove heavy mill scale from the surface. Castings too are often cleaned by this method. In this type of cleaning a blast of sand-laden air is directed at the surface to be cleaned. Large pieces are usually cleaned by directing the sand blast by means of a special nozzle as the operator moves around the work smaller pieces, such as castings, are often cleaned by placing them in a specially constructed tumbler which causes the castings to rotate while a blast of sand-laden air is directed at them. The surface produced by either the stationary or tumbler type of cleaning is rough and excellent for ceramic-type finishes. However, a heavy paint coat must be applied so that a smooth finish can be obtained. Also, initial paint adhesion on this surface is very good, but the corrosion resistance is relatively poor and therefore the surface will deteriorate. Another weakness of sandblasting is that it cannot very effectively be applied to sheet steel surfaces, as it may cause buckling.

With this brief consideration of the mechanical applications let us go on to the chemical methods, emphasizing that the mechanical applications are primarily used on specific problems in the steel field. The chemical methods are wider in scope and find application in all phases of the industry.

Solvent cleaning is one of the oldest methods to be applied for the removal of soil from the surface of metals. Originally, and even today in a few instances, petroleum products such as gasoline, kerosene, etc., were widely used to remove oil and dirt from metal surfaces, because they were the only known materials in which the soil was readily soluble. One of the drawbacks in using a petroleum solvent is that the oil film has merely been reduced in degrees and not completely eliminated. Another factor against its use is the relatively high cost of these products as compared to many commercial cleaners now on the market. Fire hazard is also an ever-present danger; this became even more of a problem when many firms began using lacquer thinners and other inflammable organic solvents to replace the petroleum products. Strict fire regulations were imposed, and today the use of many of these materials is prohibited. Only solvents having a flash point of over 100°F can now be used, and these only under properly approved conditions. As a solution to the fire problem, a group of non-inflammable of the chlorinated type solvents was developed.

One bad failing of these chlorinated solvents, however, was that they could not be used as wipe-on materials, nor could they be used in open tanks, for they were highly toxic to the operators. This led to the introduction of vapor degreasers. In the vapor degreasing method, the solvent is contained in a deep tank. Only a little of the solvent is present and this is vaporized. The hot vapors rise in the tank and the work to be degreased is submerged in the tank where it is completely immersed in the hot vapors. After the metal is degreased it is removed and allowed to cool. To prevent the vapors from escaping into the room there is a series of cooling coils around the inside of the tank, a short distance from the top. These condense the vapors and the condensed liquid is returned to the lower portion of the tank, where it is again vaporized. The resulting metal surface is free of grease. However, too often neither the pigments of drawing compounds nor any other solid soil is removed. This results in a smutty surface.

Another factor that has been found detrimental in these types of systems is that they must operate at high efficiency. Moisture must be kept out of the system and the vapors must be kept in the tank. If even small quantities of moisture get into the system some decomposition of the chlorinated solvent takes place, producing hydrochloric acid, and these corrosive chloride rusting agents will be deposited on the work. These decomposition products will also attack the equipment if the vapor escapes into the atmosphere even in small quantities; the vapor will decompose and leave rusting agents in the atmosphere which can be deposited on the work. As pointed out earlier in this chapter, rusting agents ultimately cause paint failure.

The vapor degreasing method of surface preparation is very effective for the removal of such soils as exceptionally heavy oil films from the surfaces of small machine parts and similar articles. Its cost however is very great compared with other systems in use. The loss of solvent is high, and therefore constant replacement must be made to maintain the most efficient systems. Another factor, though not a minor one, is the high maintenance cost.

Generally evaluating the solvent-cleaned surface, we find that it is a better surface for the reception of paint than was the oily surface. However, on the basis of corrosion resistance it is not very good. This method can very effectively be used for degreasing parts that are to be painted, but which have a short use life, that is, where the durability of the paint finish is not a prime requisite.

Alkali cleaners are a diversified field of chemical cleaning compounds. Here, by the blending of alkaline salts, soaps and resins, one finds a wide range of cleaning compounds practically tailored to fit each degreasing job. The cost of these materials is extremely low. They are sold in a concentrated powder which is diluted according to specifications for various types of work. Their use, however, is limited to definite types of application, as they can be used only in spray-washing equipment or dip tanks. A slightly cleaner surface than that produced with the solvent cleaners is obtained with this type of material, for they can be compounded to remove all the soil, including drawing compound residues. The soap that is incorporated in the product helps emulsify the soils in the pores of the metals.

After an application of this type of metal cleaner, the surface must be very thoroughly rinsed to remove the maximum amount of the alkaline residues. Any of these residues which remain on the surface will be the culture point for the start of corrosion. Even after thorough rinsing, the cleaned parts must not be left around before painting, as rust will start in a period of hours. If the parts are painted after rust has started, failure of the paint finish will occur after a short time.

To improve paint adhesion and reduce the possibility of corrosion many alkali rinses incorporate a small percentage of neutralizer. Although surfaces resulting from the alkali-cleaning methods are somewhat better than the solvent-cleaned surfaces they too are primarily for short life terms. Because of their low cleaning cost the alkali cleaners find wide use in industrial systems, usually in conjunction with other preparatory systems prior to painting.

Emulsion cleaning is an old type which has found a wide use in the field of metal cleaning during the past few years. Basically these cleaners are petroleum products suitably blended with emulsifying agents. In the past these cleaners did not prove too effective because they were a very limited number of emulsifying agents and these were not very good. During the past few years, however, a great many new synthetic emulsifying agents have been produced, and these are much more compatible and effective than the old natural emulsifiers. As a result of these developments emulsions are now produced that can be diluted to almost any desired consistency. This wide range of dilution also means better applicability to specific industrial cleaning problems. Cleaning with these emulsions usually leaves a micro-film of oil which, although not too desirable a surface for paint reception, is at present the recommended pre-clean prior to the application of some types of phosphate coatings.

An innovation as the result of the new synthetic emulsifying agents has been the ability of forming emulsions of solvents other than petroleum products such as chlorinated solvents. All emulsion cleaners are usually used at elevated temperatures and surfaces treated in this manner are left in a good clean condition. When paint is applied directly to an emulsion-cleaned surface the resulting work will have about the same durability as that obtained by solvent cleaning. Emulsion cleaning does have the advantages over solvent cleaning, however, that it is less expensive and that it can be used at elevated temperatures both in dip and spray systems.

A more recent development in the emulsion-cleaning field is the acid-emulsion solutions. In these, a small percentage of phosphoric acid is blended into the emulsion. As a result of this the parts cleaned in the emulsion should have better paint durability and adhesion. If they work according to theory, the resulting surface should be somewhat better than that produced by ordinary emulsion cleaners and should fall into a class probably close to the surfaces resulting from alkali-cleaning followed by a neutralizing rinse.

The next classification has to do with pickling. This term is generally taken to mean the use of strong mineral acids for the removal of oxides from metal surfaces. However, alkali pickling is also considered. This is due to the fact that during the war years a new method of pickling steel surfaces was developed in steel mills. This is known as the Sodium Hydride process. It has been found to be more effective than the older sulfuric acid pickling method in the steel mills, many of which are gradually incorporating it in their processing procedure. The method utilizes a molten solution of sodium hydride through which the steels are passed and are readily descaled without fumes and corrosive vapors escaping about the plant. Naturally this process is primarily limited to the removal of mill scale at present. Undoubtedly the resulting surface is alkaline in nature and the same bad features apply in paint durability as with alkaline cleaners.

Acid pickling has been part of the steel industry for many years. Sulfuric acid is probably the best known and most widely used pickling agent, although practically all the strong mineral acids are used for this purpose.

Since iron oxides are basic oxides, it is natural that acids should react readily and dissolve them. This leaves behind the iron salt of the acid used. Unfortunately, the iron salts of all strong mineral acids—sulfuric, hydrochloric and nitric—are very readily soluble in water; as a result they act as corrosion agents, often speeding up the process of rusting the steel. One can see from these facts that metals treated by this process also fall in the short paint-life field, since the porous nature of the painted surface permits moisture to reach these salts.

Phosphoric acid, another mineral acid, is sometimes used, rather than the three above-mentioned pickling acids. It is somewhat less active and more expensive than the others. However, in its favor is the fact that its metal salts are insoluble in water. It does not give off noxious odors or corrosive fumes. The surface that results from such a pickling operation is ideal for paint reception and durability, for all soils have been removed, including chemical soils and rusting agents. Whether or not this material will be used is primarily a question of evaluating the end result against cost.

Acid metal cleaning is a very diversified field. Its applications can be incorporated into any industrial set-up, regardless of production or size of parts. It can be used in manual systems, dip units, or spray-washing equipment. The manual systems find most of their application where the production is relatively small and the parts comparatively large, such as trailers, caskets, etc. In this method of application the surface is thoroughly wet with the acid metal cleaner, either by brushing it onto the surface or by wiping the surface with a rag that has been thoroughly wet with the solution. It should be pointed out here that the latter means of application is not desirable, as the rag soon becomes saturated with soil, and this is then carried back onto the surface being cleaned.

Heavy rust should be scrubbed with steel wool dipped in the solution. After the surface is thoroughly wet, the surplus material is removed by wiping the surface with clean dry cloths. This operation leaves a slight film of phosphate on the surface, which has been found to give an excellent bonding base for paint. The durability of the paint finish is also greatly increased, since any moisture that may penetrate the paint film is kept from reacting on the metal surface by the insoluble phosphate. Another factor leading to increased durability of the paint film is the fact that the phosphoric acid treatment has neutralized all corrosive agents and left a surface having a pH between 5.0 and 6.5. This has been found to be the most desirable condition for good paint adhesion.

It is evident that the acid metal cleaners are effective in eliminating all types of soil from the surface.

The dip and spray-washing applications of the acid metal cleaners depend largely on the space and equipment available in a manufacturer's plant. Often, too, the availability of heat is a deciding factor. Probably the most important factor, however, is the extent to which the equipment can be tied into the production system without disrupting the production layout. Each of these two types of applications has specific uses.

The dip systems require higher concentrations of material, as the job of removing the soil depends on "soaking" it off, combined with slow chemical action. Heat is generally required if the soil is heavy in thick oils or drawing compounds. Usually in these types of systems, the acid cleaners are preceded by some type of precleaning operation, such as alkali cleaners, emulsion cleaners, or degreasers. This removes all the surface soils, leaving only rust and corrosive agents to be removed or neutralized by the acid cleaner. By combining the two systems, a much less expensive operating system is obtained and a much more effective painting surface produced.

Basically, the same facts apply to the spray-washing systems. In these, a lower concentration of material can be used to produce results similar to those obtained from the dip systems. It is found also that the solution has the added aid of mechanical action from the spray in removing soil. Here again, for the least expense in operation, some method of precleaning is recommended. The surface produced by this system is also excellent for paint reception.

Paint films applied over either of the two surfaces produced by the methods mentioned above will have far better adhesion than any of the methods mentioned prior to the use of phosphoric acid. As we have seen, the resulting phosphate surfaces are excellent for the reception of paint and for the elimination of corrosion. It is therefore logical to assume that the greater the amount of phosphate present, the greater will be the resulting protection under paint films. This is the basis for the phosphate type of metal coatings. It is the purpose of these systems to produce a sufficient phosphate coating on the surface of the metal to give the maximum possible protection under the paint.

Phosphate coatings can be produced on metals in one of two ways. In the more generally used method, a solution of acid phosphate salts plus some activating agents is prepared and heated to about 140°F. The part to be phosphate-coated is then thoroughly cleaned, preferably in an emulsion-type cleaner. This is followed by thorough rinsing. Then the part is immersed in the phosphate solution, where the phosphate salts are deposited on the surface of the article in crystalline form. The final step is a sealing dip in a bath of diluted chromic acid. This method today is considered to give the maximum paint durability. Unfortunately, this method has a few drawbacks. Because the phosphate coating is crystalline in nature, it is often found that paint will chip off if a sharp blow is given the surface thus treated. The system is also costly.

More recently phosphoric acid solutions have been introduced in the field of phosphate coatings; these produce fairly dense phosphate coatings on the surface of the metal. Although the coatings thus formed are not as dense as those obtained by depositing the coating on the surface, they do have two distinct advantages. First, they are formed by the chemical reaction of the phosphoric acid on the metal surface being treated, and secondly the resulting coating is amorphous in nature. These two facts tend to insure better bond between the metal and the paint. Since the coating is a part of the metal, there is definite assurance that the coating will adhere to the metal; also, since the coating is amorphous, it will not cleave as will a crystalline coating under paint.

The system used in applying this type of phosphate coating is primarily the same as for crystalline coatings. Some means must be employed to remove all the soils from the surface. This step must be followed by sufficient water rinse and then by dipping into the phosphoric acid solution. This solution does not have to be hot, but can successfully be used at room temperature. A hot solution at about 140°F is usually recommended to accelerate the drying time of the surface. This coating operation is usually followed by a dilute chromic acid rinse to passivate the surface.

It would be well to call attention to the fact that in both of these systems precleaning of oils, dirt, and so forth is a necessity. However, in the crystalline system, rust must also be removed, while in the phosphoric acid system the rust is taken care of in the process of coating.

By laboratory tests, it has been found that the crystalline coating will stand a slightly greater number of hours in the salt spray tests. Conversely, the amorphous material has stood up better under water-soak conditions, mandrel tests and impact tests after the paint had cured for two weeks.

From this consideration of surface metal preparation one can see that there are a great many means of preparing metal surfaces for paint. In the first place, it is necessary to remove soils. How this can be done most effectively is something that only the manufacturer can answer. Each manufacturer and his engineers must always take into careful consideration the value of a metal preparation process to their product. Basically, the question resolves itself into, "Will the cost of the set-up be worth that much more to the product?" In figuring cost many factors must be determined. What will be necessary? How much space is available to put in the equipment? Will it require additional plant space? What kind of water is available? Will it require any water-softening equipment? What will be the maintenance cost? Is sufficient heat available (in the form of power house equipment) ? These are but a few of the questions that must initially be answered.

In evaluating surface preparations the following basic paint durability and adhesion tests are made: salt-spray, water soak, humidity, mandril, scratch, impact and weather. Evaluation is made on panels treated in the proposed system and painted. These painted panels are then subjected to those tests that most closely approach actual service conditions, that is, refrigerators, washing machines, etc., must withstand water soak, humidity, mandrel and impact; automobiles, etc., must stand up under salt spray and weathering as well. By using these tests one may readily evaluate the end paint durability.

It is only by the proper preparation of the steel surfaces that maximum protection can be obtained.

OTHER METALS

Although steel is still the most widely used metal, there has been a great deal done since the war to replace it with a lighter metal, such as aluminum. Chemically, aluminum is very different from steel. Its oxides, unlike those of steel, form a protective blanket against further oxidation and ultimate destruction of the metal. Uniform oxide surfaces of aluminum form excellent paint adhesion surfaces. Many chemicals that give excellent cleaning of steel cause drastic corrosion of aluminum.

Physically, aluminum is considerably softer than steel and it cannot as readily be stamped out without surface failures.

It can be seen that many of the methods employed in the cleaning of steel can readily be used on aluminum. However, it must be kept in mind that removal of the oxide film, without replacing it with some suitable substitute, leaves the aluminum surface in a less paint-receptive condition than if the oxides were present. On checking the prepaint methods employed in the cleaning of steel and applying them to aluminum, it would be found that the mechanical methods would not be desirable, for the oxide surface would be removed, leaving the less desirable surface of aluminum for paint reception.

It might be well to point out that the mechanical methods do find considerable use in decorative work which is not to be painted. For instance, scratch brushing is often employed to give a satin finish to the surface. Sandblasting produces matte surfaces, but must be used at a much lower pressure than with steel in order to prevent warping of the metal.

Cleaning by chemical means finds much greater application in the preparation of aluminum for paint. Solvent-cleaning finds wide use for grease and oil removal and leaves the natural oxides untouched. However, the same difficulties apply here as are found in their use with steel.

Alkali cleaning is used quite a bit. However, strong caustic readily attacks aluminum and therefore special formulations must be made. This method of cleaning is usually employed prior to some form of surface preparation.

Emulsion cleaners are found to produce very good results in this field for they remove the soils, leaving the natural oxides untouched. Unfortunately, the natural oxides are often not very uniform and the paint adhesion may fail.

Pickling of the oxides is generally applied only to remove the natural oxide prior to the application of suitable paint-receptive surfaces. Care must be employed in using the strong mineral acids since they readily attack and corrode the aluminum surface.

Acid metal cleaning which employs phosphoric acid as its base finds wide usage, for the phosphate surface left is an excellent surface for paint. Another advantage is that many of these type of cleaners can be made to work for all kinds of metals that are being used in the plant, thus eliminating the need of special cleaners for each metal.

The phosphate coatings have also been greatly improved and developed. Here too one of the advantages is that special compounds can be prepared to handle all metals in the plant that have to be prepared for paint.

In the field of aluminum there are found special treatments which are applied to aluminum to produce a very uniform oxide coating. This surface has excellent corrosion resistance even without paint. With paint the adhesion is excellent. One of these treatments is called "anodizing." In this process the metal is made the anode instead of the cathode, as in the case of electroplating. Any electrolyte that is capable of giving off oxygen is used in proper strength for the bath. The current is turned on and the oxide film is formed which is more dense at the outer surface than at the metal surface. This film is then sealed by one of many sealing chemicals and is ready for use or painting, whichever may be the case. There are many patented variations of the process but basically they are the same. Another method of producing the uniform oxide films is by using chromate baths at elevated temperature. However, it is found that the resulting oxide film is not as good as that produced by the "anodizing" processes. Both the electrolytic and chemical methods of producing the oxides give excellent paint-receptive surfaces and paint adhesion.

Zinc has been used in industry for a good many years. Even with this long record of usage it still is found to be a trouble maker when it comes to paint durability. It reacts with the paints to produce soaps, and this ultimately results in paint failure.

It is not uncommon to see where some playful boys have thrown a stone against a painted billboard, causing the paint to flake off because of the sharp impact. This is the result of improper preparation of the surface. Paint failure of this type occurs on zinc die castings as well as on the sheet metal surfaces of galvanized, galvanealed and electrogalvanized metals.

Some attempts have been made to eliminate paint failure difficulties right at the mill by giving a phosphate coating to the zinc-coated metal surface before it leaves the mill. One difficulty of this process has been found that surface cracking may occur in manufacturing of items from the sheets. Another problem has been trapping of soil on the surface; this must be removed very carefully or the protective coating may be destroyed.

In considering the cleaning of the surface of zinc prior to painting it must be remembered that removing the soil without conditioning the surface for paint reception means only ultimate paint failure. It should be also kept in mind that strong preparatory materials may be used on zinc die castings and galvanized metal, but these same solutions may completely remove the zinc from surfaces such as electrogalvanized metal.

Evaluation of the methods for cleaning mentioned in the section on steel shows that none of the mechanical methods afford good paint adhesion. Solvent alkali and emulsion cleaners do nothing more than remove the soil but leave a very poor paint-receptive surface. Acid pickling causes drastic attack of the zinc surface. Phosphoric acid cleaning produces good cleaning without too much action on the metal surface, and this process is being used more and more. The paint adhesion is good. Phosphate coatings deposited on the zinc surface also give good paint adhesion.

The latter two methods of preparing zinc surfaces for paint have the added advantage that special compounding will produce a material which can be used on other metals, as well as eliminating high costs of equipment installations.

Chapter 26

Methods of Applying Surface Coatings

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The methods of applying surface coatings vary widely, from a ten cent-store brush and a 4-ounce can of paint to the investment of $250,000 worth of equipment to paint a thousand washing machines a day. A modern high-speed newspaper printing press costs half a million dollars. Printing ink of course, is one form of surface coating.

Engineering enters largely into the application of paints. A *mechanical engineer* may design a satisfactory conveyor line and oven; an *electrical engineer* designs the heating elements in the oven to bake the product, or an infrared baking oven, or in the case of electrostatic spraying, the proper electrostatic field to deposit the paint.

The *ventilating engineer* supplies the proper amount of clean air in the finishing room, in the ovens, at the proper humidity and reasonably free from drafts. Many other kinds of engineering enter into the successful application of surface coatings. Finally the *paint engineer* and formulator must make coatings which will fit the mechanical equipment and produce a satisfactory job—by means of either the ten cent-store brush or the half-million dollar printing press.

The application of coatings involves three *parts*: preparation of the surface, the method of application, and finally the drying cycle, either air-dry or baking.

Preparation of the Surface

Surface preparations are necessary, no matter whether it is a house job on the kitchen chair with a cheap brush or an automobile. The kitchen chair may have some half-loose curled paint, kitchen grease, or wax on it; if this is painted over without removal, the new coating will not adhere well. The best surface coating made is of no value unless it has adhesion. Hence, good surface preparation is *essential.*

Leveling and Filling. *Putty Knife.* A putty knife is a tool that every painter in the architectural field uses, both for taking off old paint and putting on heavy, plastic paint such as putty. Nail holes and cracks require filling with putties and crack fillers if the finished job is to present a new appearance. Automobile and other sheet-metal finishers use a putty knife to fill in scratches, solder joints, weld marks and joints with a knifing putty.

Wiping. Another method of filling and leveling a surface is used in the case of open-pore woods, such as oak or ash. A paste wood filler is thinned to brushing consistency with a volatile thinner such as turpentine or mineral spirits. A heavy brush coat is applied to the wood and this is allowed to dry for about 10 or 15 minutes. It is then rubbed across the grain with a piece of burlap leaving the pores of the wood filled and levelled.

Iron Filler. Porous castings are leveled by applying several brush coats of iron filler, letting the thinner evaporate or flash off and then wiping the surface to a smooth finish with a leather pad.

Methods of Application

There are three major methods of application: brushing, spraying and dipping. These cover about 90 per cent of the coatings used. There are about a dozen other methods which make up the other 10 per cent.

Brushing. It is estimated that 60 per cent of all paint produced is brushed. Most architectural paints for office and public buildings are brushed, as well as dwellings and apartment houses. Railroads and ships use a great deal of brushing, though both use spraying as well. Nearly all the paint sold at retail paint stores and hardware dealers is brushed, as their customers have no other way of applying it.

Spraying. Most factory-made products are sprayed, including automobiles, refrigerators, freight cars, ships in drydock, metal partitions, furniture and a long list of other fabricated products. Factory buildings are sprayed inside and out if conditions are right. Most spraying is done by hand, but automatic spraying is rapidly gaining ground.

Dipping. A product of such a shape that it can be immersed in a tank of surface-coating material and then withdrawn and the surplus drained off without trapping the surplus paint is usually dipped. Metal shelving, hoods of automobiles, many small parts that go to make up an automobile, wooden shingles, many fabricated sheet metal products, insulating varnishes for motors and electrical coils, toys, etc., are examples of products that are dip-coated.

Spinning. One form of the dipping process is to immerse the product packed in a wire basket, and after immersion to spin the basket at high speed to remove the excess coating material. Coated nails, metal buttons, and metal reels for camera film are a few of the many small parts which are finished in this manner.

Deep Impregnation. Deep impregnation of porous products under pressure is another form of dipping. Railroad ties, wooden telephone poles and, during the last war, aluminum airplane engine castings were impregnated by pressure. The product to be finished is placed in a suitable container capable of standing high pressure and a vacuum is first applied to exhaust all the air possible. Then a hot impregnant is forced into the porous parts. Railroad ties are impregnated to a depth of several inches with creosote; the life of a tie is increased several times by this method. In the case of aluminum castings for engine work the impregnants—China wood oil, phenolic resin solution and other types—were applied to fill up tiny pores which developed during casting. Many a costly casting was saved by this method during the last war.

Squeegee. Another form of dipping is the squeegee or gasket process. The product to be finished is dipped and the excess is squeezed off by a gasket which fits tightly around the outer surface. Broom handles are an example of the gasket method. Automotive-cable lacquers are applied in this manner. Vinyl compounds are applied to copper wire by means of metal dies to produce the best grade of magnet wire. Solutions of high viscosity can be applied by this method if the article to be coated is of suitable shape.

Tumbling. Another method of dipping is by tumbling. Articles to be coated are placed in a revolving barrel; just enough coating material is added to cover the surface of the objects and the barrel is revolved for ¼ to ½ hour. If too much paint is added, the pieces will stick together when baked or dried; if too little is added, bare spots will appear. Tumbling is usually a two-coat job. Golf tees, shoe buttons, shoe eyelets, and small parts are examples of items coated by the tumbling process.

Roller Coating. A product which can be painted in flat sheets and then fabricated afterward without disturbing the coating is often roller-coated. A roller coater is similar to the printing press in principle. The tin-can industry is the greatest user of the roller coater. Cosmetic tubes, lithographing and reproduction of wood grains on metal are examples of the products of roller coaters. This subject will be expanded later.

Silk Screen Process. Decorative designs, lettering, and identification marks are applied to objects by means of the silk screen process. Silk screens are made by cutting out the outlines of the design in a flexible metal, paper or similar backing and then cementing a piece of silk over the surface. Nylon has replaced silk since the war, due to its higher tensile strength and durability. The screen to be used is placed firmly on the object and paint forced through the meshes of the fabric by means of a stiff brush or a rubber squeegee. For cheaper work the silk is omitted and the paint is either sprayed or brushed on through the stencil.

Decals. Decals are just like postage stamps. A design is printed on paper, cellophane, sheet nitrocellulose and an adhesive is put on the back to fasten it to the surface to be decorated. The adhesive may be rubber cement, an oleoresinous or alkyd varnish, or a vinyl cement. The face of the decal is protected by a thin glue-sized paper which is softened with water and removed after the decal is in place. Decals usually require a clear finishing coat to protect the edges.

The Di-Noc Co. of Cleveland has made a great many variations and artistic improvements in the decal field. Most of the grained instrument panels for automobiles in recent years have been Di-Noc decals.

Gold leaf is applied by means of a sizing varnish except that the varnish is first applied to the surface in exactly the outline required. After the varnish is set, the gold leaf is rolled on, and after drying overnight carefully wiped with a dry sponge or a brush. Where no varnish is present the gold leaf crumbles, leaving a clear sharp edge.

Brushes. When the Egyptians first produced paint they sought some means of applying it. Turning to nature, they shredded the end of a palm leaf stock and made a swab out of it. Later the Chinese observed that the hog had long bristles; they cut a piece out of the hog's hide with the bristles still intact and dipped the butt end into shellac. This was fastened to a stick which acted as a handle. Thus the rudimentary basis for present-day brushes was established.

The modern brush consists of a hard wood handle, bristles of selected length and quality, and a metal ferule to attach the bundles of bristles to the handle. The butt ends of the bristles are firmly cemented together by vulcanized rubber or a heat-reactive phenolic resin. A "rubber-set brush" has the butt end vulcanized with rubber; dry brushes may be glue-set.

Bristles. The difference in quality between a poor brush and a good one lies in the bristles. Seventy-five per cent of brush bristles are hog bristles imported from China. Hog bristles are quoted on the commodity market as Manchuria, Tientsin, Hankow, etc., depending on what part of China they come from. Hankow and Manchurian bristles are coarse, due to the cold climate in these sections, while those of southern China are softer and finer. Some of the Chinese hogs must be fierce-looking animals judging by the length of the bristles they produce. Hogs in this country do not have hair long enough or stiff enough to be of any value as brush bristles.

The value of Chinese hog bristles over other animal or vegetable fibers lies in the fact that the outer end of the hog bristle divides into two or more branches like a tree; this is known as the flag end of the bristle. Branching or flagging has several advantages over bristles containing no flagged ends:

(1) It gives two or three times the number of points of contact with the surface, thus leaving finer brush marks.

(2) It has greater power to hold the excess paint by capillary attraction so that when pressure is applied, the surplus paint does not run out.

The Chinese gather all the available bristles, even from the fences in hog lots, together with the bristles obtained when the hogs are slaughtered. These are boiled in water to remove dirt, and while wet are straightened out and bundled. Hog bristles form a major export item for the Chinese people, who have very few. Russian Siberia used to have the hog bristle market before World War I, but China captured it and has apparently retained it for the last 30 years.

The way in which the bristles are selected and bundled together to form the final paint brush is rather complicated. A brush is made up of various lengths of bristles ranging in the case of long-bristle brushes (5″) from 3 to 5 different lengths. As a result, when the flag ends of the longer bristles have been worn off through use, the brush will still be of value.

Likewise, the brush must have the right flexibility; if made from 100 per cent cold-country bristles, it would be too stiff. Hence finer and softer bristles are intermingled with the coarser ones. Finally, the cost of the product determines whether cheaper fibers are included in the final piling.

House-paint brushes are usually square-ended, whereas enamel brushes are likely to have chiseled shapes. This chiseling is done by placing shorter bristles on the outside and longer ones in the middle. Artist's brushes are made from the hair of the weasel or his relative, the skunk. So-called camel hair brushes may be made from squirrel tail. Badger-hair brushes actually are made from the hair of a badger. In the old carriage days every expert finisher carried a set of fine badger-hair brushes with him; these cost as much as fifty dollars for a set of five. Cheap brushes are made up partially or wholly of horse hair, tampico fiber, and others. By law, the brush must be marked as pure bristle, or at least the amount of pure bristle must be indicated. It is well to look at the label when buying a brush for an indication of its quality.

Now why does a horse hair not make a satisfactory paint brush? Its wearing qualities are as good as or even better than those of pig bristles. Yet horse hair is not desirable because it does not have flags or branched ends to hold the paint; hence it has only one-half or less the number of contact points of a hog bristle. There is an old saying in the paint trade that one can tell how good a painter is by looking at the toes of his shoes:

an excess of paint on his shoes means a poor painter. However, it can mean that he is using a poor brush which does not hold paint well.

This brings up a subject which developed during the war. When the Burma road into China was closed, the supply of hog bristles from China was cut off. The government required a large number of paint-brushing operations around ship-yards, army cantonments, and new war buildings, and the soldiers required brushes for applying camouflage paints to equipment in the field. Nylon, which had been produced in about 1938, was proposed as a substitute for hog bristles. Although it has three times the wearing power of hog bristles, nylon fibers are straight-sided cylinders, lacking flags, and they do not hold paint. In the manufacture of the nylon fibers, right angle kinks were put in every so often, and in this way they were improved to a considerable extent. Moreover, the ends of nylon fibers were also split by a rather expensive procedure, and this also helped. These nylon brushes answered the purpose very well during the war, but since then the average contract painter has been insisting on hog bristle brushes, since he had little or no experience with nylon brushes during the war. Though the synthetic chemist has a hard time imitating nature, it is probable that the nylon paint brush will eventually displace the hog-bristle type.

Another wartime product to replace non-existent paint brushes for civilian uses, was the roller, usually about six inches long and 2 inches in diameter. The surface is covered with a fabric like a Brussels carpet. A two-pronged handle supports the cylinder on a shaft running through its axis, which permitted revolving. The gadget is in effect a hand roller coater. Water-emulsion paints are thus successfully applied to wall paper and to other flat surfaces. A sticky type of paint such as a turpentine-thinned gloss enamel could not be so applied. With the return of brushes the roller coater disappeared.

Some Economic Factors of Brush Application. Retail paint stores sell $15.00 worth of paint brushes with every $85.00 worth of paint; therefore they are very much interested in pushing the sale of brushes. As mentioned before, about 60 per cent of all paint produced is applied by brush. A trade journal recently reported that with wages of union painters at $2.00 an hour it would cost $27.00 to apply one gallon of paint. The automobile manufacturere would get 35 to 100 gallons of paint applied for $27.00 by spray methods. If the paint costs $5.00 a gallon the application by brushing would cost roughly 5 times as much as the paint. Before the war the cost of paint for brush application on the exterior of a house was estimated at 25 per cent of the total cost of the job. The moral to be drawn from this is that the best possible paint obtainable is actually the cheapest. Poor paint should never be applied outside.

An amusing instance arose out on the Pacific coast over union rules. In that particular locality the union painters were not allowed to use spray guns except on roofs. A painting contractor took a contract to paint about 200 quonset hut type buildings and figured on spraying them. The union objected to spraying, claiming that a quonset hut had no roof. The contractor contended it was *all* roof! So the case went to court.

Roller Coating Machines. The modern roller coating machine is a modification of the printing press. It usually consists of three or more rolls. The lowest steel roll runs horizontally, half immersed in the paint to be applied. This roll transfers the paint to a second steel roll parallel to the first. A third roll, rubber-covered or of a gelatin composition, is parallel to the second, from which it receives its supply of paint. All rolls are power-driven. The flat sheet passes under the gelatin roll and receives a coating; the distance between the second and first roll determining the thickness. This is very carefully controlled, and is determined by the number of grams per square inch. This is the most accurate method of applying a uniform coating known to the industry. The tin can industry coats millions of cans each year both inside and out by the roller coater.

The cost of roller coating is probably the least of all methods of application.

Dip Tanks. If an article is so shaped that it can be immersed and that gravity will remove the excess paint without trapping it, the article is usually dipped. This method has the added advantage of coating interior parts which are not accessible with a spray gun or a brush. The longer the pieces, the greater the quantity of paint required in a dip tank. When the tank is connected with a chain conveyor and the pieces are automatically dipped, the tank must be considerably longer, to permit the pieces to be withdrawn without touching the sides of the tank. Hence as much as 5000 gallons of paint are involved in some dip tanks. To reduce the amount of paint, a conveyor dip tank is often cone-shaped at the bottom; this minimizes the volume of paint required. A drain board for a distance of 10 minutes' travel time must be provided to take care of the dripping of surplus paint. Some method of agitation must be provided to keep a uniform mixture of pigment and vehicle. In some tanks the paint is drawn from the bottom and pumped into a point near the top which is still under the surface. This is done to prevent too much motion on the top surface of the liquid, thus avoiding bubbles. Other tanks have worm augers in the bottom of the tanks to provide a gentle agitation. The viscosity of the coating material used in dip tanks is from 14 to 25 seconds in a number 4 Ford cup.

The thinner used is an important factor in the operation of a dip tank. In some dip tanks the amount of thinner added is equal to the volume of paint used. The recommendation of the supplier of the paint should be followed in the matter of choice of thinner. With all the remarkable new aromatic petroleum solvents and synthetic ketones and alcohols available, the troubles previously encountered with the coating materials separating in the tanks should be lessened.

The stability of a dip tank is the problem of the manufacturer of the coating. However, if the turn-over of a tank, that is the amount of new paint added in a month is not equal to the volume of the tank, trouble may ensue. It may be more economical to use some other means of application. However, the cost of dipping is very low. Dipping does not give a uniform thickness of coating, since it is about twice as thick at the bottom as at the top. Also some sticky drips are sometimes left at the bottom of the piece; this gives trouble and presents a bad appearance. In a later section of this chapter information will be given on a method of eliminating drips by the electrostatic method.

The simplest tanks for dipping are just plain tanks filled with paint. The object to be dipped is immersed and then hung on an overhead rack to drain. In a semi-automatic tank the material is hung on a frame and then the whole thing is lowered and raised by power. The same general defects are manifested no matter what type of tank is used.

Wood Grains Reproduced on Metal. Printing ink is a specialized form of paint and an entire monograph would be required to cover this subject completely. Much of the art and science of the printing ink industry has been borrowed to accomplish the reproduction of wood on metal.

The first step is to photograph a piece of wood with a film the same size as the wood specimen. A screen is used on the lens with a series of circles, diamonds or squares, spaced equidistant but not touching. This film is a negative, and from it a positive film is made by the usual photographic means. The film is then laid tightly on a copper plate on which is a photosensitized gelatin solution. The positive film on the copper plate is again exposed to light and the picture of the wood is transferred to the gelatin coating on the copper plate. The copper plate is then etched with acid, which eats out the unsensitized portions to various depths. The figures are outlined by the series of small diamond- or circle-shaped openings, depending on the type of screen used. In this method of coating a surface, a ground coat is sprayed or dipped on the object to be grained and this is then baked. An ink is applied to the copper plate and the excess scraped off with a doctor blade. A gelatin roll is run over the surface of the copper, and this picks the outline of the wood grain out of the tiny etched holes. The gelatin roll is then run over the ground-coated object and the grain is transferred to the ground coat. The ink is then baked on and a clear coating is applied over the entire surface. This is the same as the rotogravure process used by Sunday newspapers. In production the copper-etched plate is wrapped around a steel core in cylindrical form and attached to a roller coater machine with a doctor blade attachment. A gelatin roll behind the doctor blade transfers the ink from the cylinder to the gelatin roll and then to a ground-coated object such as garnish mouldings, compartment doors, etc. In the rotogravure process newspapers use colored film; then they make three such cylinders by a colored screen—one for each color—and do a four-color process.

Drying and Baking Equipment

Protective coatings are applied in liquid form and must be converted to a solid form before they are useful. The first stage of conversion to a solid form takes place by evaporation of the volatile thinners. For example, the nitrocellulose lacquers are converted to the solid form when all the thinner and solvent has evaporated. In the case of an oxidizable base paint, such as a liquid house paint, drying proceeds by two methods, *i.e.*, evaporation of thinner and the oxidation and polymerization of the linseed oil to a solid stage. Lacquer thinners evaporate rather rapidly, but vegetable drying oils require hours for conversion to the tack-free stage and days to the dry-hard stage. Obviously in any factory where a product requiring a finish coat is made, the necessity for shortening this conversion time is paramount. Baking ovens were the answer to this problem. The oven may only be a room with an extra steam coil in it which reaches a temperature of 105°F, such as is the case where furniture is force-dried, or it may have an electronic heating device that reaches 1000°F in 10 seconds.

Box Type Oven. The oldest and simplest ovens were of the box type. The roof was high enough to permit a man to walk upright in it. One end had full-opening doors which permitted racks on casters to be rolled into the oven. The material with the wet coating was hung on the racks and placed in these ovens. The box ovens were heated by steam coils along the walls or by gas pipe burners located where the floor and side walls met. A natural draft chimney connected the top of the oven to the outside air. Some ovens had a suction fan to help in the ventilation. When the oven was full of racks the doors were closed and the heat turned on. A mercury thermometer was usually inserted in the door for temperature readings. By trial and error the time and temperature required for baking was determined. When the baking was finished the doors were opened and the trucks pulled out. Every time this occurred the oven cooled off and a great deal of heat was lost.

Improved Type Box Oven with Conveyor. Floor conveyors or overhead monorails with power were installed in bigger and longer box ovens. They had doors at both ends for entrance and exit and the work to be baked was hung or loaded on carriers. When the oven line was full of fresh work the conveyor was stopped and the doors closed for the necessary baking period. Better ventilation, better heating units and better insulation were characteristics of the semi-intermittent ovens.

Continuous Conveyor Oven. When the Ford Motor Co. started to assemble automobiles on a continuous conveyor line the natural outgrowth was a continuous conveyor oven in which the work entered and departed from the oven continuously. The oven then became tunnel-like in shape. It could be located anywhere—floor, ceiling or even roof, if necessary. Or it could be as high as three stories, the conveyors taking a low level through the oven to the back wall, turning and coming back at a higher level inside the oven. Proper heat distribution then became a major problem, which ventilating engineers solved, but not always too successfully. The type of conveyor was dependent upon the product to be baked.

Requirements of Baking Oven. A baking oven is nothing more than a heat exchanger. By bringing the wet-coated work up to an elevated temperature the volatile thinner is quickly driven off and the process of oxidation or polymerization is greatly accelerated to produce a dried solid coating. The processes of oxidation and evaporation give off certain products which are volatile at elevated temperature. Some of these volatile products are explosive if allowed to reach certain concentrations; therefore they must be kept below this explosive limit. General Motors safety engineers specified a minimum of 1200 cubic feet of air to be added for every gallon of volatile solvent evaporated in baking ovens.

Another requirement of a good oven is that the temperature must be uniform from the top to the bottom, giving every part of the work the same heat. If one part of the object is underbaked and another overbaked, the color, gloss and hardness may be affected. The pieces would not match in color or sheen, when assembled.

Finally the oven must be as economical as possible, consistent with results. This all adds up to proper ventilation, conservation of heat, type of heat, insulation, and such other factors as adequate heat controls, etc.

Ventilation. The biggest improvement in new ovens over the old ones has been made in ventilation. Some manufacturers of ovens withdraw air every 10 feet through openings in the top of the oven and force new heated air in at the bottom. Others have side entrances and exits. About 75 per cent of the air withdrawn is sent back through the oven; the other 25 per cent is replaced with new air. This keeps the concentration of volatile thinners below the explosive limits. Some ovens discard the air drawn from the entrance of the oven, as it contains the highest concentration of thinners. A good circulation of air gives an even distribution of heat in all parts of the oven and this promotes proper heat exchange. The air must not carry any dust or dirt, as this might deposit on the wet coating and leave a dirty, specky finish. Hence the better ovens have elaborate cleaning devices for filtering the air before forcing it into the oven.

Air Seals. In order to prevent cold air from rushing into open end tunnel ovens and cooling them off, the better ovens have air seals. These consist of a set of slotted ducts that line the opening of the ovens, including the bottom. The sets are spaced about ten feet apart and a fan draws air from one set and forces it through the next. This prevents cold air from displacing the hot air in the oven but it does not interfere with the passage of the conveyor into the oven.

Type of Heat. Gas, oil, electricity and steam are the main sources of heat. The choice depends upon the location, availability, and electric power and gas rates. Steam is used only if baking temperatures are 250°F or lower. Electricity is usually higher in cost than gas or oil but it is a cleaner heat, leaving no products of combustion. Likewise, strip heaters or calrods can be placed in any position along the walls, ceiling or even the floor of the oven. Natural gas and oil are the cheapest source of heat in most cases.

Location of Heating Equipment. Ovens are either directly or indirectly heated. A direct-heat oven has the burner, the electric strip resistance coil, or steam coil inside the oven. The indirect-heat oven has the heat source outside, the air being preheated and forced through the oven.

Steam and electric heating units are invariably located inside the oven. Gas and oil burners may be either inside or outside. The better ovens, which are fired by gas or oil, are indirect. Indirect gas-fired ovens eliminate some of the products of combustion of the gas which may often be harmful to light-colored high-gloss paint coatings.

A new type of gas burner has recently been developed known as the Burdett burner. It looks like a laboratory Meeker burner which has a short blue flame. These burners are mounted in rows six to ten feet apart along the floor of the oven. By means of very efficient ventilation and air circulation, white enamel can be baked at 325°F and can pass within 8 inches of the tip of the flame without any discoloration. This is the best direct-fired oven on the market.

Infrared Baking Oven. A new departure in baking equipment was the infrared heated oven. About 1938, the Ford Motor Co. started baking its undercoats at the Rouge Plant with banks of infrared lamps and in this way shortened the baking time from one hour to about ten minutes. These lamps are of the short wave length type and are high in the infrared. The bulbs with gold-plated reflectors are mounted on frames; the frames are in the form of an arch and the lights are mounted as close together as possible. These arched frames form a tunnel through which the automobile bodies or painted objects pass on a conveyor. When the infrared rays strike an object the heat bakes the coating. No insulation is used around the bank of lights and the fumes from the baking process pass off into the air. Gold-plated reflectors are used because gold reflects the infrared better than any other substance. Since black paints absorb more infrared, these bake faster than white paints, which tend to reflect part of the rays.

There is no doubt that infrared is one of the fastest ways known to transfer heat into a painted object. The closer the lamp is to the object, the hotter the object becomes. If, however, the rays do not strike some part of the object, it will not bake. The door hinges on an automobile body, which are three times as thick as the body metal, always come out soft. Not enough heat is generated at this point to raise the extra quantity of metal up to baking temperature. Ford has never been able to bake the lighter-colored finishing coats in infrared ovens due to the fact that the parts closest to the lights turn darker than the areas which are farther removed. Assembled parts which have a wide variation in metal thickness give trouble.

The cost of an infrared oven is low in comparison with the other types and the over-all length is shorter; therefore it takes up less space. The operating cost is high; lamps require replacing and the gold reflectors need frequent cleaning or the baking efficiency drops fast. Condensation of fumes deposit on this surface and must be removed. If the object to be painted is of such a shape that all of its surface can pass the lamps at the same distance, good results are obtained. A flat sheet is ideal. Metal temperature is the thing that counts in baking. One of the companies selling infrared baking equipment has a full-size demonstration set of lamps at its laboratory; before infrared baking equipment is installed a demonstration baking of the actual pieces that are to be finished should be made. This type of equipment can be very satisfactory or it can be a complete failure. The public utility and power companies have given the infrared baking equipment a lot of publicity in newspapers and magazines. However, these ovens are not the final answer to every baking problem.

Controls. All enclosed types of ovens have or should have automatic temperature controls. Controls in both the gas and electrical fields have been greatly improved in recent years. Whereas a few years ago temperature control of ±10°F was considered good, controls of ±2°F are now common. A traveling recording pyrometer should be a part of every oven operator's equipment to determine heat curves. A means of determining metal temperature especially in an infrared oven is a necessity. A pyrometer with a long lead wire attached to the object traveling through the oven is satisfactory.

Safety Factors

Ovens and paint thinners are all dangerous materials that can cause serious fires and explosions. All dip tanks of any size should have carbon dioxide, Foamite or some system of protection other than water. Water only spreads the fire. All gas- or oil-fired ovens should have the best automatic controls in case fuel supply, pilot lights or electrical failures take place. All unused paint should be stored in a separate building having fire walls.

A body builder in Detroit several years ago lost 50 lives by having a mercury arc lamp break; the hot mercury fell into a tank of lacquer, causing a severe explosion and fire. Adequate ventilation is necessary in any room in which volatile thinners are exposed to the air, both from a fire and health standpoint.

SPRAY PAINTING

L. W. LAMMIMAN

The DeVilbiss Company, Toledo, Ohio

We all know the contribution of the paint industry to the beauty and protection of our everyday surroundings. Now let us consider the contribution made by the greatest paint dispenser known, the spray gun.

This modern air tool made its debut in 1907 and shortly thereafter small industry began to adopt it for faster, finer finishing. Its effect was immediate and substantial. The industrial finishing revolution was soon under way. Almost every week marked the introduction of some new use of this amazing new technique. The furniture industry became a great spray-finishing advocate. Then later the automobile industry promoted the new process. It had brushed, flow-coated, and finally sprayed color varnish on wheels, chassis, and finally on automobile bodies.

But the big impetus to spray painting came with the practical development of lacquer. In 1922, the Oakland automobile made its appearance with a lacquer-sprayed body, and the big push was on. Now it was possible to finish an automobile in hours where previously a week was necessary. No longer did whole warehouses full of drying automobiles—all of them highly susceptible to contamination—have to be immobilized.

Today if all the automobiles manufactured in Detroit in a single day were stored for drying in the old manner an enormous storage space would be required, and the price would soar out of the average man's range again. But with the development of a quick-drying lacquer, which could be applied quickly and faultlessly, the spray gun came into its own. A few men armed with spray guns quickly relieved the finishing bottleneck of a great industry.

It was estimated that these new efficiencies had reduced the cost of an automobile well over $100 at that time. Such production lessons were quick to spread to other industries. The demand for spray-finishing equipment grew continuously until today 85 to 95 per cent of all the final finishing materials used by industry are spray-applied.

Spray-painting equipment, of course, is used extensively outside of industry. It has a great and well-deserved market in the refinishing field. This includes the fabulous volume of automobiles refinished each year. A wide range of equipment from small portables to thousands of well-equipped garages and shops all over the country accomplish this work.

The contract spray-painting field alone is a great user of such equipment. Portable outfits enable the painter to move rapidly from job to job and to bring factory production spray methods to bear on a great volume of maintenance work, in both domestic and commercial establishments. Many factories with elaborate finishing departments use portable outfits to keep the buildings bright and efficient inside and out.

The farm market too has a great potential for spray-painting equipment. This tool provides the labor-worried farmer with an opportunity to give his buildings the protection and beautification they need, which he can well afford to do with spray-painting equipment. Even the urban householder has taken to portables to maintain his house and its contents in a proud, colorful atmosphere. Thus the spray-painting machine has established itself as a great tool not only to industry but also to the ultimate consumer. In fact, today almost half of all the paint manufactured is applied with spray guns.

The war, with its urgency for huge volumes of production, imposed an immense task on spraying equipment. The answer was automatic spraying—and the results were tremendous. Modern industry is looking more and more to this solution to its increasing problems of getting out more production and of meeting rising costs. Automatic sprays have proved themselves over and over as economical instruments which not only save time and material but which accomplish unbelievable quantities of work with faultless uniformity. Automatic machines are used extensively to coat a great variety of products, such as refrigerators, plywood panels, venetian blinds, lamp shades, pipe, golf balls, leather hides, acoustic panels, adhesives of photographs, and multiple small parts. In fact, almost any sprayable material can be automatically applied economically where the production is warranted.

But whether paint is automatically sprayed or not, we are living in a spray-painted world. From Diesel locomotives to supersonic airplanes, from structural steel to hairpins, from prefabricated houses to china through an unlimited range of coatings, we find spray applications doing the job. Porcelain enamel is sprayed on bathtubs, ranges, wall tile, and kitchen utensils. Rugs are sized; pottery is glazed; tobacco is moisturized; cereals are vitaminized; baked goods are sweetened; coal is trade-marked; crackers are cheesed; and so on ad infinitum.

Essentially the spray-painting machine is not big or complicated. It consists of an air compressor to supply air power to the spray gun. An air transformer filters out dust and dirt, condenses oil and moisture, and regulates the flow of air. A paint container, either cup or tank, is needed to contain the material being sprayed and to meter it out to the spray gun. Hoses conduct both paint and air to the spray gun. Finally, the heart of the spraying operation—the gun itself—is vitally necessary to apply the material properly to the surface.

This combination of equipment is available in all sizes, shapes and degrees for a great many flexible purposes. Air compressors range from fractional horsepower portables to larger stationary outfits running into big water-cooled industrial units. The air transformer may vary from a small-capacity unit to the large production type. Containers may be pint or quart cup attachments to the spray gun, or they may be separate pressure feed tanks ranging anywhere from 2 to 120 gallons capacity. A wide range of spray guns includes touch-up guns, small cup guns, medium production guns, standard production guns, and automatic guns. The proper diameter and length hoses are matched to the capacity of the hook-up they serve. In industry they may go to stationary piped air lines and circulating systems for fluid delivery.

Whichever of these combinations of equipment is chosen depends entirely upon the requirements of the job. The size, coating material, type and area of the surface, and the production rate, all must be considered in selecting spray equipment.

In choosing the spray gun, for instance, we look at the job it is expected to do. If we are to finish small parts or do a decorating job, a small gun with a suction feed cup attachment may suffice. This gun, with container attached, is used when it is not considered practical to use a large, separate container with its considerable quantity of one type or color of material.

In the suction feed gun, air flowing past the nozzle of the spray gun creates a vacuum which pulls paint from the cup attachment through a fluid tube. This fluid feeding is further aided by an air vent in the top of the cup. The vent allows outside atmospheric pressure into the cup to aid the upward flow of fluid created by the suction process. When the fluid stream meets the air stream which pulled it from the cup, an atomization process begins. Air picks up minute particles of paint and whirls them violently outward in a round spray. As air from the two horn holes on the outside of the air cap meets this round, center spray of paint and air, it breaks it up further into a finer mist and flattens the pattern into a fan shape to give it wider coverage. The atomization we are after is one which results in a full, wet pattern with the least amount of air needed to break the paint flow into a fine spray of uniform density.

It may be said for suction feed that it is more convenient where spraying is limited to small quantities and to different colors. It also simplifies the cleaning up job. There is no fluid hose or tank to clean. It is easy and quick to slosh a little solvent around in the cup and to shoot a cleansing squirt through the tube and cap. On the other hand, some operators consider it harder to handle a cup gun when spraying small, confined areas.

The pressure-feed tank or separate container is used rather where fast, continuous production is needed, and refilling a small cup would be a bothersome waste of time. With a pressure-feed arrangement, the material is pushed through a fluid hose to the gun by a regulated air pressure on the paint in the tank. Such a device permits a more accurate and independent control of paint feeding at higher production speeds and reduces the possibility of off-color. In addition to the pressure-feed container or tank, it is also possible to use a pressure-feed cup attachment to obtain the same results as that resulting from the use of the tank.

Switching from pressure feed to suction feed or *vice versa* does not necessarily mean that it is necessary to change spray guns. It is quite possible to change only the air cap and fluid tip designed for the different purpose. The tendency with new spraying developments, however, is toward simplification and away from complicated combinations of gun caps and tips.

Most spraying jobs of any volume, whether they are in the contract spray-painting field, in automotive refinishing, or in industrial production, will prove most practical with the production-type spray gun. This is a high-capacity spray gun with a variety of air caps and fluid tips to accommodate a variety of purposes. It should be used generally whenever the air supply is sufficient to support it. With certain air caps on continuous, high production it may take as much as 20 cubic feet per minute. Operating in average intermittent jobs where the spraying is not continuous and the gun is triggered as it should be, one of these guns may be expected to consume about 10 cubic feet per minute. A compressor producing 100 pounds of pressure will suffice to operate one or more such guns, depending upon the volume of air produced.

To understand the flexibility a variety of air caps and tips give to a spray gun, let us look briefly at their function and incidentally at the basic principle of the spray gun—the proper balancing of air to fluid.

Fluid is metered into the air stream through the fluid tip. The factors determining how much fluid is pushed out are the size of the orifice in the fluid tip, the type of the material itself and its viscosity, the air pressure and volume exerted upon it, and the degree to which the fluid needle is withdrawn to permit passage of the material.

A given amount of material requires a certain amount of air to atomize it. The character and volume of the atomizing air stream are determined by the air cap, its type, the number of holes in it, and their size. Particular air caps are built to pass a volume of air adequate to atomizing the volume of material a given nozzle will pass. This volume of air is adjusted in the spray gun to conform not only to the size of the fluid tip but also to the other variables previously mentioned as influencing the fluid flow.

This relationship of air to fluid is a vital principle in spraying. When the balance is right, the spraying is perfect. When the balance is off, however, it can usually be adjusted easily by rearranging the variables we have mentioned. The first fundamental variable is the choice of air cap and fluid tip. This depends largely upon the material being used and the amount of air available. Once this choice is established according to the manufacturer's recommendation, the refinement of the air-fluid balance can be reached by adjusting one or more of the remaining variables affecting this relationship.

One of these variables can affect the fluid flow. Changing the viscosity or fluidity of the material tends to make it feed faster or slower, especially where suction feed is used. In few cases only would one want to go to this extreme. It is important that the operator follow the paint manufacturer's recommendations both as to the type of solvent used and its proportion in the spraying material. To change a recommended viscosity merely to make it more sprayable is to invite trouble. Balancing the air-fluid equation is more easily achieved by other means.

One of these is the use of the fluid-adjusting screw on the spray gun to restrict the flow of fluid in relationship to the air being used. There are two other more practical ways of achieving the perfect balance, but restricting fluid flow can be used when the others are not sufficient. The reason we prefer not to use it is that restricting with the fluid needle screw puts a tension on the fluid needle and a drag on the trigger with each pull. This tends to discourage triggering the gun or feathering the stroke in a prolonged operation; besides, restricting the fluid flow is probably not the answer to the balancing result unless we want to slow up the operation.

It may be more desirable simply to distribute further the fluid being atomized. This can be effected with the spreader or pattern adjustment on the spray gun. Its purpose is to allow air out of the horn holes on the outside of the cap to flatten the originally round pattern so that more area is covered by the longer shape. This addition of air and area to the same fluid flow is, practically speaking, the equivalent of reducing the fluid factor in the equation.

The last of the variables mentioned, and the one which is most practical and therefore most often used, is the simple adjustment of more or less air to the formula. When a pressure feed tank is used, this actually means that two independent adjustments are possible: (1) the air pressure on paint in the tank can be adjusted so as to deliver more or less fluid to the gun; (2) the atomization air supply to the gun can be increased or decreased while the fluid pressure is kept constant if desired. In this manner perfect balance of air to fluid can be quickly and surely obtained.

Using the suction-feed gun, however, we do not have this independent control of air and fluid, as with the pressure feed tank above; rather, the single air supply not only feeds fluid to the gun but also atomizes the material at the same time. Thus to a degree it is self-adjusting. Nevertheless, it is still an important variable in arriving at the perfect balance we have been pursuing.

A word of warning in closing this discussion of air-fluid balance in spraying: perfect atomization is not the only objective of perfect alignment of these two factors. There is also the matter of getting a uniformly dense pattern of the proper shape. Too much fluid concentration may give a heavy-centered pattern, and too much air concentration may give a split pattern. Again, adjustment of the variables just discussed is necessary. Other defects of the pattern may be caused by dirt in the tip or cap. Proper preventive straining of material and cleaning of hoses and spraying equipment will largely eliminate this bother.

Most guns have a variety of caps and tips to handle a considerable range of materials; the limiting factor is very often the amount of air available. Spray-gun manufacturers make a number of guns designed to handle the spraying needs of almost any material, with outfits from ¼ horsepower up to those capable of powering production-type spray guns.

The subject of air production by the compressor is vital to spraying operations. The spray gun is air-powered, and generally it is impractical and uneconomical for the operator to have to wait for air. Therefore, in choosing an air compressor, it is necessary to select one with ample volume (cubic feet per minute) as well as ample pressure (pounds per square inch). It is wise to cover the needs of all air tools when selecting an air compressor and to make allowance for emergencies as well as for any future increases in air tool usages which may be likely.

In making these provisions for air supply, we must know the actual delivery of air volume of a compressor as well as its top pressure capacity. Displacement of air is the theoretical output of the compressor. Delivery is the actual output and is always lower than the displacement. The difference lies in the mechanical efficiency of the unit and its loss of power in leakage and heat.

In spraying operations the air transformer is an indispensable requisite to good finishing. It filters out impurities and dirt, condenses moisture, and provides a steady, uniform flow of regulated air to the spray gun. To eliminate the human error of forgetting to drain them daily, it is possible to attach an automatic drain to this valuable air control.

Other considerations in setting up efficient spraying operations are those of proper conduction of air and fluid to the spray gun. Internal diameter and length of hoses restrict the flow of air within them. Consequently air hose which is too small in diameter for its length will tend to starve the spray gun or take an abnormal amount of pressure to feed the gun. Correct sizes are necessary to feed the spray gun properly. Air hose to the spray gun is seldom less than 5/16 inch internal diameter; air hose from compressor to pressure feed tank generally is 7/16 inch.

Galvanized pipe lines are desirable where air operations are permanently established. Air lines are seldom too large but are often too small. One-half inch pipe can be used for main air line that does not exceed 50 feet, for a single operator. If more than one operator is used on the same air line, the piping should be increased to 3/4 inch. It should be slanted toward a drain leg to allow moisture to be run off. All take-offs should be from the top of the main line to avoid moisture which may accumulate at the base of the line.

While a number of variables and common errors in spray painting have been discussed, there is no implication that spray operations are complicated or full of pitfalls. It is true that mechanical painting is not simply a matter of turning on the air and spraying. The average operator might "get by" with such a procedure, but this is a pretty poor procedure in any line of work. In the old days brush painters used to serve years of apprentice training before they were ready. Today with excellent spraying equipment at his disposal, the spray operator does not need a wealth of background, though it always helps. He does need some mechanical training in his equipment, however, and he should be acquainted with the bare fundamentals that any painter is required to know, regardless of the type of application; that is, the nature of his materials and their proper uses. He should certainly know the value of superior materials and must realize that he needs to follow the manufacturer's mixing recommendations in order to get excellent results. Besides these important material fundamentals, which any smart operator can learn to get right and keep constant, there are human deviations which, however simple, are neglected again and again. These are the basic rules of spraying technique.

Perhaps the most important of them all is the simple rule of holding the gun the proper distance from the work. It is estimated that this one essential alone is responsible for 85 per cent of the quality of the job. Spray guns are designed to be held six to eight inches from the work for ordinary work. In the process of spraying, solids are atomized and solvents are vaporized. This optimum distance is calculated to permit the maximum effect in both, with the proper amount of thinner losses between the spray gun and the work. Actually, the operator should hold the gun not six *and* eight inches from the work, but one or the other, depending upon the pattern and the speed of material flow he happens to be getting on his particular job. Then he should keep this distance constant for uniform results.

Another simple technique, which can save organizations much money in the course of a spraying period, is the proper stroking of the gun. It is perhaps natural for an uninitiated operator to wave the gun as he sprays. This arcing the gun turns it directly off the target, especially at the ends of the stroke. Naturally, arcing the gun on a surface causes overspray to bounce obliquely off the surface; and when the gun is pointed directly at the surface (at the middle of the stroke), a heavier film will be deposited than at the end of the stroke when the gun is arced.

To correct this bad habit, with its excessive misting and contamination of nearby work as well as uneven film build and waste of material, the gun must be held at right angles to the work and move in a line equidistant from and parallel to the work. This can be done by flexing the wrists at the ends of the stroke rather than waving the gun. In Figure 94 the right and the wrong ways of making the stroke are shown.

Another point of technique which helps the operator to get a full, wet and uniform coat is overlapping. This means that he will overlap each stroke 50 per cent by directing the middle of his spray (merely aiming his gun) at the bottom of the preceding stroke. In effect he is applying two coats in shingle fashion, laying each new one half way over the just completed pass.

One of the problems in keeping the finish coat continuously smooth is

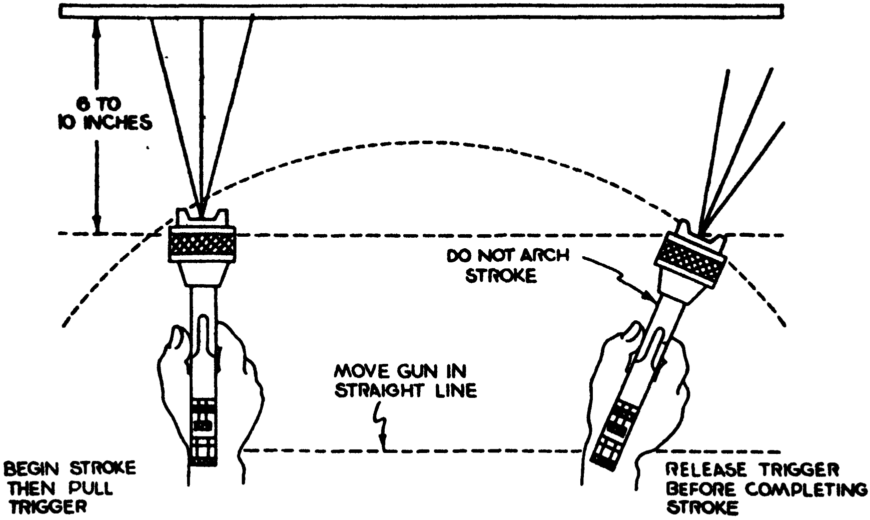

FIGURE 94. Proper method of making a spray gun stroke.

joining, or connecting adjacent areas in an unbroken, even film build without trace of lateral lapping. This can be accomplished by simply feathering each stroke of the gun. To do this the operator must pull the trigger just before he commences his stroke and release it just before he stops his stroke. This means that the gun will always be in motion when the trigger is pulled and that the ends of the stroke will be graduated in such a fashion that they can be joined without abruptness.

ELECTROSTATIC COATING PROCESSES

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Among the important developments in production painting and coating is the use of an electrostatic field to secure maximum efficiency in the deposition of the coating material through the electrostatic spray process, and of its companion process, electrostatic detearing, which removes objectionable accumulated excess material resulting from dipping or flowcoating. Both of these Ransburg processes accomplish their purposes by use of the well known electrical principle that like electrical charges repel and unlike charges attract.

Electrostatic Spraying

In applying electrostatic spraying methods the exact nature of the application will vary, depending upon the piece or item being coated. In general the part is hung from or supported by a conveyor and is carried while thus supported into the spray booth or spray zone. In the spray zone the objects are surrounded by an electrostatic field maintained by a suitable source connected between the item and a set of electrodes appropriately positioned along the conveyor. Coating material atomized into this field by automatic guns becomes ionized to the same polarity as the electrodes and is attracted to the object under the action of the field. The object thus gradually collects its full coating over some four feet as it moves along the conveyor between the electrodes. The way in which the coating material is efficiently utilized is shown in Figure 95. That material not attracted to and deposited upon one object becomes coating material for those which follow. The small amount of coating which escapes this extended precipitating force, together with the evaporating solvent fumes, is exhausted in the usual manner. The object, after receiving its coating, is carried from the spray zone to adequate drying or baking facilities.

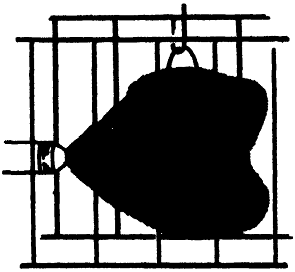

FIGURE 95. Principle of electrostatic spraying.

Figure 96, selected for its clarity in showing the gradual deposition of paint on the work, is a photograph of an electrostatic spraying installation being used to paint water-heater parts. In this application the parts are loaded on an overhead conveyor and are carried into the spray booth from one side. Once in the booth, the conveyor turns and advances centrally through it. In this region the object is surrounded by the electrostatic field and the appropriate electrodes are clearly visible at either side. In this application two guns, one on either side, are used to atomize and distribute the coating material into the field. Once coated, the objects are removed from the conveyor and placed on an oven conveyor to have the finish baked.

In this particular installation the objects are supported from overhead and are rotated as they pass through the field. A spindle, belt, or other type of conveyor may be used with this process, depending on the user's desires and on the object. Rotation or non-rotation of the object likewise is determined by its size and shape. Radio tubes, auto air filters, water-heater jackets, electric motors, chairs, light fixtures, bathroom-scale housings, water pumps, stoker parts, some space heaters, and cylindrical containers of all types are rotated because their external symmetry permits of such motion; increased efficiency of application is obtained by combining the advantages of mechanical rotation with those of electrostatic spray. Such objects as flat sheet stock, corrugated panels, cabinet panels (assembled or unassembled), pipe of small diameter, venetian blind slats, and structural steel members can be coated either overall or on one side only without rotation. They present to the field and the atomizers a flat,

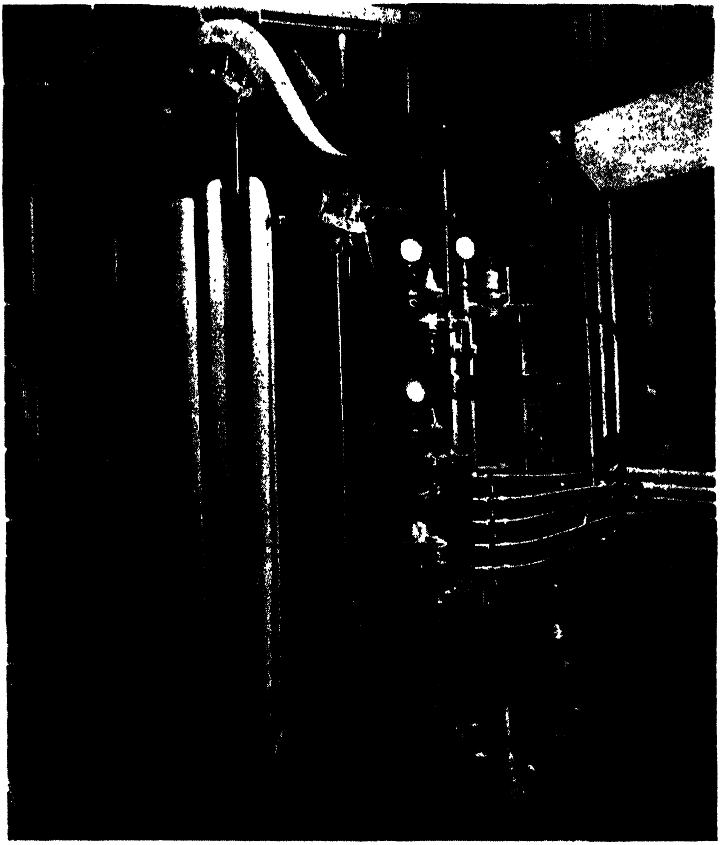

FIGURE 96. Electrostatic spray. Paint mileage was almost tripled on these water heater jackets and frames with electrostatic spray.

extended surface which appears continuous as the separate parts are moved along the conveyor.

Still other very irregularly shaped articles which are normally not visualized as possibilities for automatic spray can be coated by this method because of the extended region over which coating material is being attracted to the items.

Automobile lift jacks, air cleaners, steering wheels, mouldings, and mufflers, as well as electric motor castings, washing machine parts and metal furniture are illustrative of such parts. They may or may not be rotated, as the individual case demands.

The electrode structure used in conjunction with electrostatic spray comprises a rigid frame mounted adjacent to the path of travel of the conveyor and spaced at about 12 inches from the surfaces being coated. Small wires (about B & S #30) are supported across the face of the electrode frame on the sides opposite the surfaces being coated. In Figure 96, for example, these wires are on the sides of the electrode frame, while others may have electrodes overhead or below. This complete electrode assembly is mounted on insulators so that it has at least 18 inches clearance to the nearest grounded part other than the parts being painted and is connected to the voltage source, which charges it to a high static voltage. When held at this voltage the small wire elements become ionizing agents which impart an electrical charge to each of the isolated paint particles. The wires simultaneously establish the field of force under the action of which these charged particles are attracted to the work.

The voltage source which maintains the necessary field is a completely oil-immersed rectifying unit capable of converting the normal 220-volt, 60-cycle, alternating current into the desired rectified voltage of approximately 100,000 volts. Designed into this unit are features which insure that the current delivered at this voltage cannot exceed a safe value. When the output of this unit is shorted through low resistance the current will not exceed .010 ampere. Under normal operation the power consumption of this unit is comparable to a 1000-watt lamp. Being constructed without moving parts, the unit requires little maintenance. Occasional replacement of tubes is the only attention normally required.

The atomizing agents are basically the standard type of automatic gun. Special fluid tips and air caps must be selected from those produced by manufacturers because the material must be broken up at lower air pressures than those used in high-pressure spray. It is the purpose of these agents to atomize the material and distribute it into the field with a minimum mechanical velocity so that the field can accomplish the precipitation. Where it is of advantage to do so, the atomizers are oscillated back and forth over a distance of several inches during the spraying operation.

This oscillation aids in the distribution of the coating material in the field and destroys the mechanical pattern produced by the individual guns on the work. In this manner more uniform coats of material are assured. Atomizing pressures are usually of the order of 15 to 20 psi. Fluid pressure is likewise reduced below that normally used in standard spraying. Three to four pounds fluid pressure is normal for electrostatic spraying with the usual atomizers.

Because the value of these pressures is important to the successful operation of the equipment, they are carefully controlled by pressure gauges provided with other Ransburg equipment. Complete operation of the equipment (including starting and stopping the guns, regulating all pressures and turning the field off and on) can be carried on from one position.

As is the case with any automatic equipment, complete correlation must be established between all related factors before electrostatic spraying proceeds successfully to produce a well coated article. Fluid and atomizing pressure must be carefully correlated with conveyor speed and film requirements. The atomizing agents must distribute the coating material into the field as uniformly as possible. The particle size of the atomized material must be reasonably fine to assure that the field will effectively act upon it. This latter feature is regulated in production by controlling the fluid pressures, solvent balance and viscosity. Since in this method of spray application a somewhat longer time elapses between atomization and precipitation of the material on the surface of the part than elapses under high-pressure methods, it is necessary to readjust the solvent balance in the coating material to make it satisfactory for this type of application. This adjustment is usually directed toward making the material "slower." Since this adjustment is only necessary because the material is in the air longer and the solvents consequently have a longer time in which to evaporate, the material precipitated onto the part is in the same condition as it is when applied by high-pressure methods. Because of this, normal baking or air dry cycles are applicable.

All types of materials are applicable by this method so long as they can be atomized at the lower atomizing pressures used and can be adjusted in solvent balance so that a satisfactorily wet film can be precipitated. Synthetic enamels, cellulose lacquers, aqueous suspensions, wrinkle and splatter finishes, oils, and some chlorinated-rubber adhesives have been successfully applied.

The material of which the part is made is of importance in determining the suitability of electrostatic spraying. The process is applicable to all parts made of electrically conducting material and is not limited to materials which are magnetic. The process can be used, therefore, on aluminum, brass and copper as well as on iron and steel parts. Objects made of non-conducting material, such as "Bakelite," porcelain, hard rubber, and wood, require special consideration. Ceramic flower pots and wood drapery hardware are listed among the applications, but such items must be handled in a special manner and should best be considered as individual cases. On items made of such materials some arrangement must be made so that the part becomes a collecting electrode for the sprayed material. Flower pots, for example, can be inverted over a conical metallic fixture and flat sheets of acoustical tile or other insulating material can be laid upon a conducting metal-mesh belt in order to create the necessary precipitating field over the surface to be coated.

Uniform flat surfaces or uniform surfaces which can be rotated offer no difficulty for the electrostatic spray method, and the film obtained on this type of object is generally more uniform than that resulting from high-pressure methods. On other objects the uniformity of coating which can be obtained is largely dependent upon the contour of the part. Since the field is responsible for the precipitation, the coating tends to be lightest where the field is weakest and heavy where the field is strong. For this reason protruding sections are favored over recessed surfaces; at the present stage of development the internal coating of comparatively closed openings is practically impossible. On some objects possessing this character the shielded or recessed sections can be satisfactorily coated by aptly directing the atomizers so that such sections will be mechanically covered by direct spray from the atomizers, while the overspray from such guns is applied to other parts of the object by the precipitating action of the electrostatic field. Such objects must be tried before actual results can be predicted or applicability of the method determined.

The electrostatic spraying method has as its major advantage the highly efficient application of coating material in a fully automatic manner. As a consequence, the application of the method affords easier quality control and sizable savings in material and labor. In addition to these features, the method often makes it possible to spray automatically objects which high-pressure automatic spray cannot normally handle with efficiency.

The exact savings which will result from the adoption of this method will vary from one application to another, since the replaced method may or may not be efficient and the item involved may or may not be one which presents a large range of saving possibility. On small incidental parts where ordinary methods are necessarily very inefficient, large savings can be expected. On large flat sheets or similar areas where hand or automatic high-pressure spraying is somewhat more efficient, savings generally are still substantial, although correspondingly less. In general, considering all these variations, the adoption of electrostatic spraying will result in a material savings corresponding to between 40 and 60 per cent of the material used with other available methods. Specifically, it is being used to finish metal radio tubes with a paint saving of 62 per cent over high-pressure automatic methods. Stove hardware and similar parts are finished electrostatically at twice the number of parts per gallon of material. Five-gallon containers are being finished at a saving of approximately 60 per cent, as compared with a previously used hand-spray method. Curtain rods are being coated five times as fast and at a 75 per cent paint saving. Twice as many electric lamp parts are obtained per gallon of coating material; and hydraulic automobile jacks are externally coated with an improved finish with 50 per cent paint saving over previous hand methods. Cabinets are painted with a 45 per cent saving; oil-burner bases with one-third the paint; and water-heater jackets with only half.

FIGURE 97. Garnish moldings are another item which could be automatically sprayed in no other way. Tremendous production savings result.

In addition to such paint saving, this method in many cases permits considerable economy in labor. In the particular case of automobile jacks, automatic highly efficient finishing at increased speed was made possible on a product which normally could not have been finished automatically by other methods without an extremely complicated mechanical apparatus. In this case, in addition to the paint saving, the method afforded considerable labor saving. One man is coating two and a half times as many jacks per hour as he could previously coat by hand methods. By making possible the automatic finishing of automobile window moldings in the plant of a large mid-western producer (Figure 97), this method allows a single operator to coat twelve times his previous hand spray production.

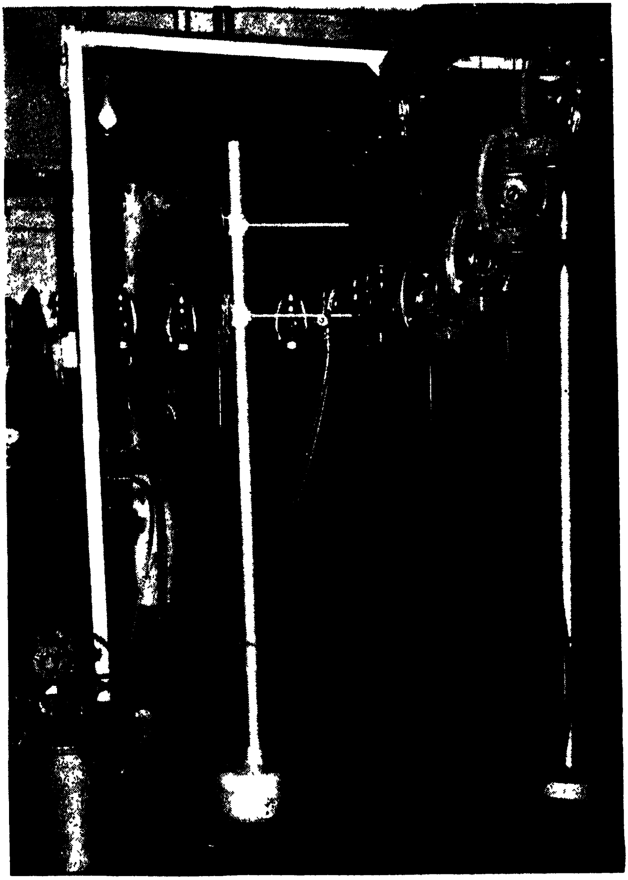

FIGURE 98. Many-faced lanterns are automatically sprayed, with substantial savings.

Figures 97, 98, 99 and 100 show items that are electrostatically sprayed with a great saving of both paint and labor.

Similar savings are reported on other objects. Such savings make this method a highly desirable one in any instance where volume and rate of production justify the consideration of an automatic finishing method.

Electrostatic Detearing

Electrostatic detearing offers to industry an automatic method of freeing an item which has been coated by the normal dip or flow-coat method of the excess accumulation of material which would otherwise remain on the drain points of such items. The general method is shown in Figure 101. In this way it extends the well known advantages of these methods of coating to many users who heretofore were forced to abandon these methods in favor of more costly processes. Either the presence of the fatty edges or tears has resulted in a finish which was below the quality required, or their removal by hand has introduced so much additional labor that it became more expedient to use some other method. Now electrostatic detearing accomplishes this removal in a fully automatic manner.

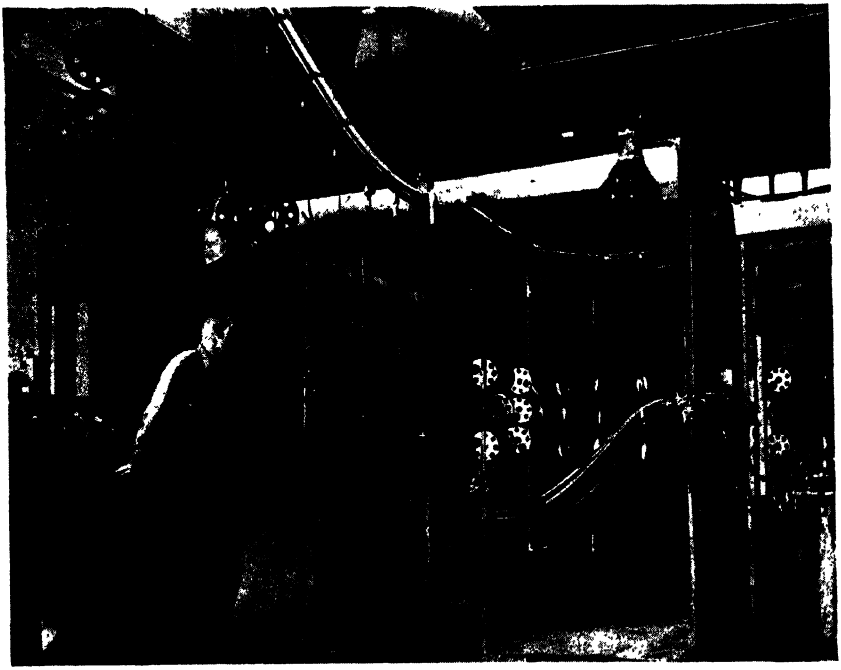

FIGURE 99. Small objects can be sprayed with a minimum of paint loss and with a large saving in labor cost.

In this process, the article supported from a grounded conveyor is dipped or flow-coated in any suitable manner. It is then carried by the conveyor from the dip tank over the usual drain board which catches and returns to the tank the principal excess material. When flow has substantially ceased and only the tears or fatty edges at the drain-off points are in a highly fluid condition, the article passes over or adjacent to an insulated conducting grid to which a static high voltage can be applied. The presence of this charged grid causes a strongly attractive electrical force to be exerted upon the grounded piece. This force is particularly strong at points or prominences where drain-off is likely to occur. Due to this attraction the excess paint which has collected at the drain-off points or edges will be removed from the piece and a smooth coating remains. The part can then be carried into the oven to be cured to a continuous excess-free finish.

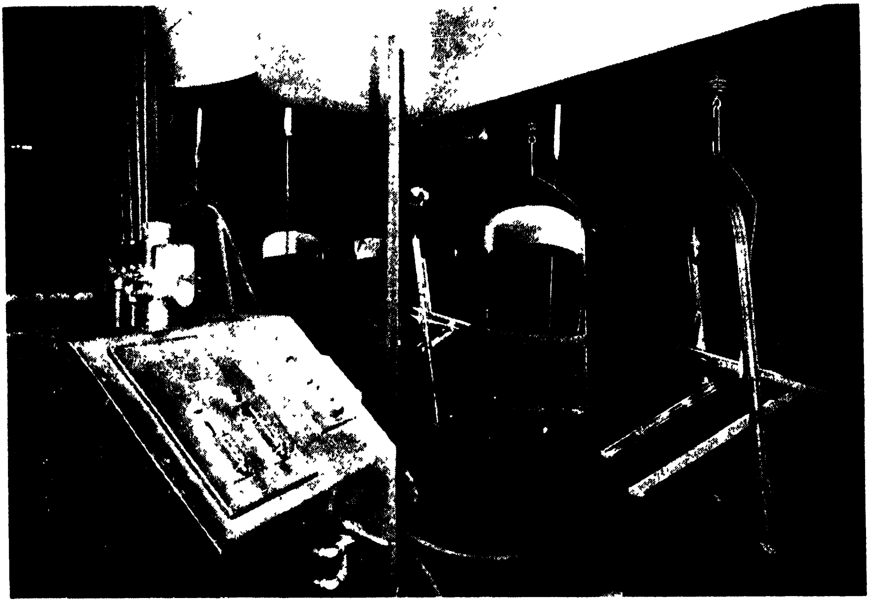

FIGURE 100. Folding chairs electrostatically sprayed. On this "wide-open" product, the paint bill was cut 50 per cent and the labor cost reduced to one-fourth.

Figure 102 is a view of a unit used for dipping and detearing refrigerator shelves. The conveyor carries the parts through a dip tank and over a drain board. After this drain period they are carried over the detearing grid, which is visible at the right of the picture. They then rise to the ceiling to the overhead oven. The parts in this application receive two coats of material, so two conveyor lines are shown in this view. The voltage source and its connection to the grids is also evident in the lower left of the picture.

Although it is normally recommended that the grids be ventilated by direct pressure or exhaust ducts located specifically for this purpose, in this particular application complete ventilation of the area is insured by having the entire operation in a dirt-free room supplied with adequate air movement. The exhaust outlets for this ventilation are visible in the ceiling above the grids. When dipping and detearing operations are carried out in spaces where such an enclosed area is not feasible, equivalent ventilation hoods are recommended to free the area of the large accumulation of solvent vapors normally accompanying such dip operations and to pass fresh air upward through the grids. The shelves coated in this way are free of tears and excess material despite their complexity.

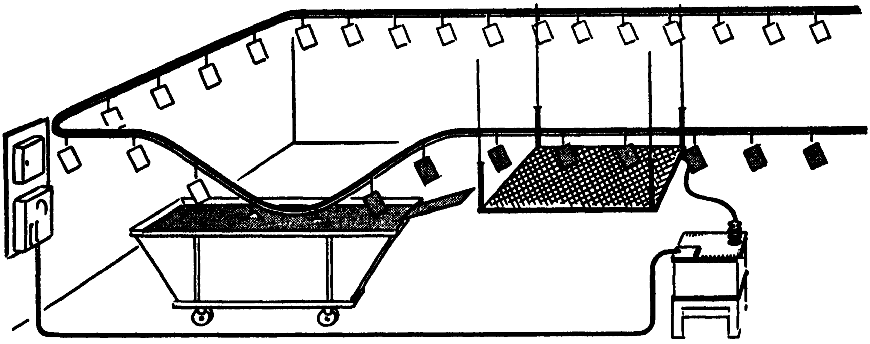

FIGURE 101. Electrostatic detearing.

This method uses a voltage supply which is structurally very similar to the one used for electrostatic spraying, except that it produces voltages which are slightly lower at correspondingly lower currents. It possesses the same over-controlled features and is limited in current output on direct short circuit to 5 milliamperes. All its controls are assembled into a self-contained control panel arranged for convenient wall mounting.

The electrodes used with this process are made from any suitable electrically conducting material and they are designed for the particular application involved, due consideration being given to the conveyor speed and type of article being treated. It is essential that each "drain-off" point from which excess material is to be removed is exposed to the electrode. Any portion of the article which is electrically shielded from the field will be less effectively "deteared" in proportion to the degree to which it is shielded.

Although the distance between the electrode and the article being deteared is held fairly constant at 8 inches because of the voltage used, the other factors involved demand a certain degree of correlation before optimum results can be obtained. Basically, the object must be of such construction that it can be dipped to obtain a satisfactory coating with the exception of tears or excess material at the drain-off points. The coating material used must also fulfill coverage and finish requirements. It then remains only to correlate the conveyor speed, the distance between dip tank and detearing electrode, and the length of the electrode itself in such a manner that the parts arrive over the grid when only the last drip remains and leave it in a tear-free condition without the possibility of subsequent reflow taking place. Although for any particular application the distance between the dip tank and the grid will depend upon the drain time and thus naturally upon the length of the item, it is seldom that this period will require in excess of five minutes. For small items it will be as short as one-half minute.

FIGURE 102. Electrostatic detearing used on refrigerator shelves.

The correlation of these factors, although they must be taken into account, places little restriction upon the flexibility of the method because of the broad limits permitted in their control. The process is applicable to all types of coating materials which lend themselves to the dipping process, except certain water-soluble materials and certain waxes. Materials which cannot be made to give a satisfactory reaction are the exception rather than the rule, and cases of doubtful applicability must be tried before a definite decision can be made.

Objects made of a wide variety of materials can likewise be treated. Those made of metallic or electrically conducting materials can be handled if their shape is such as to make dipping applicable. Pottery, wood, and plastic products can be deteared, but they deserve special consideration. Whether such objects can be deteared depends upon whether or not a field can be established at the detearing point. In many cases this can be decided only by trial and therefore such items should be carefully considered before they are ruled out of the group of applicable cases.

There are two limitations confronting the method. One is obviously encountered when the coating material is sufficiently thermoplastic to cause harmful reflow in the baking process after the object has left the detearing grid. The other limitation is encountered on those objects whose drain-off points are surfaces of relatively large radii. The process will only partially remove material from such surfaces. It is therefore essential, in order to enjoy the maximum benefits of the method, that the article be hung in such a manner that the drain-off material accumulates on edges or corners which do not exceed one-quarter of an inch in radius.

The process is being, or has been, used in the coating of all manner of wire goods, metal die-cast and formed toys, padlock bodies, automobile head lamps, metal stools, rectifier units, small machine parts, hand tools, wooden blind parts, wooden drapery fixtures, and many other items of which these are but a representative sampling. In most applications labor has been saved and the coating quality improved. In some cases dipping, as made possible by the detearing operation, has saved the coating material which would have been used by other less efficient methods.

Both the electrostatic spray method and the electrostatic detearing method are daily finding new and unique application in the finishing field. The wide range of materials and objects to which they are applicable, their low maintenance and operating costs, their increased efficiencies over other available methods, and the improved and repetitive character of the coating which they make possible render them suited to any highly repetitive production.

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Chapter 27

Resin and Varnish Making Equipment

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The Patterson Foundry & Machine Co., East Liverpool, Ohio

This chapter contains pertinent suggestions for the selection of equipment for a modern synthesizing plant. In the selection of the equipment for such a plant, the governing factor should be its versatility and adaptability to the preparation of a wide variety of products.

This is possible in a system of modern design which may be heated, and cooled as well, making it ideal for synthesizing, polymerization and reaction processes. With such a system the preparation of synthetic resins, plastics, adhesives, varnishes, various chemical compounds, numerous types of food products, etc., is most expeditiously and economically carried out. Oil-bodying, refining, processing, distillation and other reactions may be carried on in a unit of this type; therefore, practically any organic or inorganic product may be prepared in these modern plants on a production basis and at the lowest possible production cost.

While any one of several different types of reaction vessels may be embodied in the complete synthesizing system, care must be exercised to select the type best adapted to local conditions and, to some extent, to the product to be manufactured. The type of metal from which the reaction vessel is to be made should also receive careful attention. Stainless steel is the widely accepted standard material, but plain steel, as well as alloys of various types, are used for many processes.

The modern producer has a choice of three general types of synthesizing plants in which relatively high processing temperatures are required. We shall discuss first the direct-fired reaction vessel, next, the electrically heated kettle for temperatures ranging up to 600 to 700°F, and then the jacketed kettle using the modern eutectic mixture known to the trade as "Dowtherm A."

The economics of any of the above types are somewhat dependent upon the locale in which the equipment is to be installed. In a natural gas area, fuel of this type will be the most economical; the same will apply in an area where electricity is relatively cheap; and of course oil-burning equipment is best in an area close to fuel-oil supplies. Economy of operation is not always dependent upon the cheapest fuel, but must also be related to the other functions required of the equipment being operated.

It is the purpose of this discussion to consider impartially the relative merits and adaptability of the different systems in order that the user may be better able to select the system which he considers best adapted to his particular needs.

Let us first consider the economics of the different types of fuel by comparing the B.T.U. value available from them. The usual fuel oil has a value of approximately 110,000 to 115,000 B.T.U. per gallon.

Natural gas is usually rated from 1050 to 1100 B.T.U. per cubic foot and artificial gas ranges from 350 to 550 B.T.U. per cubic foot. Electricity has a value of 3415 B.T.U. per kilowatt hour. Efficiency in the use of any of these fuels depends to a very great extent upon the type of user to which it is adapted, the degree of insulation provided and the type of equipment used in burning the fuel.

To make an exact comparison of the relative fuel costs per gallon of material produced would usually result in the determination that natural gas is the most economical, fuel oil second, artificial gas third, and electricity fourth. However, to make this determination, it would be advisable to discuss these problems with local utility services to determine the best earned rate, predicated upon the experience of the supplier of the equipment.

Direct-fired Synthesizing and Processing System

Let us first consider the direct-fired kettle for general process work, including synthesizing, polymerization, preparation of synthetics, plastics, adhesives, varnish, oil-bodying and refining (Figure 103). These kettles are supplied in sizes of 500, 1000, 1500, 2000 and 2500 gallons. The type of fuel usually used is either gas or fuel oil. The gas may be either natural or artificial, depending upon the locality. There are many different types of equipment for the burning of gas, but perhaps the most efficient for this service is the radiant type burner.

The first thing to consider is the design of the furnace in which the kettle is to be mounted. This usually consists of an outer or supporting wall, with an inner lining of high-temperature insulating fire brick. The kettle is usually constructed of stainless steel, Alloy 347 or 321 A.I.S.I., which are the stabilized types of stainless steel. The shell is directly exposed to the flame and is usually baffled in order to give a circuitous path to the gases to increase the overall efficiency. The agitator and other auxiliary equipment are common to all types of plants and will be discussed later.

The disadvantages of direct-fired units can be compared to those found with ordinary varnish and similar kettles, as there is usually considerable difficulty in keeping the bottom free of carbonization, due to the extreme amount of heat applied to a relatively small area. This often causes the bottom to warp and fail owing to these excessive stresses.

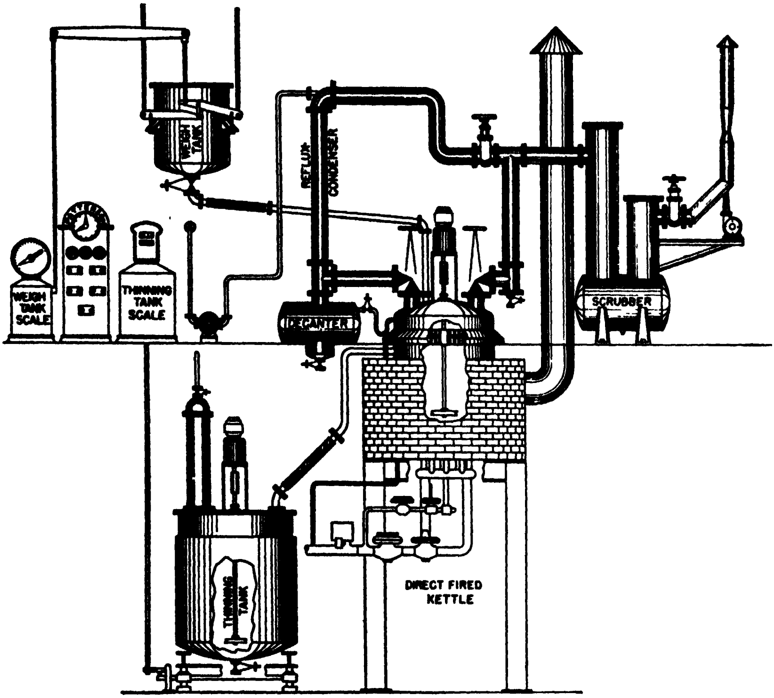


FIGURE 103. Patterson direct-fired synthesizing and processing system.

The only adequate cooling arrangements are by the circulation of cold air through the furnace interior, which of course has a deleterious effect on the lining; as an alternate, quite often internal coils are provided through which cold water is circulated to remove the heat rapidly. However, these coils are subjected to considerable thermal shock, and unless very specially designed, they require rather frequent replacement. They also interfere with the cleaning of the kettle, as it is desirable to have the surface kept clean to prevent scorching of the product or buckling of the shell.

The rate of heat-up with this type of kettle is usually 2.5 to 2.7 degrees per minute. Later mention will be made of improvements in the speed of heating. In case of exothermic reactions, this type of kettle is rather hard to control, as the heat stored in the lining usually causes a carry-over, and it is not always possible to get sufficient cold air through the furnace or sufficient water through the cooling coil to control it before spilling has occurred.

There is another type of direct-fired unit, often referred to as the Dutch-oven type, where the products of combustion are not carried directly to the kettle walls, but are used to heat air which is circulated in contact with the walls of the kettle. However, this indirect method is so inefficient in its operation that only a relatively few installations have been made, and it is not considered a practical approach to the problem.

In the use of fuel oil, the refractory walls required for the proper burning of the fuel usually have a higher heat capacity than those used with gas, and therefore the problem of accurate control of kettle temperatures is more difficult, as usually the heat capacity is so great as to cause an over-run of temperature.

In all direct-fired units the problem of discharge of the finished product is usually complicated, because to discharge through the bottom involves special valving arrangements, and considerable trouble is encountered in protecting the discharge pipe. The preferred method is to employ an evacuating pipe by the use of pressure inside the vessel, forcing the liquid out through a top connection. The disadvantage of this method is that the entire contents of the vessel cannot be discharged, as usually considerable liquid remains in the bottom, at least as high as the top of the discharge pipe opening.

Electrically Heated Synthesizing and Processing System

Let us now consider the electrically heated kettles that have been in general use. The first type of unit was designed to use strip heaters, which are bent to the curvature of the vessel, with pie-type sections on the bottom and strip heaters arranged circumferentially on the shell. The pie-shaped elements and the strips are held in place by shoes, which permit the element to expand as its temperature increases. These elements are usually furnished in either the 700° or 1200° maximum sheath temperature. The 700° elements are satisfactory only for the very low temperatures. As these types of elements are not in close enough proximity to give good conduction, they have to depend considerably upon radiation to attain their heating value. These elements have a tendency to work away from the shell, and as they grow older their efficiency materially decreases. The maximum recommended voltage is 230 to 250 volts, although they have been used on 440 to 480 circuits.

As an alternate to this method of electric heating, there is the immersion type of element, which has been used in rather limited numbers, particularly where the amount of heat required was of any magnitude, the disadvantage being a high concentration of heat in each element, creating a tendency toward carbonization and destroying the color of the product.

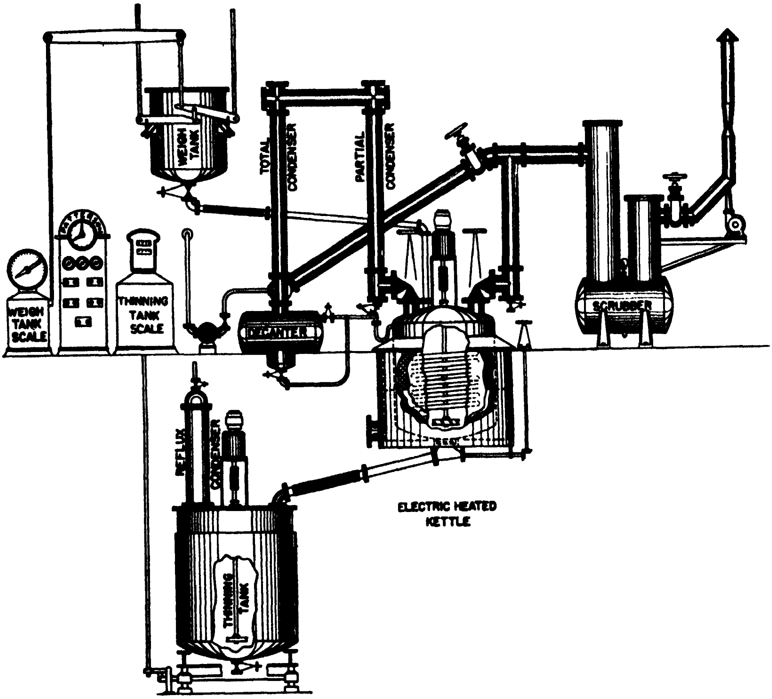


FIGURE 104. Patterson electrically heated synthesizing and processing system.

A new type of element called "Flasheat" has been developed; it operates on an entirely different principle. The heating elements are of relatively low heat capacity (that is, stored heat in insulation). They have been successfully used for very rapid heat-ups and have been developed to the point where the efficiency is 15 to 20 per cent better than any other type of electric heat application to kettle construction. Figure 104 shows an electrically heated synthesizing and processing system.

The disadvantage of this type of electric heating is in the cost of construction and, again, it is recommended or preferred that it be used on 230 volts rather than on 460 volts. It has the distinct advantage that the heating elements can be changed without removal of the insulating jacket, being readily accessible through sectional doors. All electric kettles have the advantage of combining the heater and user sections in one piece of equipment, with the exception of the controls, which occupy relatively small space and are usually placed in an external room.

The control of the kettle in cooling, particularly during an exothermic reaction, is rather difficult inasmuch as again circulation of cold air over the heating elements, or the use of a cooling coil inside the vessel, is required. Cleaning over and around the coil is rather tedious.

"Dowtherm" or Other Fluid or Vapor-Heated Synthesizing and Processing System

Let us now consider the fluid or vapor-heated system. We shall first enumerate the essential equipment required to make a Dowtherm System the equivalent of that which we have outlined for the direct-fired and electrically heated units. A typical unit of this kind is shown in Figure 105.

The "Dowtherm" vaporizer or heat generator is usually selected to fit each individual kettle, although a central "Dowtherm" vaporizer or heater is sometimes used, to which many users may be connected. However, we shall consider at this time the one that directly compares with the direct-fired and the electrically heated vessels.

Usually for a 1,000-gallon vessel a 1,000,000 B.T.U vaporizer or heat generator is selected. The vaporizer or generator may be oil-fired, gas-fired or electrically heated; it is designed for a working pressure of at least 90 psi and is constructed in accordance with the A.S.M.E. Code for fired pressure vessels. It very much resembles a steam generator or boiler, but has special construction features which make it more readily adaptable for liquid heating or "Dowtherm" vaporization. The unit is equipped with liquid level gauge glasses, liquid level controller, off-on type burner control, all required safety devices such as low liquid cut-off, over-pressure control, "Protect-o-glo" and necessary pressure relief valves which are vented to the atmosphere. The "Dowtherm" or other liquid is maintained between predetermined levels in the vaporizer; the advantage of using this heating medium is that it can be raised to a relatively high temperature of approximately 725°F at 125 lbs pressure per sq in P.S.I. absolute. The boiling point of "Dowtherm" is 500°F at atmospheric pressure, which is considerably higher than that in an ordinary steam boiler.

The usual heating processes for the higher temperatures are in the vapor phase and usually the maximum temperature of the "Dowtherm" is 600°F at 43 psi.

The user, or kettle, is generally constructed of either 347 or 321 A.I.S.I. stabilized stainless steel. The usual arrangement is to jacket the bottom and 25 per cent up on the side as one section, and then an additional 25 per cent jacket adjacent as the second section to cover approximately 50 per cent of the volume of the kettle. By the use of this two-zone jacket, it is possible to process half batches if required. The necessary valves are provided to isolate these separate sections. It is possible with this unit to attain heat-up rates up to 3.2°F per minute, which is approximately ½° per minute faster than in the direct-fired unit.

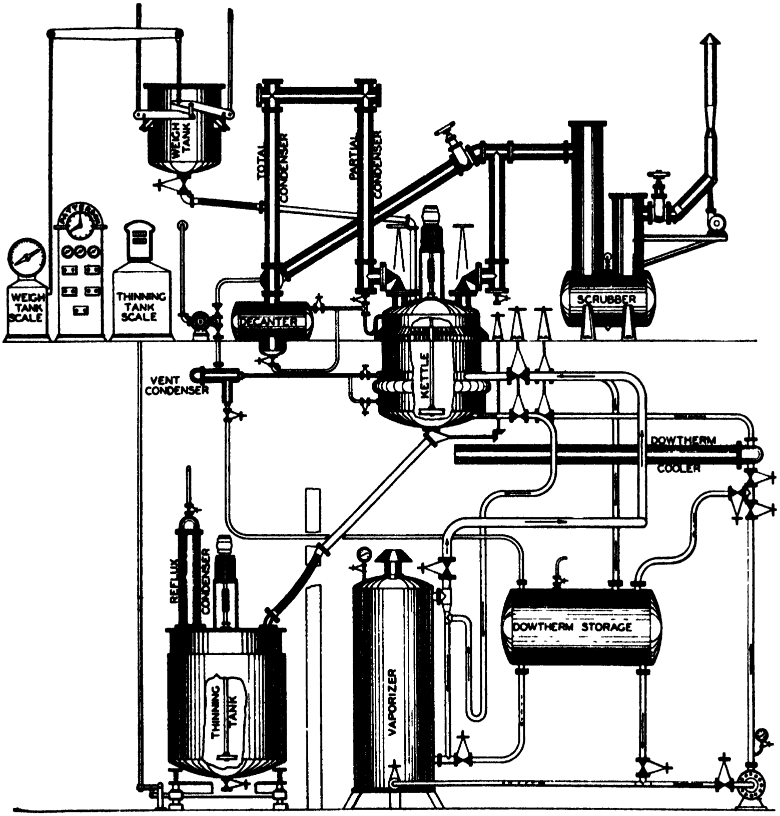


FIGURE 105. Patterson complete synthesizing and processing system.

With the "Dowtherm" unit auxiliary equipment, consisting of a storage tank, cooler, and circulating pump can be used to control the temperature of the material being processed by the use of proper valving arrangements, where the heat can be shut off almost instantly and cold "Dowtherm" circulated through the upper and lower jackets. Exothermic reactions also can be controlled almost instantly, the liquid being circulated by the pump through the cooler, into the jacket, and then returned to the storage tank. As soon as the temperature is lowered sufficiently in case of exothermic control, the cooling is cut off and the heat restarted; or, if it is desired to cool the contents of the vessel before passing to the thinning tank, the temperature can be brought down to almost any degree desired, but usually it is in excess of 350°.

With the "Dowtherm" or similarly heated unit it is usually necessary to elevate the vessel above the vaporizer so that the liquid may be returned to the kettle by gravity. However, by proper engineering, building heights have been materially reduced and a two-story system with "Dowtherm" is quite common practice. "Dowtherm" units can also be set up to operate on a one-story basis, but the condensate return must be handled by pumps, and it does not give as nice a flow arrangement for the finished product as the two and three-story types of construction.

The kettle itself is designed for 60 lbs working pressure in the jacket, and the internal pressure is for either 15 lbs pressure or full vacuum. The kettle is usually provided with a bottom discharge opening equipped with a flush type valve. Insulation is applied directly to the wall of the vessel, thereby giving a very compact arrangement, as no air cooling is required to obtain proper control.

Up to this point, we have considered only the bare kettles and their heating agents. It would be well now to take into consideration the auxiliary equipment that is usually common to the various types of vessels.

Let us first mention the question of agitation. The usual procedure is to use a turbine type agitator, operating at proper speed to give the correct degree of agitation, though other types are sometimes employed. Too rapid agitation will cause discoloration, and too slow agitation will not give the proper heat transfer at the interface and the heat-up rate will be lowered. The drive unit is usually of the vertical type, with an explosion-proof motor and totally enclosed reduction unit, of either the single or the double reduction type. The drive is usually mounted on a substantial base on the head of the processing vessel, with a compression load-carrying type coupling joining it to the stainless steel stirrer shaft, which enters the vessel through a stainless steel lantern-type stuffing box, carbon dioxide gas being introduced through the lantern gland.

The cover or top of the vessel should be provided with at least one sight glass and a light window, the necessary inlet connections for liquids, a sufficiently large, quick-opening manhole for charging of dry materials, as well as for inspection of the contents. The usual practice is to provide the manhole with a CO_2 sparger ring to prevent oxygen reaching the surface of the product; CO_2 is also introduced at the bottom of the vessel through a sparger ring directly underneath the agitator. The flow of this sparger ring is measured through a rotometer and is a calculated quantity most desirable for proper processing.

The necessary condenser and fume connections should be made, along with a sampling connection for the continuous removal of samples from the vessel during the course of processing.

The regulation of temperature of the product is usually controlled by a recording pyrometer, the thermocouple of which is introduced through the side of the processing vessel, its bulb being in direct contact with the material being prepared. This controller can operate in conjunction with a rate controller or in conjunction with a program control, so that the length of heat-up time, the whole time and other functions can be handled for any process.

The usual instrumentation includes pressure gauges to record the pressure in the jacket as well as the pressure inside the vessel.

Weigh Tank

The usual practice is to weigh all liquids entering the process on a suspended type scale, either dial or beam, the liquids usually being pumped or arranged to flow by gravity to this tank. The tank is usually of stainless clad steel and is provided with or without cover, as requirements necessitate. The weigh tank is connected to the vessel by means of a flexible metallic hose, so that it is never necessary to disconnect it from the vessel; due to dripping, this causes a messy condition around the plant.

Fume Scrubber

Fume scrubbers of the wet-plate type are usually provided, and a design has been worked out which is very efficient in the abatement of obnoxious odors. As a result, the equipment can be installed in residential districts. This system can be arranged for the recovery of certain products by the use of a continuous process, the decision as to this resting with the owner or operator and is usually governed by the economic value of the products recovered.

Condensing System

The condensing system can be either of the plain reflux type with decanter, or of the azeotropic type whereby certain of the products are refluxed and the balance recovered or discharged from the system. The condensers in any case are constructed of stainless steel in order to prevent contamination of the refluxed or recovered materials.

Thinning Tank

The thinning tank is usually constructed of stainless clad steel and is provided either plain or jacketed. The usual procedure is to set the thinning tank on weigh scales, to obtain accurate weights of the product from the kettle and the thinners entering the thinning tank (both through flexible connections). The type of thinning tank preferred is round, with dished bottom, and is provided with agitation in order to obtain the proper blend between the thinners and the varnish, resin or other product. The tank is also provided with a reflux condenser, so that when the hot resin, varnish or other product enters the thinner already in the thinning tank, any volatiles that are vaporized are condensed and returned to the tank. The use of a thinning tank on scales provides a more accurate method of obtaining desired specific gravities.

All materials coming in contact with the product are stainless steel. The agitation is similar to that of the kettle, but at this point the degree of agitation is not as critical.

PAINT MANUFACTURING

GORDON MUTERSBAUGH

The Glidden Company, Cleveland, Ohio

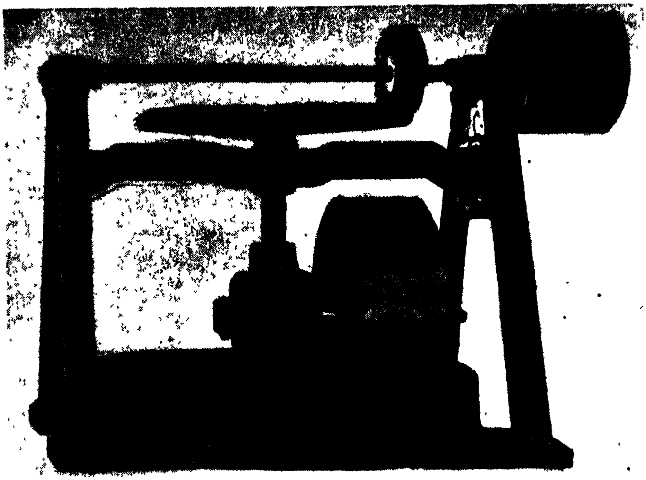
The manufacture of salable paint products depends just as much on proper manufacturing technique and good equipment as on good formulation and good raw materials. There is no substitute for this experience or know-how which means the difference between success and failure as it does in most industries.

The importance of manufacturing technique can easily be demonstrated by sending the same formula and raw materials to different paint plants. There will be variations depending on the skill and type of equipment used in the manufacturing process.

Paint manufacturing is the process of mixing pigments with a suitable vehicle and grinding to a satisfactory fineness, color and consistency. The equipment necessary to accomplish this end is relatively simple and has been improved with the progress of the years to reduce labor and operating costs and to do a better technical job.

Study of plant layout from the point of view of flow of production will pay for itself in low labor costs. Most paint plants were built in days when high labor costs were not of primary concern and when it took many more man hours to produce a gallon of paint than it does today. During the last twenty-five years there has been a steady decrease in labor costs of mixing, grinding and filling by use of better equipment until today there is more labor cost in handling raw materials and finished products than in the manufacturing process.

An important factor in low cost operation is to use the smallest number of raw materials. This requires standardization of each type of raw material so that as many can be purchased in carloads and tank cars as possible. This requires skill on the part of the formulator. It is not too difficult to meet competition with a limitless number of raw materials but to make competitive products with a limited number of raw materials is a real test of formulating skill. This is one reason why it is often desirable for a young chemist to start in the plant and thoroughly understand the process and available equipment before starting to formulate in the laboratory.



(Courtesy The Patterson Foundry and Machine Company

FIGURE 106. Putty chaser.

Another factor in low cost operation is adequate room for storage of pigments and tankage for vehicles and for economical handling and storage of finished products. The business is partly seasonal and to properly utilize labor enough room should be available to produce for stock during the slack season so that machinery can be constantly utilized and labor can be regularly employed. Unless this is done, the machinery will only be fully used in peak seasons and it will be necessary to hire inexperienced people in peak seasons and lay off people in slow seasons which does not result in efficient employees.

The standard plant uses a three or four story building where liquids are stored in tanks on the top floor and pigments are stored on the floor below. The production then proceeds by gravity to mixing, grinding, filling and storage of finished products on the floors below. This makes for a low cost plant for manufacturing but elevators are a bottleneck in the flow of raw materials so that costs for handling raw materials are high.

A one story plant where raw materials and finished products can be handled with fork trucks and pallets reduces material handling costs. The equipment can be arranged on one floor and loaded from a mezzanine floor. This requires the use of pumps to replace the gravity process. The cost and availability of land will determine the layout of the plant.

Proper records for ordering raw materials and scheduling of production is necessary to operate with lowest possible investment and cost of labor.

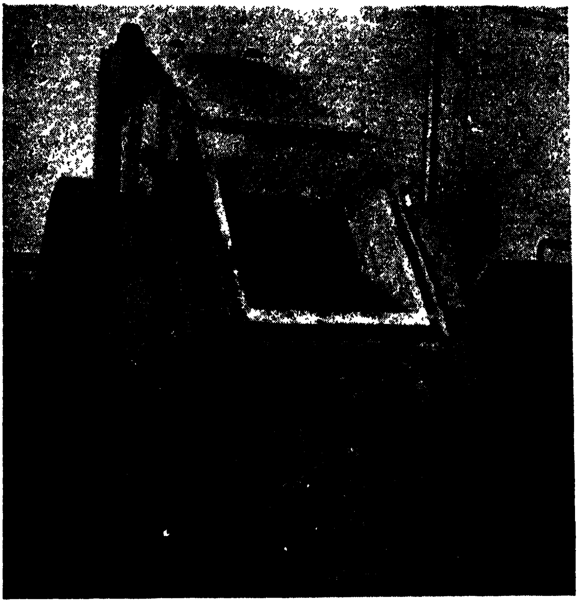


FIGURE 107. Dispersion mixer.

The first step in the manufacturing process is mixing. Pre-mixing is required if stone mills or roller mills are used. This is done in a mechanical mixer. A standard lead mixer or a putty chaser (see Figure 106) or edge runner is used. Proper mixing reduces the grinding operation as the pigments are partially wetted and some of the agglomerates broken up by the shearing action that is developed.

Some easy wetting pigments can be dispersed so that no further grinding is necessary by using dough mixers which depend entirely on the shearing action in the mixer. A dispersion mixer is a heavy duty mixer with a small clearance between the blades of the mixer and the side of the mixer which results in enough shearing action to disperse most pigments (Figure 107). Large size motors are required to develop this action. The heaviest type of dispersion mixers are the Banbury mixers used in the rubber industry. These develop fine dispersion and gloss especially for nitrocellulose lacquers and synthetic enamels.

The ordinary lead mixers that are normally used for mixing are made in 50 to 100 gallon sizes (Figure 108). Recently, these have been made in 500 gallon sizes which reduce labor costs of mixing. It is important to keep these mixers clean because contamination from one batch to another of different formulas may cause trouble in the final product.

FIGURE 108. Lead mixer.

The purpose of grinding is to thoroughly disperse the pigment in the vehicle. There is little reduction of particle size in the process although it is necessary to break up all agglomerates of pigments and thoroughly wet each particle of pigment with the vehicle. Most pigments are purchased so fine that less than 1% is retained on a 325 mesh sieve. The time of grinding especially in the case of hard inerts can be reduced by buying micronized pigments.

The fineness of grind desired can be measured by an experienced operator by rubbing the paint between two spatulas. This can be measured more accurately by using a North grind meter. Enamels are usually ground very fine but some paints, especially house paints, should not be ground too fine.

One of the oldest types of mill used is a stone mill which is a variation of the old grist mill (Figure 109). The mill consists of a hopper which

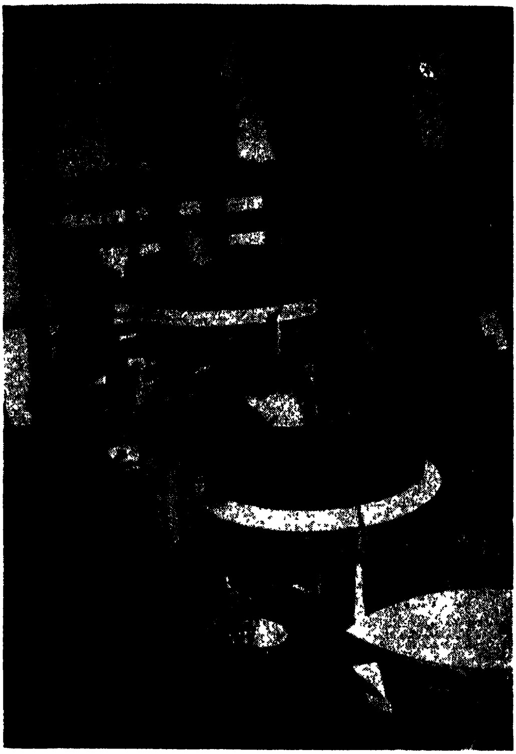


FIGURE 109. Stone mill.

FIGURE 110. Three roll mill in operation.

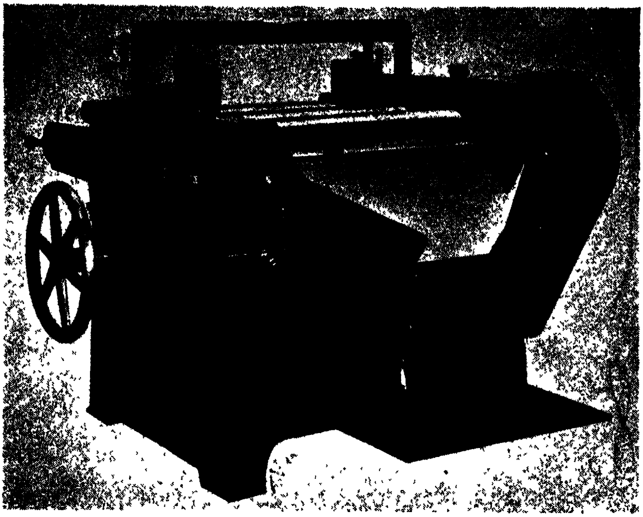


FIGURE 111. Brasington three roll mill with one point adjustment.

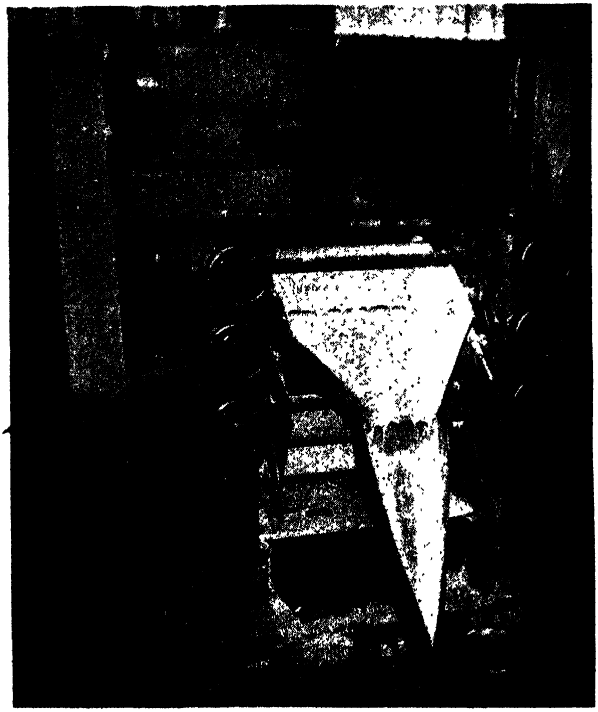


FIGURE 112. Five roll mill in operation.

feeds the pre-mixed paste into the opening or eye of a cylindrical stone with a hole in the center; which revolves on another stone of equal diameter. The grinding surface of both stones is cut into deep furrows running from the center of the mill to the periphery. Small feeding channels run at right angles to the main furrows. These stones are made of buhrstone or synthetic materials like silicon carbide or alundum. The stones can be arranged in single pairs or in tandem fashion so that a double grind can be obtained. The operator adjusts the pressure with which one stone presses on the other and this determines the fineness of grind and the output through the mill. Fineness of grind is necessary to develop the full strength of expensive dry colors. The stones are usually 12 to 32 inches in diameter.

Stone mills give good flexibility of grind and consistency but have a relatively low output and high labor costs and for this reason are rapidly being replaced by other grinding equipment.

Another type of mill that has been used for many years is the roller mill. These mills have chill hardened rolls between which the pre-mixed paste is passed. The rolls are 12 to 15 inches in diameter and 32 to 40 inches long. Some European mills use only one roll and a scraper. American mills use three to five rolls. The rolls in the three roll mill are arranged either horizontally or one above the other. The rolls in the four and five roll mills are always arranged with the rolls one above the other. The rolls run at different speeds and the paste is transferred from the lower roller to the roll above. Roller mills have been improved in recent years to run at faster speeds and improve the output. Several roller mills are shown in Figures 110, 111, 112 and 113.

Roller mills produce good results especially with soft white pigments and they produce good luster. They are flexible regarding type of grind and consistency of paste. If used to grind hard pigments like inerts the rolls score quickly resulting in high maintenance costs. Labor costs are relatively high and also loss by evaporation of volatile solvents.

Pebble mills and ball mills are rotating cylindrical shells and accomplish both mixing and grinding. Labor costs of operation are low and there is practically no evaporation of volatiles. They lend themselves to 24 hour operation. A typical mill of this type is shown in Figure 114.

These mills can be lined with porcelain blocks and used with porcelain balls. Some mills are lined with buhrstone blocks and used with flint pebbles. Other mills are lined with a special type of high specific gravity clay called Berylite and used with balls of the same material. This type of mill is shown in Figure 115. Steel ball mills are not lined and the shell is made of tough chrome manganese steel.

These mills are made in different diameters and lengths. Pebble mills

FIGURE 113. Five roll vertical mill.

FIGURE 114. Ball mill.

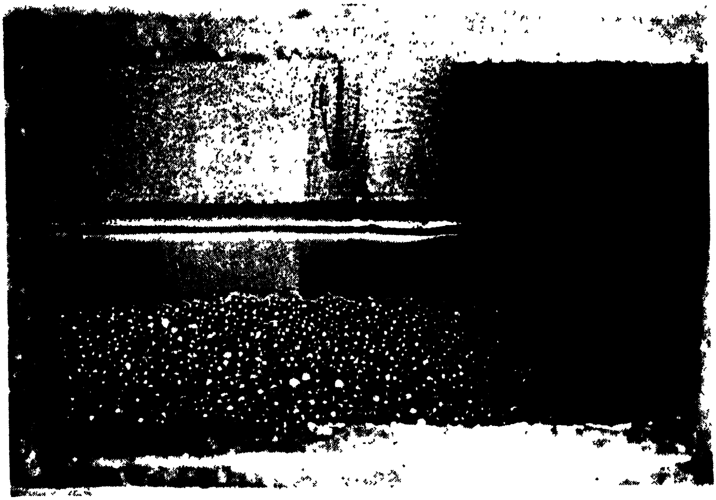
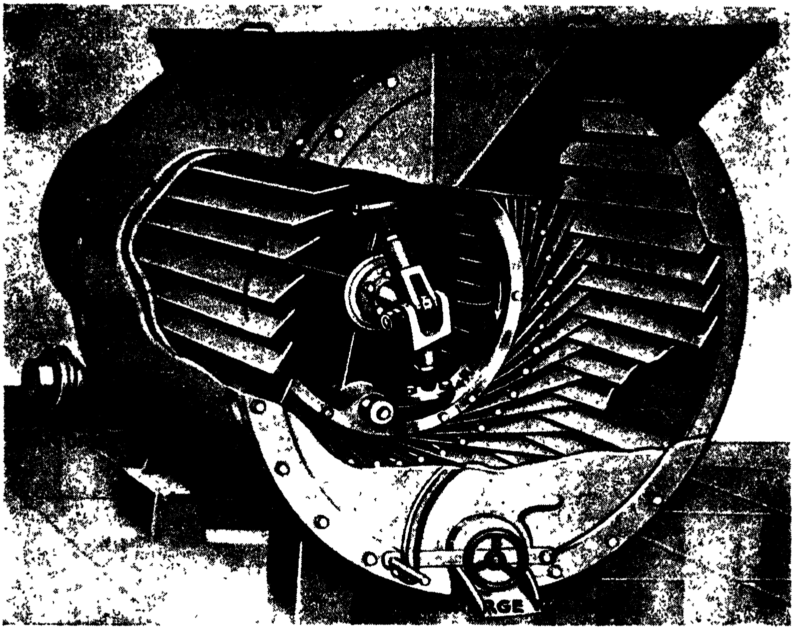


FIGURE 115. Berylite lined mill and balls.

FIGURE 116. Hy-R-speed mill.



(Courtesy The Bramley Machinery Corporation, New York)

FIGURE 117. Inside view of a 38 inch Bramley mill.

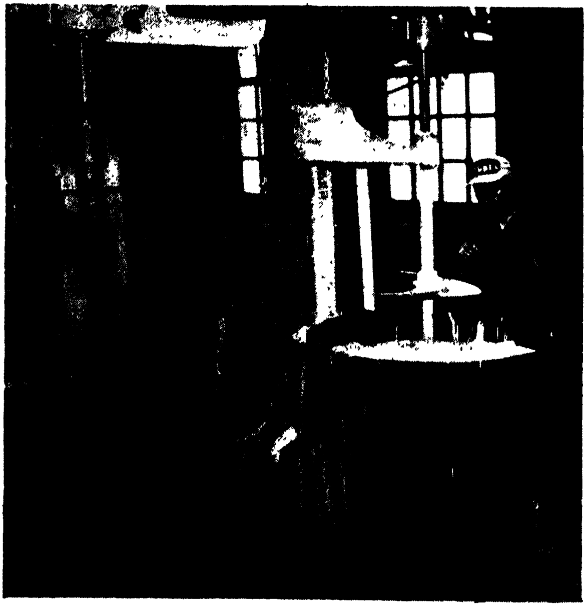


FIGURE 118. Portable mixing kettle.

are not usually water-cooled except for grinding heat sensitive pigments. Steel ball mills should be water-cooled in sizes over 90 gallons as they develop considerable heat.

Steel ball mills discolor white pigments and some dry colors. Porcelain and Berylite mills are used where minimum discoloration is desired.

Steel ball mills produce the best luster and pebble mills the poorest luster. Berylite mills produce good luster especially with white pigments and are primarily designed for this purpose.

Steel ball mills cause some contamination of iron and, since iron is a drier, baking enamels seem shorter when ground in steel ball mills and the formula must be adjusted accordingly.

Grinding time in steel ball mills is about half that of pebble mills and Berylite mills grind white enamels nearly as fast as steel ball mills.

The consistency of the paint must be such that the balls or pebbles cascade freely inside the mill. The mills are equipped with lifter bars to aid the cascading of balls or pebbles.

Steel ball mills and Berylite mills cost nearly twice as much as pebble mills because of their greater weight and have a much shorter operating life.

Factors Determining Output of Ball and Pebble Mills

Several points should constantly be considered to attain good grinding results.

1. Ball or Pebble Charge—Weight

Size Mill	Pebble Charge	Steel Ball Charge
3′ x 4′	939#	2837#
4′ x 5′	2310#	6281#
5′ x 4′	2954#	7963#
5′ x 6′	4603#	11904#

2. Ball or Pebble Charge—Size

Diameter Mill—Feet	Ball Charge of Porcelain Balls		
1–2	½″–70%	1″–30%	
3–4	½″–30%	1–1½″–60%	1½–2″–10%
4–5	¾–1″–85%	2–2½″–15%	

In the case of pebbles, the size should be increased by 50% and the proportion of large pebbles increased by 30–40%.

3. Ball or Pebble Mill Speeds

Interior Diameter of Mill (feet)	6½	5	4	3	2	1
R.P.M.	17–18	19–21	20–22	25–26	30–32	49–52

4. Select the best wetting liquid ingredients for the grind. To increase the wetting properties of the liquids use wetting agents such as Lecithin or Zinc Napthenate.

5. Thin the vehicle to 25% solids, if possible.

6. Bring up the viscosity of the mill grinding base with pigment. In this way a maximum amount of pigment may be ground thus allowing a great deal of thinning down and subsequent higher yields.

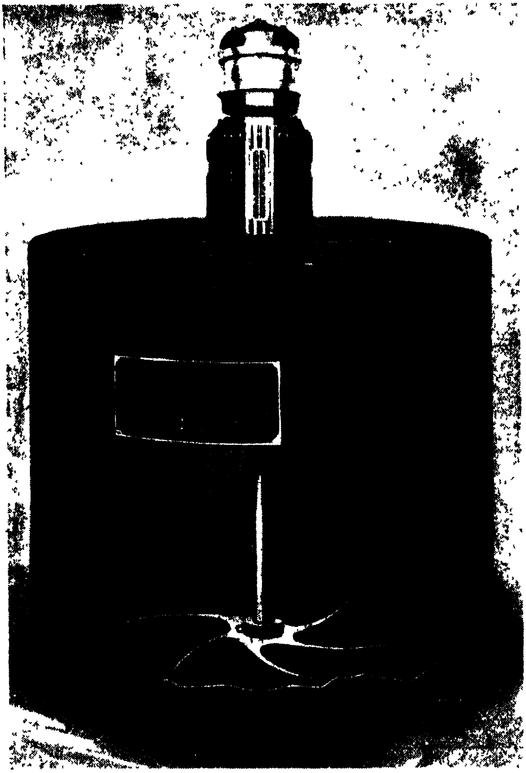


Figure 119. Stationary mixing tank (showing stirring device.)

7. The grinding base should be 100–120 KU for loads just covering the grinding media. Their viscosity depends upon how high the ball and pebble mill temperatures run. In the case of blacks, reds, and puffy batches the viscosity will be too high to draw the mill and at the end of the grind about 30–40 gallons of vehicle must be added to draw.

The viscosity listed above is for loading only 2 or 3 inches above the pebble or ball mass, so that the pebbles or balls pull the paint along up the side as they "ride." On the full mill loads, usually over week-ends, or in the case of short grinds such as 24–40 hours for full mills, the viscosity should be in the 86 KU to 95 KU range. This thinner body is used so that the batch above the pebble mass is drawn in more easily.

Colloid mills, like the Charlotte mill, can be used for dispersing soft pigments where an enamel grind is not necessary. The paste is passed through high speed discs. They have a high capacity for certain type paints.

FIGURE 120. Wire mesh strainer.

The Hy-R-Speed mill (Figure 116) is really a combination stone mill and colloid mill. The paste is passed through silicon carbide stones that revolve at high speed. They produce a good volume of house paint and flat wall finishes but are not satisfactory for grinding high grade enamels.

Another type mill that is used in some plants is the Bramley mill. It consists of a steel shell with internal blades that press against the inside of the shell with varying pressure. An inside view of a Bramley mill is shown in Figure 117. These mills have a good output and good flexibility of grind but cannot be easily changed from one color to another and maintenance costs are relatively high.

Some mention should be made of flush colors. Most dry colors and white pigments are made by a wet precipitation method. In this form the particle size is very small. It is possible to replace the water phase with vehicles so that the usual agglomeration in the drying process of pigments is avoided. The resulting pastes need no further grinding. The economics of flush colors compared to grinding dry pigments is open to question and they are not generally used in the industry.

Some paint companies grind concentrated pastes which are used as bases for making finished enamels. This offers a quick way to give service when making small batches of special colors and reduces costs compared to separate grinding of small batches. They can also be used for tinting purposes.

After the paint is ground, it is transferred either to portable kettles or to stationary mixers depending on the size of the batch. Here it is shaded and thinned to the proper color and consistency. A portable kettle is shown in Figure 118 and a stationary mixer (with cut-away view) in Figure 119.

A sample from the batch is then tested to insure uniformity. It should be tested in the same manner that it will be used by the customer.

The paint is then filled either by weight or volume into containers. A filling machine is usually used for filling small cans.

The paint is strained before filling through a wire mesh strainer of various mesh fineness such as is shown in Figure 120 or in the case of high grade enamels is centrifuged or passed through linen or silk. Cleanliness in the manufacturing process prevents skins and contamination and minimizes the necessary straining.

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