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# Colloidal Dispersions



# Colloidal Dispersions

*by*

The Late Earl K. Fischer

National Bureau of Standards  
Washington, D. C.

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## Preface

This monograph is planned as a guide to the theory and practice of the dispersion of solids in liquid media.

Throughout the writing I have had in mind readers in several professional categories: one is the physical and colloid chemist who is unfamiliar with the technical aspects of the subject; another is the scientist in industry who is compelled by the exigencies of his work to concentrate on product development but finds that an understanding of theory is the most effective basis on which to design new products; a third is the production supervisor who is interested in the science and engineering underlying the operations in his care but who is too busy to seek their exposition in widely scattered places. There are others, I hope, who will also find the volume interesting and usable.

The topics forming the substance of this book are part of the large province of colloid science. An effort has been made to provide a coherent account of the physical properties of colloidal dispersions and the methods for producing them. Innovations and refinements in research techniques have brought a new insight to the structure of these dispersions. In particular, mention should be made of methods for particle-size measurement, experimental means for gauging the interaction of dispersed particles, and new reagents that offer a measure of control for some of the physical properties. There remain, of course, unanswered questions, and the subject abounds with engaging and important research problems.

This book is intended to supplement the well-known and easily accessible monographs on surface and colloid chemistry. Information has been drawn from diverse sources. In an effort to keep the book of moderate size I have been perplexed by the inevitable problem of selection, for pertinent material is to be found in the literature of many industries and branches of science. I have endeavored to document the work adequately and to bring subjects into their correct historical perspective. Where available information ran low, I have, on occasion, taken the liberty of speculating, and the reader will find hypotheses advanced at various points through the book. I hope that errors are infrequent or of the kind that will not mislead the scientist; if serious



errors of fact or interpretation are found, I shall appreciate having them called to my attention.

Although the writing of this monograph has been a personal venture on leisure time, it represents in some measure gainful discussions and collaboration with many friends and sometime colleagues. I wish to mention, in particular, the following: C. R. Bragdon, D. M. Gans, A. E. Gessler, the late Henry Green, W. D. Harkins, E. N. Harvey, Jr., C. H. Lindsley, L. W. Ryan, and Ruth N. Weltmann.

In a very tangible way I am grateful to many persons and organizations who gave permission to reproduce material. Included are publications of the American Chemical Society, the American Institute of Physics, the American Society for Testing Materials, the National Paint, Varnish and Lacquer Association, Inc., the MacNair-Dorland Co., and the Textile Research Institute, Inc. The photocopying service of the American Chemical Society, operated in cooperation with the U. S. Department of Agriculture Library, has been an invaluable aid in supplying articles difficult to find.

I wish also to record indebtedness to my late wife, Catherine Fischer, for assistance with the reference material and for literary criticism, to Margaret Carver Ernsberger for careful proofreading and help with the indexing, and to Susan Taylor for efficient typing of the manuscript.

EARL K. FISCHER

*Washington, D. C.*  
*September, 1950*

# Contents

1. Introduction	1
2. Particle Size	3
3. The Solid-Liquid Interface and Wetting	73
4. The State of the Dispersed Solid	104
5. Rheological Properties of Dispersions	147
6. Surface-Active Agents	224
7. The Process of Comminution	258
8. Mixing	268
9. Roll Mills	279
10. Ball and Pebble Mills	304
11. Disc, Cone, and Colloid Mills	329
12. Dispersion by Phase Transfer—the Flushing Process	348
Author Index	365
Subject Index	375



# 1. Introduction

The arts of grinding and of decoration with colors are among the oldest of man's achievements. They came down to us through the centuries with only gradual alteration, but, when mechanical inventions grew apace and cheap mechanical and electrical power became abundantly available, the refinements in our machinery and our skills expanded immeasurably. Today the machinery of our production, although identical in principle with the earliest hand-wrought and hand-turned mills, utilizes all the innovations of engineering. The materials of our production in like measure have utilized all the resources of pure and applied science.

The subject of this monograph, the dispersion of finely divided solids in liquid media, is of great industrial importance. Industries whose production value aggregates several billion dollars annually in the United States alone depend on this basic process. Paint, in all its varieties, is essentially the dispersion of a mixture of pigments in liquids which serve finally to bind these particles into a coherent and resistant film. Printing ink, akin to paint in important respects, has the special task of conferring high opacity in extremely thin films. Textile colors need to be securely bound to the fibers so that washing and abrasion do not severely affect the durability of the printed fabric. Ceramic technology depends on an aqueous dispersion of clay and coloring substances so formulated that molded objects hold their shapes until permanently fixed by firing. Rubber dispersions of carbon black form the body of the tires we use for mileages that rival the life of the mechanism of the automobile, and the remarkable endurance of the tires can be credited to reinforcement of the rubber hydrocarbon by the fine, discrete particles of carbon black. These are only a few examples of the many products that depend on the properties of colloidal dispersions.

The subject in its essentials is the study of the formation and the properties of the solid-liquid interface. It is in this region, where the

solid comes into contact with the liquid, that the physical properties of the bulk mass are largely determined, for resident within this interface are forces whose magnitude and nature are now only partly known. The study of this region is the fascinating province of surface and colloid chemistry. For our understanding it is necessary to examine the means for determining the sizes of particles, to consider the experiments and theories revealing information on the wetting of solids, and to analyze, as best we can, the state of the dispersed solid. These are the subjects of Chapters 2 to 5. The manufacture of colloidal dispersions is covered in Chapters 6 to 12. This section constitutes, in effect, a second part of the monograph, and includes details on processes and machinery. Dispersion equipment is considered from the following viewpoints: design and construction, capabilities, methods for operation, and performance.

There is a central idea threading through the discussion. The powdered solids of commerce consist of aggregations of smaller particles. To convert them to dispersions in liquids, mechanical work is performed, and the forces and stresses imposed on the aggregates through the liquid cause them to break up into the smaller units. At the same time the liquid suspending medium is brought into contact with each particle. Once dispersed, the particles in their new environment are free to move about and to form new associations, differing, however, in important respects from the original aggregations. The flow properties of these dispersions help to characterize them and to a great extent the formulation of special products is concerned with this property alone. By somewhat indirect means we can also use the information derived from a study of dispersions during flow to explain the state of the finely divided solid.

It will be necessary to consider the size of the dispersed particles at all stages. In most respects the dimensions we shall be considering are in the realm of colloidal. The limits of colloidal particles have been variously stated, but sizes between 1 micron and 1 millimicron encompass the usual extremes, and, for the most part, the materials of this discourse are in this range. For convenience in reference the several units employed are given in the accompanying tabulation.

	inch	cm	mm.	$\mu$	m $\mu$	Å
inch	1	2.54	25.4	25,400	25,400,000	254,000,000
cm.	0.393	1	10	$10^4$	$10^7$	$10^8$
mm.	0.0393	$10^{-1}$	1	$10^3$	$10^6$	$10^7$
$\mu$	0.0000393	$10^{-4}$	$10^{-3}$	1	$10^3$	$10^4$
m $\mu$	0.0000000393	$10^{-7}$	$10^{-6}$	$10^{-3}$	1	10
Å	0.00000000393	$10^{-8}$	$10^{-7}$	$10^{-4}$	$10^{-1}$	1

## 2. Particle Size

Particle sizes of the finely divided substances that are common to everyday experience cover a wide range. Starting with sand grains, easily visible to the unaided eye, the roster of particle sizes, in decreasing magnitude, includes dust, unicellular organisms, emulsions such as milk, pigments, smokes, and viruses and ends with particles that are of molecular dimensions. In even a small quantity of a finely divided material there are countless particles, but more important, from the point of view of the investigator, are the variable sizes and shapes of the particles. It is rare, indeed, for the particles present in such a system to be of uniform dimensions and shape, or "monodisperse." Instead they are most frequently arrayed in a distribution of sizes, although there may be a similarity in shape. Consequently the methods of statistical analysis are required to bring some meaning to any recorded dimension.

Inadequate information on the sizes of particulate substances has been the cause of much uncertainty. Rough empirical methods have long been employed by manufacturers of pigments and other powdered materials with, it should be recognized, considerable success in arriving at a compromise of properties which provided satisfactory commercial properties. The optical microscope, using visible light, was employed to advantage with particles greater than 0.2 micron in size and with ultraviolet radiation to about half this size, but precise information on the crystal habit and the specific surface of finely divided materials below this limit was unobtainable. The fine particles of carbon black and organic colors, for example, could not be examined with any degree of success. The introduction of a commercial model electron microscope, refinement of adsorption techniques for surface-area measurement, and application of methods based on sedimentation equilibria, all since about 1930, have brought a far more precise knowledge of particles so small that formerly only guesses could be made as to their sizes and shapes. It is still too early to expect more than a preliminary assay of the size

characteristics of many finely divided materials, especially when this information is intended for correlation with rheological and optical properties of suspensions, but future research will undoubtedly furnish the data now lacking.

The literature on particle size is extensive; a useful monograph has been written by Dalla Valle<sup>1</sup> which covers many industrial fields with emphasis on engineering applications. The nomenclature of size distribution was notably clarified by the papers of Perrott and Kinney,<sup>2</sup> Green,<sup>3</sup> and Martin.<sup>4</sup>

Various methods for particle-size measurement have been discussed by Work,<sup>5</sup> and Schweyer<sup>6</sup> reviewed critically the data and methods in the region from 0.2 micron to 75 microns. In 1941, the American Society for Testing Materials held a symposium on methods, and the papers are available in monograph form.<sup>7</sup> In 1947 Harvey<sup>8</sup> discussed the application of these methods to the study of pigments and presented new data for some 30 pigments.

### The Concept of a Particle

There are many concepts connected with the term particle, and all of them agree only on the idea of relative smallness. For the following discussion it will be necessary to have a rather clear conception of a particle in its several technical meanings. To start with the smallest division, a particle can be considered a single minute crystal formed, for example, during a reaction that precipitates an insoluble substance. Such a crystal may be so small as to be invisible in an optical microscope, yet it represents an entity; on the other hand, the crystal may grow so large that it weighs many pounds. The large crystal would hardly be considered a particle, commonly associated with the idea of smallness, but, if the crystal were pulverized into very small pieces, the fragments would be properly considered particles. We could partially fuse the fragments

<sup>1</sup> J. M. Dalla Valle, *Micromeritics*, Pitman Publishing Corp., New York, Second edition, 1948.

<sup>2</sup> G. St. J. Perrott and S. P. Kinney, *J. Am. Ceramic Soc.*, **6**, 417-39 (1923).

<sup>3</sup> H. Green, *J. Franklin Inst.*, **204**, 713-29 (1927).

<sup>4</sup> G. Martin, *Trans. Brit. Ceramic Soc.*, **23**, 61-109 (1923).

<sup>5</sup> L. T. Work, *Chem. & Met. Eng.*, **45**, 247-49 (1938).

<sup>6</sup> H. E. Schweyer, *Chem. Revs.*, **31**, 295-317 (1942).

<sup>7</sup> American Society for Testing Materials, "Symposium on New Methods for Particle Size Determination in the Subsieve Range," Philadelphia, 1941.

<sup>8</sup> E. N. Harvey, Jr., *Interchem. Rev.*, **3**, 59-70 (1944); "Symposium on Paint and Paint Materials," *Am. Soc. Testing Materials, Special Tech. Pub.* 75, pp. 60-84, Philadelphia, 1947.

into a porous mass and then pulverize again; the fragments would once more be particles but quite different in structure from those formed by breakdown of the original crystal. Instead of fusing the fragments into aggregates, they could be connected together with any kind of binder.

The solid intended for dispersion in industrially useful compositions, such as a paint, a ceramic glaze, or a surfacing for a road, is often a naturally occurring material that has been treated to isolate some desired ingredient. In processing a pigment or an ore, the first step is crushing (as in a stamp mill) followed by fine grinding (as in a ball mill). The product is one of great complexity: particles of different materials are present, most of them the result of actual fracture; others, originally very small, are merely freed from a matrix of imprisoning materials. Ordinarily the particles formed by pulverization are in the so-called sieve range, greater than approximately 40 microns in any given dimension. The production of finer material, in the subsieve range, calls for further processing. Separation processes depend on the size of the particles, their chemical and physical properties, and the uses to which the classified material is to be put.

In the majority of materials with which we are concerned, it has been found economically possible to obtain the requisite fineness only by chemical reactions involving precipitation from an aqueous solution or by deposit, as in the special case of carbon-black manufacture, from a luminous flame. The particles so deposited are the primary particles. They are far smaller than sieve sizes and range from about 0.005 to 1 micron. When each of the primary particles of a precipitated solid in an aqueous medium retains an isolated individuality, it settles only very slowly. Processing them becomes difficult: washing by decantation, for example, is protracted, and filtration may be impossible. Hence it is desirable to increase the effective size of the particles by causing them to clump together or flocculate. This result is often achieved merely by the addition of electrolytes, by changing the pH of the suspension, or by addition of a surface-active compound. The floccules so formed act as if the particle size were many times larger, and, since they do not pack closely, the resulting dried filter-press cake is more porous and is more easily pulverized.

The aqueous slurries of precipitated particles almost always contain soluble salts which are incompletely removed by washing. Further, reagents that are added to aid processing or to impart some desired property to the finished powder also remain in the filter-press cake. During drying, these substances tend to cement the particles together. Commercial chrome-yellow pigments, for example, frequently contain as



much as 3 percent of soluble residual salts. In the precipitation of organic colors by dilution of an acid paste, and, in the wet grinding of natural materials and of artificial color masses such as ultramarine blue, the retention of soluble salts, giving rise to cementation, is equally possible. For some other materials, sintering occurs during drying of the filter-press cakes; lithol toners to which an appreciable amount of a fusible metallic resinate have been added are examples of this class. Aggregates of the individual particles result in this manner.

The extent of cementation is reduced by subsequent pulverization of the dried material, but the aggregates with strongest bonds persist. Aggregation to a controlled extent is not undesirable; instead, it aids in isolation of powdered materials and in subsequent handling and packaging. The advantage of compacting fine powders is obvious; fly ash and carbon black, as typical examples, are so bulky that a small weight occupies a very large volume, and the material is easily carried by even small air currents. Carbon black is now marketed in small beads or spheres because this form contributes greatly to economy and cleanliness in packing, transport, and storage.

Since all powdered materials contain aggregates of the primary particles along with other particles that are present either as an incident in manufacture or as a residue from the raw material, it is necessary that the selected dispersion procedure break the aggregates to some acceptable minimum size. The process of dispersion of powdered solids in liquids has as an essential duty the comminution of aggregates. Should any particles larger than the accepted minimum size remain in the suspension, they contribute to the physical properties of the system, not in relation to the size of the primary particle, but instead in relation to the size of the coarser aggregate. The material that persists through dispersion processes without breakdown is often designated "hard aggregate," "agglomerate," or "grit," and frequently necessitates prolonged mill operation to bring the maximum aggregate size to limits for satisfactory performance. Manufacturers of pigments and colors have expended considerable effort in producing "soft-grinding" products. The measures adopted for this purpose are varied: centrifugal separation removes oversize particles; reagents are added to "coat" the individual particles to avoid cementation; drying procedures designed to produce a readily pulverized cake employ immiscible solvents and flocculating reagents. In addition, transfer of the pigment from an aqueous dispersion directly into a component of the vehicle, avoiding the separate steps of drying and pulverizing, has been used for pigments and colors that readily form hard aggregates. These processes are described in detail in Chapters 6 and 12.

The extent to which a given dispersion process reduces aggregates to the primary particles of which they are composed is a question that has not been completely answered. There is evidence that only in rare instances is complete breakdown achieved; but the aggregate size in a commercial dispersion is so small as to meet all practical standards. To meet the need for a definition that rationalizes the difference between an ideal and a practical state of dispersion, the term *ultimate working unit*<sup>9</sup> was proposed. Such a unit is a primary or individual particle or a group of primary particles that retains its structure throughout a dispersion process and subsequent application.

### Methods of Expressing Particle Size

Numerous expedients have been adopted for expressing the dimensions of particles. The simplest is, of course, merely a qualitative statement obtained by scanning a microscopic field or a photomicrograph, but the more quantitative methods have a statistical basis. In the following discussion, the various ways of designating particle size are described.

#### Size distribution

Size data of particulate materials are usually represented by a graph plotted to show the relation between frequency of occurrence and some measured dimension. As obtained from a particle-size count, the dis-

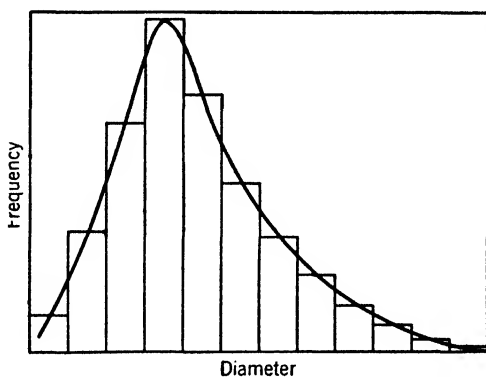


FIGURE 1. Typical histogram or size-distribution curve as obtained from a particle-size count.

tribution is shown by a sequence of “cells” or size groups, and a smooth curve is usually drawn connecting the tops of the different cells, to form a histogram as shown in Figure 1.

<sup>9</sup> American Society for Testing Materials, Standard Test E 20-33T (revised 1939).

Size-distribution data for most particulate materials are not symmetrical, and the curve slopes gradually to the larger sizes. Such a distribution is skewed to the right, in contrast to a symmetrical or left-skewed

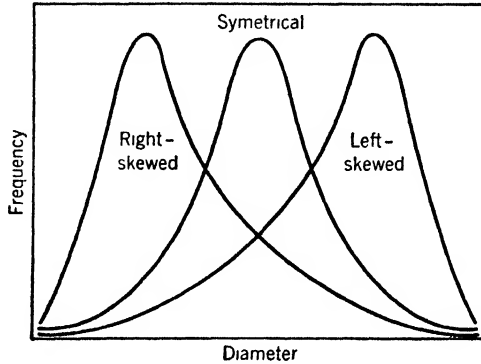


FIGURE 2. Generalized types of size-distribution curves. (Powdered materials invariably give right-skewed size-distribution curves.)

skewed distribution shown in Figure 2. When the numbers of each particle are added and the results plotted as shown in Figure 3, a cumulative frequency curve results.

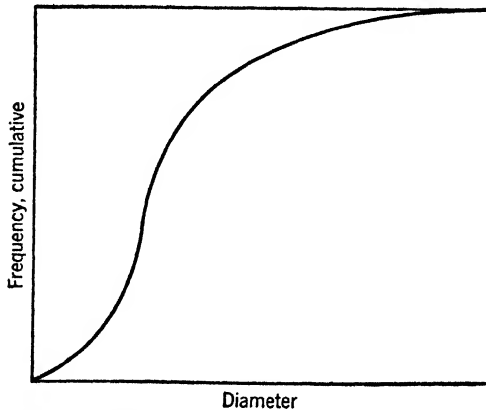


FIGURE 3. A typical cumulative frequency curve derived from a right-skewed size-distribution curve.

### Particle diameter

A frequency distribution is the first step in an analysis of size. It is necessary, however, to determine what dimension is to be measured, since the particles in a typical powdered material do not have a regular

geometrical shape such as a sphere or a cube. Instead, the sample is likely to be a mixture of some crystals (either perfect in form or distorted), clusters of primary crystals (which may have a regular shape), and fragments. To speak of a particle "diameter" or "size" poses a formidable problem in mathematical definition. We are inclined mentally to reduce the shape of an irregular object to some form that can be easily visualized. Most frequently this shape is a sphere or a cube, but, as the complexity of the form increases, we are forced to adopt a parallelepiped as the product of our mental simplification. Determination of a single dimension then is necessarily an approximation. If we consider a hypothetical particle, a rectangular parallelepiped in shape, we can assign the dimensions of length  $l$ , height  $h$ , and width  $w$ . Several dimensions can then be calculated. Thus  $(l + h + w) \div 3$  is a statistical average;  $(l \times h)^{1/2}$  is the side of a square with area equal to one surface of the object;  $(l \times h \times w)^{1/3}$  is the edge of a cube equivalent in volume to that of the particle. These dimensions can be readily imagined. The harmonic mean diameter is computed from the reciprocals of the separate dimensions.

It is not feasible, of course, to attempt the measurement of three dimensions on each particle, and, instead, one measurement on each particle is usually made. For example, if the particles in a photomicrograph are scanned in a given direction, and a measure of the dimension is taken on each particle (regardless of the position of the particle), then an approximate summation of  $(l + h + w) \div 3$  is obtained. Admittedly this method is an expedient.

Since not all the particles present in a sample will have the same dimensions, it is necessary to consider, further, the manner in which some selected dimension will be averaged. The most obvious method is to select some dimension and to add the different dimensions of all the particles and divide by the total number; thus  $d_{av} = nd/n$ . Although such an average corresponds with the arithmetic of ordinary experience, it has serious defects. Undue importance is attached to the small particles; for example, a small weight of the sample in the form of extremely small particles, present in large numbers, would reduce the computed average excessively. Some investigators, for this reason, consider the arithmetical average dimension to be of minimum utility in industrial problems.

These considerations indicate the difficulty, in dealing with size analysis, with respect to both terminology and computation. The term "diameter" in its most general meaning refers to a dimension through an object and does not imply a regular geometric form. It is used in this sense in particle-size analysis. Several "average" diameters can be com-

puted for non-uniform particles, and it thus becomes necessary to specify which of the average diameters is actually used. The literature on particle-size analysis is difficult to follow because *average particle diameter* is often used without definition; the presumption is that an arithmetical mean is intended, but some other average diameter may be implicit in the computation.

A general definition of average particle diameter has been given by Green<sup>3</sup> as the diameter of a hypothetical particle that represents in a special way a property of the total mass of particles. The actual magnitude obtained in a calculation of average particle size in a given sample depends on the relative importance assigned to the total number of particles, some linear dimension, the surface area, the volume, and the weight. The nomenclature continues to be variable, but many investigators have adopted the system essentially as it is developed in this chapter. (See Table I.)

TABLE I. EFFECTIVE AVERAGE DIAMETERS

Symbol	Name	Formula
$d_m$ or $d_{mod}$	Modal diameter	From frequency maximum
$d_{med}$	Median diameter	From cumulative frequency
$d_1$ , $d_{me}$ , or $d_{av}$	Mean diameter	$d_1 = \frac{\sum nd}{\sum n}$
$d_2$ or $d_l$	Mean length or length average diameter	$d_2 = \frac{\sum nd^2}{\sum nd}$
$d_3$ , $d_{vs}$ , or $d_a$	Mean volume-surface or average surface diameter	$d_3 = \frac{\sum nd^3}{\sum nd^2}$
		$d_3 = \frac{6}{\text{Density} \times \text{specific surface}}$
$d_4$ or $d_w$	Weight-mean diameter	$d_4 = \frac{\sum nd^4}{\sum nd^3}$
$\Delta$ or $d_s$	Mean surface diameter	$\Delta = \sqrt{\frac{\sum nd^2}{\sum n}}$ $= d_1 \times d_2$
$D$ or $d_v$	Mean volume diameter	$D = \sqrt[3]{\frac{\sum nd^3}{\sum n}}$ $= \sqrt[3]{d_1 \times d_2 \times d_3}$

*Qualitative rating.* When a pigment dispersion is mounted on a microscope slide, considerable information may be obtained by viewing sep-

arate fields, provided, however, that the microscope is fitted with a calibrated scale in the ocular, and that the magnification is adequate for proper delineation of form. It is possible then to judge the largest number of particles within some given size range and to express the results in a manner somewhat as follows: "majority of particles between  $a$  and  $b$  microns, few (or many) particles  $c$  to  $d$  microns, largest  $f$  microns, few particles smaller than  $a$  microns." When different specimens are studied in this way, comparative data are obtained. Although the specification is largely qualitative, it is useful, especially in grading dispersions quickly for the presence of oversize aggregates, and in estimating the shapes of particles departing appreciably from a cube or sphere.

*Nominal diameter,  $d_n$ .* The nominal diameter, as defined by Wadell,<sup>10</sup> is the diameter of a sphere with the same volume as the particle. This is an easily visualized diameter: the volume of an irregular object can be found, for example, by measuring the amount of water displaced by it, and computation of a sphere of the same volume is simple.

*Effective diameter,  $d_e$ .* The effective diameter is the diameter of a sphere that acts in the same way as the particle of irregular shape. Data obtained by sedimentation, using Stokes' law for the computation, lead to effective diameters. The  $d_e$  diameter is usually less than other diameters. One condition for the measurement from the movement of particles in a liquid is that complete deflocculation is assumed; if any flocculation exists, the settling rate is accelerated and  $d_e$  is not representative of the primary particles.

*Modal diameter,  $d_m$  or  $d_{mod}$ .* This diameter is obtained from the peak of the size-distribution curve. It is the diameter of the largest number of particles present in the sample. Since most pigment size distributions are unsymmetrical and right-skewed, this diameter emphasizes the contribution of fine particles. It is the smallest of the diameters computed from a frequency distribution.

*Median diameter,  $d_{med}$ .* This diameter is most conveniently obtained from a cumulative-frequency curve but it may be estimated also from tabulated data showing frequency against size group. It represents a particle of such diameter that the particles larger than the median are equaled in number by particles smaller than the median.

*Mean diameter:  $d_1$ ,  $d_{me}$ , or  $d_{av}$ .* This is an arithmetical average. As noted previously, the small particles in a pigment dispersion influence unduly the computed average. Most investigators consider the  $d_1$  diameter of least value and Dalla Valle<sup>1</sup> (p. 36) states that the arithmetic mean (as well as the median) have no physical significance and recom-

<sup>10</sup> H. Wadell, *J. Franklin Inst.*, **217**, 459-90 (1934).

mends averages that relate to measurable physical properties such as surface and volume. Despite the limitations of the  $d_1$  diameter, it is widely used.

*Mean length or length average:  $d_2$  or  $d_l$ .* This diameter is obtained by dividing the areas of the particles as projected by the summation of the diameters. It is evident that various dimensions may be employed for this calculation. For example, the area may be considered in terms of an equivalent square or circle. The total surface area of the particle is not involved in the computation.

*Mean volume-surface diameter,  $d_3$ ,  $d_{vs}$ , or  $d_a$ .* This diameter is obtained by dividing the total volume of all particles by the summation of the cross-sectional areas. It is, perhaps, the most important of the statistical diameters for analysis of fine powders, since it is now readily determinable by two reliable methods: adsorption of gases and particle-size counts from an electron micrograph. Computation of  $d_3$  from surface area, as determined from gas-adsorption data, is made by means of the following equation:

$$d_3 = \frac{6}{\text{Density} \times \text{specific surface}}$$

The factor 6 is valid theoretically for individual spheres of different sizes. When a shape factor is involved, as it is in the majority of powders, another factor must be used. Because of the difficulty in estimating such a factor with precision, it is usually assumed that 6 will give an adequate representation of the size. There is some experimental and theoretical justification for this assumption, except for particles of extreme asymmetry.

*Weight mean diameter,  $d_4$ .* This diameter is based on the surface area of a unit weight of particles. The fourth power in the equation is difficult to interpret, but the diameter is considered physically significant, giving a value larger than the other diameters. Perrott and Kinney<sup>2</sup> provide an example of a distribution in which the weight of one half of the particles is smaller than  $d_4$ , and that of the other half is larger than  $d_4$ .

*Mean surface diameter,  $\Delta$  or  $d_s$ .* This is the diameter of the particle of average surface area.

*Mean volume diameter,  $D$  or  $d_v$ .* This is the diameter of the particle of average volume.

Certain properties of the different statistical diameters are important. When the particles in a sample are perfectly uniform, the diameters become numerically identical. These diameters are also related mathematically in certain instances as follows:

$$\Delta = d_1 \times d_2$$

$$D = \sqrt[3]{d_1 \times d_2 \times d_3}$$

If the particle-size distribution is symmetrical, i.e., does not exhibit skewness, then the modal, median, and mean particle diameters are equal.

Of all the diameters listed above, the easiest to visualize in terms of geometrical shape and the size distribution are  $d_m$ ,  $d_{med}$ , and  $d_1$ . The

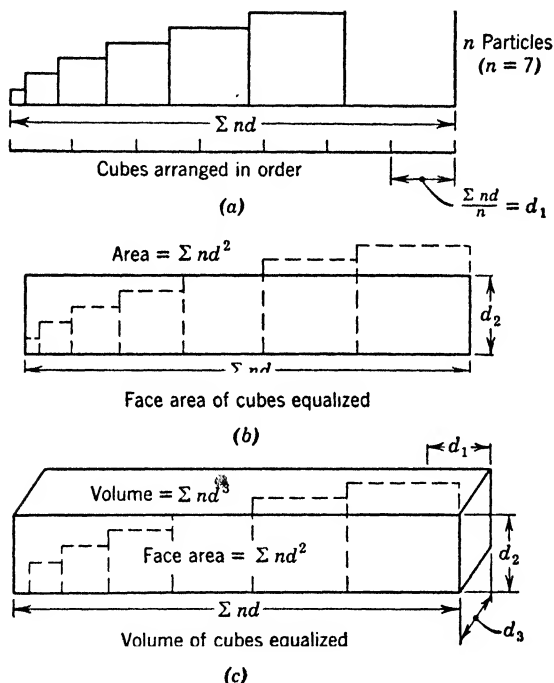


FIGURE 4. The geometrical relations between the diameters  $d_1$ ,  $d_2$ , and  $d_3$ . (After E. N. Harvey, Jr., with permission.)

idea of an equivalent sphere or a nominal sphere to represent an irregularly shaped particle can also be imagined. The relationship between  $d_1$ ,  $d_2$ , and  $d_3$  is more difficult, however, and the illustration devised by Harvey clearly shows the distinction. In Figure 4, a sample of cubes is shown. The top figure shows the face of the cubes, and the mean diameter  $d_1$  is the total length divided by the total number. If part of the face of the largest cubes is removed and added to the areas of the smaller cubes to give a rectangle equal in area to the total faces of the cubes, then  $d_2$  is the side of this rectangle (center figure). In a



similar way, a rectangular parallelepiped can be constructed with a volume equal to the total volume of the cubes in the sample; the dimension  $d_3$  results (bottom figure).

A particle-size distribution for a medium chrome-yellow pigment is shown in Figure 5. This curve was constructed by Harvey<sup>11</sup> from an

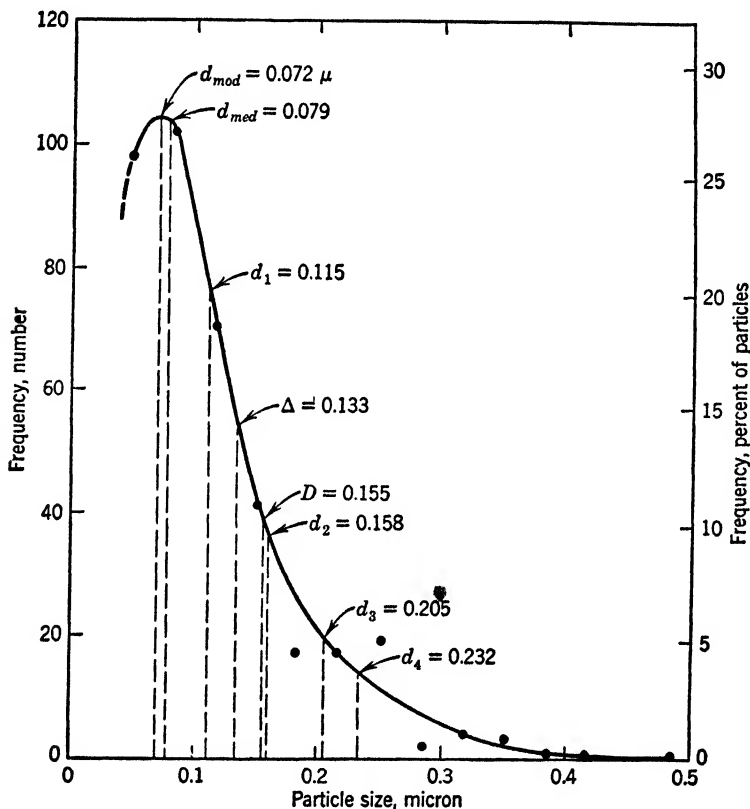


FIGURE 5. Particle-size distribution in a sample of chrome yellow, illustrating magnitudes of different average diameters. Data from an electron micrograph. (After E. N. Harvey, Jr., with permission.)

electron micrograph. The magnitude of each of the diameters described above is indicated on the curve. For special methods of computation from size-distribution data, the reader is referred to the papers by Austin,<sup>12</sup> Roller,<sup>13</sup> and Watson.<sup>14</sup>

<sup>11</sup> E. N. Harvey, Jr., *Interchem. Rev.*, **3**, 59-70 (1944).

<sup>12</sup> J. B. Austin, *Ind. Eng. Chem., Anal. Ed.*, **11**, 334-39 (1939).

<sup>13</sup> P. S. Roller, *J. Franklin Inst.*, **223**, 609-33 (1937).

<sup>14</sup> J. H. L. Watson, *Anal. Chem.*, **20**, 576-84 (1948).

## Uses of the different diameters

Which particle diameter should be assigned for specific applications is of considerable importance. Information available is not always sufficiently extensive to determine this point with certainty, but a few examples will illustrate. The total range of  $d$  values in the chrome-yellow size distribution cited by Harvey was 0.72 micron ( $d_m$ ) to 0.232 ( $d_4$ ), a factor of three. More than a tenfold difference was computed for pulverized coal by Perrott and Kinney.

In considering the optical properties of pigments, Clewell<sup>15</sup> states that in the region of Rayleigh scattering, the  $D$  diameter should be used since this is a volume effect. The arithmetical mean diameter  $d_1$  should be used in the diffraction range since this property depends on linear dimensions of the particle, and the surface-area diameter  $d_3$  should be used in the reflection range.

Gamble and Barnett<sup>16</sup> state that both the  $d_3$  and the  $d_4$  diameters have been correlated with pigment properties in rubber dispersion, but that the  $D$  diameter, frequently used, fails to account for the extent to which the larger particles determine the physical behavior of the rubber compound. The  $d_1$  diameter is considered the least significant of all for this purpose.

In the study of photographic plates for grain size and sensitivity, a diameter based on the projected area of the silver grains is used.<sup>17</sup> The projective area is useful for this purpose since it is proportional to the light-collecting power of the silver halide grains. Further, the effect of particle shape is minimized. The projective area is usually symbolized by  $\bar{a}$ .

Since the properties of a solid-liquid suspension are established in large degree by interfacial surface for a given volume of dispersed substance, the  $d_3$  diameter is one of the most useful of the statistical diameters. On the other hand, problems in coal and ore handling are considered most effectively analyzed by the  $d_4$  diameter.

## Surface roughness

Various methods have been devised to express surface roughness or *rugosity* (Latin, wrinkled). Robertson and Emödi<sup>18</sup> define coefficient of rugosity as the ratio of the measured specific surface to the hypothetical

<sup>15</sup> D. H. Clewell, *J. Optical Soc. Am.*, **31**, 521-27 (1941).

<sup>16</sup> D. L. Gamble and C. E. Barnett, *Ind. Eng. Chem., Anal. Ed.*, **9**, 310-4 (1937).

<sup>17</sup> C. E. K. Mees, *The Theory of the Photographic Process*, Macmillan, New York, 1946, pp. 50-1; R. P. Loveland, H. M. Menihan, and A. P. H. Trivelli, *J. Franklin Inst.*, **246**, 459-81 (1948).

<sup>18</sup> R. H. S. Robertson and B. S. Emödi, *Nature*, **152**, 539-40 (1943).

surface area computed from spherical particles. The reciprocal of rugosity is *sphericity*.<sup>19</sup> Several applications of the coefficient of rugosity are suggested, including the flow properties of dry powders, degree of aggregation of particles, and the compressive strength and plasticity of molding sands. Little information, however, is available on this correlation. Anderson and Emmett<sup>20</sup> compute a "roughness factor" as the ratio between the surface area measured by nitrogen adsorption to the area computed from electron micrographs. This ratio provides a measure of porosity, since the electron micrographs would not be expected to exhibit the fine capillary spaces which are available to nitrogen. As an example, one treated lampblack was found to have a roughness factor of 7.3, whereas an acetylene black gave a factor of 1.08. The latter value indicates an essentially non-porous structure.

### Measurement of Particle Size

Methods for particle-size measurement are listed in Table II and discussed briefly in the following sections.

TABLE II. RANGE OF METHODS FOR PARTICLE-SIZE MEASUREMENTS

Method	Approximate Useful Limits	Diameters Usually Computed
Sieving	> 45 $\mu$	$d_4$
Microscopy (white light)	100-0.25 $\mu$	$D, d_1, d_3$
Microscopy (ultraviolet)	1-0.11 $\mu$	$D, d_1, d_3$
Microscopy (electron) *	1-0.004 $\mu$	$D, d_1, d_3$
Ultramicroscopy †	2-0.01 $\mu$	$D$ only
Adsorption (gases) †	20-0.002 $\mu$	$d_3$ only
Adsorption (from solution) †	50-0.01 $\mu$	$d_3$ only
Sedimentation (gravity)	50-1.0 $\mu$	$d_e$
Sedimentation (centrifuge)	10-0.05 $\mu$	$d_e$
Elutriation	100-1 $\mu$	$d_e$
Permeability †	100-0.5 $\mu$	$d_3$ only
Diffusion †	100-0.1 $m\mu$	$d_3$
X-ray ††	10-0.01 $m\mu$	...
Turbidimetry †§	50-0.05 $\mu$	$d_1, d_3, D$

\* Theoretical limit of resolution variously stated but is estimated at ca. 6 Å; certain instruments now resolve to ca. 0.0015 micron.

† Single value: method does not give size distribution.

‡ Grain size in the microscopic range may also be observed.

§ Diameters in different ranges:  $d_1$  in diffraction;  $d_3$  in reflection;  $D$  in Rayleigh scattering.

<sup>19</sup> Cf. H. Wadell, *loc. cit.*

<sup>20</sup> R. B. Anderson and P. H. Emmett, *J. Applied Phys.*, **19**, 367-73 (1948).

## Sieving

The simplest method for an analysis of particle-size distribution is by means of a series of sieves of graded mesh. In practice, the powder is placed on the wire cloth and tapped or shaken until a separation of the material finer than the mesh size has passed through the sieve. By stacking a series of sieves, with the finest mesh at the bottom, fractionation of a sample may be accomplished in one operation. Each fraction is weighed, and the results are usually expressed in terms of sieve sizes, e.g., "plus 100," representing particles larger than the openings in a 100-mesh screen; "minus 100," representing particles finer than the openings in the 100-mesh screen. The fractions so obtained may be charted in a curve of size vs. weight.<sup>21</sup>

Sieve sizes commonly used in this country follow the U. S. Sieve Series proposed by the National Bureau of Standards in 1919 and adopted by the American Society for Testing Materials.<sup>22a</sup> In this series, a 1-mm. opening is used as the basis for spacing, and the gradation in size progresses in the ratio of  $\sqrt{2}$  to 1 for the fine series. The range of the sieves is from 5,660 micron (No. 3 $\frac{1}{2}$ ) to 37 micron (No. 400). (A second "coarse" series of sieves ranges from  $\frac{1}{4}$ -inch to 4 $\frac{1}{4}$ -inch openings.)

Precise details for making sieve analyses are given in various standard test methods. For coarse particles, sieving is the only method that can be used to classify the size fractions. With finer particles, such as pigment-grade materials, sieve analysis is used to standardize the product for shipment and to determine the amount of oversize material present. Generally the methods may be classified either as dry or wet sieving, and various mechanical means, such as shaking and vibrating machines, are employed to obtain uniformity in agitation. Many dry powders "ball up" on agitation, and separation into fractions then becomes impossible. For such powders and for dispersions of pigments in the form of pastes or paints, various modifications of the wet method are used.<sup>22b</sup> In these procedures water or a suitable solvent is mixed with the material, and the suspension is run through the sieve. Additional water or solvent is

<sup>21</sup> Additional information on particle-size determinations by sieving will be found in Dalla Valle, *Micromeritics*, Chapter 5; A. F. Taggart, *Handbook of Mineral Dressing*, John Wiley & Sons, Inc., New York, 1945, pp. 7-01 to 7-72; A. M. Gaudin, *Principles of Mineral Dressing*, McGraw-Hill Book Co., Inc., New York, 1939; Chapters 3 and 7.

<sup>22a</sup> American Society for Testing Materials, "Sieves for Testing Purposes," E 11-39.

<sup>22b</sup> American Society for Testing Materials, "Coarse Particles in Pigments, Pastes, and Paints," D 185-45.

then sprayed onto the residue on the sieve, and, to facilitate passage through the screen, the residue is stroked with a camel's-hair brush in prescribed manner. These methods isolate oversize particles, grit, tailings, skins, etc., but can offer no indication of the actual particle size of the powder.

Sieving has been found to take place in two stages. The fine particles pass through the sieve in the first stage of shaking, but particles approximating the dimensions of the openings come through more gradually and at a diminishing rate. Wet sieving greatly increases the total amount of material passing through.

The accuracy with which a sieve analysis can be made depends on many factors. One source of error, which is frequently overlooked, is the gradual distortion of the wire cloth through abrasion, corrosion, and abuse. If only a small percentage of the openings in the sieve is enlarged, an appreciable error occurs in the fractionation. In order to reduce such errors, it is advisable to retain one set of sieves for calibrating purposes and to replace the service sieves at intervals. Rittenhouse<sup>23</sup> found that the effective size of the sieve openings was larger than the rated size. Two factors were considered: (1) the presence of a few oversize openings in the sieve and (2) the passage of flattened grains diagonally through the sieve openings. Fritts<sup>24</sup> offers some experimental evidence that the 325-mesh sieve separates at 45 microns, but many investigators take 60 microns as the upper size limit of particles that pass through the mesh.

Simple, low-cost methods for preparing powders, suitable for reference standards, are described by Gooden and Updike.<sup>25</sup> Glass beads used for coating projection screens are separated by sieving, and non-spherical particles are removed by causing the particles to roll down an inclined vibrating plane surface. Separation is accomplished because the non-spherical particles are stalled on the slope. Particles so prepared are relatively coarse, however, being in the neighborhood of 100 microns in diameter. The second method described preparation of rod-shaped particles from glass wool by grinding in a hammer mill. A product made from a laboratory grade of glass wool was quite uniform in diameter (8 microns) and varied from 30 to 500 microns in length. The preparation of glass spheres has been described by Bloomquist and Clark<sup>26</sup> and by Sollner.<sup>27</sup>

<sup>23</sup> G. Rittenhouse, *Ind. Eng. Chem., Anal. Ed.*, **15**, 153-55 (1943).

<sup>24</sup> S. S. Fritts, *ibid.*, **9**, 180-1 (1937).

<sup>25</sup> E. L. Gooden and R. L. Updike, Jr., *ibid.*, **18**, 802 (1946).

<sup>26</sup> C. R. Bloomquist and A. Clark, *ibid.*, **12**, 61-62 (1940).

<sup>27</sup> K. Sollner, *ibid.*, **11**, 48-49 (1939).

### Optical microscopy

Until the electron microscope became available in the 1930's in a form practical for commercial use, the optical microscope was the only instrument that could be used to delineate form and size. The limit of resolution was fixed by the laws of optics, and painstaking effort was expended by many investigators to make every possible gain in resolution. Expedients that improved the technique included refinements in mechanical adjustment, rigid supports, control of illumination with special light sources and filters, selection of lenses, etc. The gain through perfection of technique was appreciable, but the barrier to the limit of resolution could not be surmounted, and many particles of great industrial interest were definitely below the visibility limit. Nevertheless, some insight was obtained on the shape and size of fine particles.

In Table III the limits of resolution for different optical systems are tabulated. This table is based largely on the compilation by Green and

TABLE III. LIMITS OF RESOLUTION FOR OPTICAL MICROSCOPY

Type of Lens	Radiation Region	Wavelength ( $\mu$ )	Numerical Aperture	Resolution Limit ( $\mu$ )
Glass	Yellow	0.58	1.40	0.25
Glass	Blue	0.44	1.40	0.19
Glass	Ultraviolet	0.365	1.40	0.16
Quartz	Ultraviolet	0.275	1.25	0.134
Quartz	Ultraviolet	0.257	1.25	0.125
Quartz	Ultraviolet *	0.275	1.25	0.11

\* Oblique illumination.

Fullam<sup>28</sup> and represents the considered experience of many authorities. In terms of actual equipment, the objectives are assumed to be selected apochromats with appropriately matched oculars and condensers. Thus under the best conditions, a particle below 0.11 micron in a minimum dimension would just be resolved with ultraviolet illuminant and quartz lenses. The usual microscopic equipment for visual observation would resolve particles 0.25 micron and above. The resolving power of a microscope is the minimum distance separating two points in an object that is just discernible to an observer.

When one is working with objectives of short focal length, necessary for resolving very small particles, the depth of field (i.e., the vertical resolution through which sharpness of the image is obtained) becomes

<sup>28</sup> H. Green and E. F. Fullam, *J. Applied Phys.*, **14**, 332-40 (1943).

very small. For example, a 2-mm. apochromat has a depth of field of approximately 0.5 micron.

The limit of the resolving power is largely a theoretical figure. To the microscopist, the images of particles too close to the limit become unsharp, or the fine detail in an aggregate is completely lost and the aggregate then appears convincingly like a single or primary particle instead of a cluster. Frequently such particles appear as spheres (or circles in the field as viewed), and actual differences in size are lost. In general there is a "rounding" of non-spherical particles as the limit of resolution is approached, and the net effect is an apparent slight change in size.

The effect of particle shape on the image formed near the resolving limit has been investigated by Borries and Kausche<sup>29</sup> and discussed in the comparison of optical and electron microscopes by Brubaker.<sup>30</sup> For regular polygons there is a limiting ratio between the resolving power of the microscope and the area of an equivalent circle above which the particle is not resolved in its actual shape. If  $d_c$  is the diameter of a circle with the same area as that of the silhouette of a regular polygon, and  $r$  is the limit of resolution of the microscope, then the ratio  $d_c/r$  must not exceed the limiting values given below:

Geometrical Shape	$d_c/r$
Equilateral triangle	2.4
Square	3.9
Hexagon	6.8
Octagon	9.5
Dodecagon	14.8

If this criterion is adopted as a bench mark for the performance of the optical microscope, the particle size should exceed the resolution of the lens system by a factor approximately equal to the number of sides of the polygon. Particles of certain typical pigments, for example, must be greater than 0.6 micron to have the optics of the microscope delineate geometrical form with fidelity.

The preparation of the microscope mount of the fine particles is a critical step in the method. For dry pigments the technique described by Green<sup>31</sup> is widely used. About a milligram of the powder is placed on a microscope slide, and a drop of redistilled turpentine is added. The

<sup>29</sup> B. V. Borries and G. A. Kausche, *Kolloid-Z.*, **90**, 132-41 (1940).

<sup>30</sup> D. G. Brubaker, *Ind. Eng. Chem., Anal. Ed.*, **17**, 184-87 (1945).

<sup>31</sup> H. Green, *J. Franklin Inst.*, **192**, 637-66 (1921); *Ind. Eng. Chem.*, **16**, 677-80 (1924).

powder and the liquid are mixed with the side of a glass rod, the dispersion being rubbed backward and forward over the central area of the slide. The slide may be warmed slightly to hasten evaporation of the turpentine, and the rubbing is continued until the particles appear fixed on the slide. On the last stroke, the rod is lifted slightly so as to leave the film in the form of a wedge. A gradient of particles is thus formed. The method has the following advantages: the particles are affixed to the slide and in a thin layer; they are free from any streaming motion (as in a fluid mount) and from Brownian motion; the particles will not have a chance to flocculate. For small particles the aggregates are broken down but there is no severe grinding action; however, where large particles (in the sieve range) are to be studied, some distortion may occur unless the mixing is very gentle.

The slide so prepared is ready for observation. The medium used for mounting should have a refractive index sufficiently different from that of the pigment to give good contrast. The preparation is then photographed in the standard way at a suitable magnification, and, in the procedure used by Green, the negative is placed in a lantern slide projector, and the particles in the projected image are measured. It is possible to adjust the projection distance in such a way as to have a simple ratio between the initial magnification and the projected image. At least 200 particles are measured and tallied, those out of focus being eliminated. The negative provides a record of the measurement. Alternatively, photographic enlargements may be made, and the particle size count taken from the print.

The difficulty with a photomicrograph is that the plane of focus is fixed and particles that lie outside the limits for sharp focus cannot be considered. This difficulty is avoided by projecting the original slide by means of a microprojector. With a remote control for the fine adjustment on the microscope, the operator, standing near the projection screen, can quickly focus each individual particle at the time of measurement. This procedure was described by Dunn.<sup>32</sup> A similar arrangement for particle-size measurements on emulsion particles was used by the author.<sup>33</sup> Calibration of the microscope and projection system is easily accomplished by means of a stage micrometer.

Other materials may be used for dispersion and attachment of the particles to the slide. Collodion or its equivalent, such as one of the general purpose household cements, is mixed with the pigment and

<sup>32</sup> E. J. Dunn, *Ind. Eng. Chem., Anal. Ed.*, **2**, 59-62 (1930).

<sup>33</sup> E. K. Fischer and W. D. Harkins, *J. Phys. Chem.*, **36**, 98-110 (1932).



kneaded with a dissecting needle. When the mass is very viscous, it is spread in a thin layer, and a small bit is subsequently reduced with additional cement or a lacquer solvent.<sup>34</sup> Dammar gum may be used for the mount.<sup>35</sup> After dispersing the pigment in turpentine, it is gathered in the center of the microscope slide, heated to evaporate the remainder of the turpentine, and covered with dammar which is melted under the cover glass.

Disruption of aggregates by these procedures is incomplete. Gehman and Morris<sup>36</sup> advocate dispersion of the pigment in rubber on a two-roll mill and subsequent solution of the mill-ground sheet in xylene. Methods intended for electron microscope mounts are also useful.<sup>37</sup>

It is frequently necessary to observe and to photograph pigment dispersions in oil or resinous vehicles. Here the pigment is present usually in a rather high concentration, and dilution is necessary. The liquid used for dilution should be the same as that of the dispersion; if it is unavailable, a quantity of the dispersion may be separated by high-speed centrifuging and the clear supernatant liquid removed. Dilution can be accomplished by placing a small quantity (1 to 2 milligrams) of the dispersion on a microscope slide, covering with a drop of the clear vehicle, and then placing a cover glass on the preparation. Gentle pressure will cause the pigment dispersion to spread along with the vehicle, and the character of the dispersion can be judged by examining the region where the clear vehicle is diluting the concentrated dispersion. A gradient is usually formed, and the material in the specimen is likely to be streaming for some time. If photomicrographs are to be taken, a very short exposure time and high light intensity are required.

If a larger field is desired, as in the scanning of mill samples for over-size particles, it is feasible to stir the small quantity of dispersion with the vehicle on the slide by means of a thin glass rod. Stirring is sometimes accomplished by mashing the cover glass on the slide and sliding it over the dispersion with a rotary motion. This procedure can lead to the formation of artifacts, and it may also set up sufficient shearing forces to break up aggregates.

It may be seen that the region for greatest utility for the optical microscope is from 0.5 micron upwards into the sieve-size range, roughly 0.5 micron to 100 microns. This is not to be interpreted as meaning that the microscope cannot be employed to advantage with particulate ma-

<sup>34</sup> R. P. Allen, *Ind. Eng. Chem., Anal. Ed.*, **14**, 92-94 (1942).

<sup>35</sup> G. S. Haslam and C. H. Hall, *J. Franklin Inst.*, **209**, 777-89 (1930).

<sup>36</sup> S. D. Gehman and T. C. Morris, *Ind. Eng. Chem., Anal. Ed.*, **4**, 157-62 (1932).

<sup>37</sup> M. C. Schuster and E. F. Fullam, *Ind. Eng. Chem., Anal. Ed.*, **18**, 653-57 (1946).

terials to a point near the limit of resolution, but the difficulties in manipulation increase, and for fine particles the electron microscope provides more certain information. It is in the region above 0.5 micron that the counting technique described by Fairs<sup>38</sup> appears useful. Special slides are prepared which hold a quantity of suspension; observation and counting are performed in a routine way. Alternatively, the haemacytometer cells used in blood tests can be used.

Many helpful suggestions for the use of the microscope and for taking photomicrographs will be found in the treatises by Shillaber,<sup>39</sup> Gage,<sup>40</sup> and Chamot and Mason.<sup>41</sup>

### Ultramicroscopy

Because of the resolving limits of the optical microscope, attempts were made to make particles below this limit visible by means of the well-known Tyndall effect. In the form of the slit ultramicroscope, described by Siedentopf and Zsigmondy in 1903, a strong pencil of light illuminates a suspension at right angles to the axis of the lens system. The particles present appear as scintillating spots of light, but an image of the particle, showing form and size, is not obtained. Particles that are observable in this way by means of the ultramicroscope but are unresolved in usual microscopic lens systems have been termed *submicroscopic*, and particles that are still smaller, undetected in the ultramicroscope, have been termed *amicrons*. Other types of illumination are used to give the so-called dark-field system; the cardioid condenser is in this class.

The ultramicroscope in various forms has been used for particle-size determination. In this procedure, a colloidal sol, containing a known weight of suspended material, is viewed, and the number of particles in a known volume of the suspension counted. From these data, and the density of the substance, the  $D$  diameter may be computed. The ultramicroscope is little used now for particle-size studies, although it provided useful information on submicroscopic particles before the electron microscope with its superior resolving power was available. Thus Gehman and Morris<sup>36</sup> obtained particle-size values for carbon black that were more credible than other values.

A description of this instrument will be found in most books on colloid

<sup>38</sup> G. L. Fairs, *Chemistry & Industry*, **62**, 374-78 (1943).

<sup>39</sup> C. P. Shillaber, *Photomicrography in Theory and Practice*, John Wiley & Sons, Inc., New York, 1944; cf. especially pp. 602-12.

<sup>40</sup> S. H. Gage, *The Microscope*, Comstock Publishing Co., Inc., Ithaca, N. Y., 1936.

<sup>41</sup> Chamot and Mason, "Handbook of Chemical Microscopy," John Wiley & Sons, Inc., New York, Vol. I, Second edition, 1938; Vol. II, First edition, 1940.

chemistry; details on its applications and limitations are given by Foster,<sup>42</sup> Freundlich,<sup>43</sup> and Zsigmondy.<sup>44</sup>

### Electron microscopy

From the theory of the microscope, it has long been known that lower resolution limits could be obtained only by use of radiation of far shorter wavelength than that of visible light. As noted above, radiation in the ultraviolet region of the spectrum permits resolution to 0.11 micron. To adopt radiation of wavelength shorter than 0.2 micron (2,000 Å) is impracticable because of difficulties in lens design and sensitivity of photographic materials. The wave character of the electron, however, offers a means to overcome this barrier: an electron beam accelerated by 60 kilovolts has a wavelength equivalent of 0.00005 micron (0.05 Å), to be compared with 0.5 micron (5,000 Å) for light. There has been considerable discussion on the resolution and detection limits of the electron microscope, but a lower limit of about 0.001 micron (10 Å) has been achieved. Commercial models as usually operated resolve effectively discrete particles of about 0.004 micron (40 Å). With a magnification approximately 100× greater than the optical microscope, the electron microscope actually opened to direct view a new realm of small dimensions bordering on molecular sizes. .

In certain respects the electron microscope and optical microscope have analogous features. The electron beam replaces the light beam and electrostatic or electromagnetic fields serve as lenses, but the analogy ends at this point. The beam is generated and propagated through a vacuum of at least  $10^{-4}$  mm. mercury, impinging on the object in the course of its path. The electrons in the beam are scattered and transmitted in proportion to the density and thickness of the object; the altered beam strikes a phosphor-coated screen where the luminescent image can be seen. This screen also serves as the shutter for the photographic plate positioned beneath it. One characteristic of electron microscopy is great depth of focus which permits studies of structure within the specimen by means of stereographs.<sup>45</sup>

<sup>42</sup> L. V. Foster, *Physics*, **1**, 154–59 (1931).

<sup>43</sup> H. Freundlich, *Colloid and Capillary Chemistry*, translated by H. S. Hatfield, Methuen & Co., London, 1926, pp. 387–90.

<sup>44</sup> R. Zsigmondy, *Colloid Chemistry*, Vol. I, Chapter 54, pp. 817–19, J. Alexander, Editor, Chemical Catalog Co. (Reinhold Publishing Corp.), New York, 1926. See also M. Poser, *ibid.*, Chapter 53, pp. 814–16.

<sup>45</sup> The subject of electron microscopy is covered in the comprehensive monograph by V. K. Zworykin, G. A. Morton, E. G. Ramberg, J. Hillier, and A. W. Vance, *Electron Optics and the Electron Microscope*, John Wiley & Sons, Inc., New York, 1945. Other references of value are E. F. Burton and W. H. Kohl, *The Electron*

Powdered solids are effectively resolved by the electron microscope, for the density of these materials is usually sufficiently high to scatter and absorb electrons, and the resulting image has high contrast. Details on the instrument and its operation are not included in this discussion, for these have been adequately covered in the references cited; instead, it appears desirable to mention some features of the technique concerned primarily with dispersion of the solid and with interpretation of the micrographs. A summary of results reported in the literature, supplemented by observations of the writer, is given later in this chapter.

In the preparation of powdered substances for the electron microscope, several procedures are currently used.<sup>46</sup> The particles require a supporting film which is attached to a fine-mesh screen (200 mesh); this screen is placed in the specimen holder of the electron microscope. A suitable mount consists of a dispersion of pigments with a sufficient number of particles to provide a representative array and spaced to allow observation and measurement. In one procedure, described by Fuller, Brubaker, and Berger,<sup>47</sup> the pigment or other powdered material is dispersed in nitrocellulose by mulling the powder first in a 1 percent solution of poppyseed oil in amyl acetate and, when this is nearly dry, adding a 2 percent solution of nitrocellulose in the same solvent. Mulling is continued until the solvent is nearly evaporated, and the paste becomes very viscous, in order to increase the shearing forces imparted to the mixture; further dilution of the concentrate with solvent then gives a fluid suspension. Schuster and Fullam<sup>46</sup> use the edge of a spatula on a glass with a finely ground surface to knead the pigment into the nitrocellulose or other film-forming binder. A mill dispersion of the pigment in nitrocellulose or other binder may be used after suitable dilution. The dispersion of powders for use with silica replicas in the electron microscope is described by Gerould.<sup>48</sup> The procedure consists in grinding the powder, by means of a mortar and pestle, into a vehicle of ethyl cellulose

*Microscope*, Second edition, Reinhold Publishing Corp., New York, 1946, and D. Gabor, *The Electron Microscope*, Chemical Publishing Co., Inc., 1948. For a popular treatment of the subject see G. G. Hawley, *Seeing the Invisible*, A. Knopf, New York, 1946. An extensive bibliography of original research papers has been compiled by C. Marton and S. Sass, *J. Applied Phys.*, **14**, 522-31; **15**, 575-79 (1944); **16**, 373-78 (1945).

<sup>46</sup> For a thorough discussion of the requirements for electron microscope mounts and procedures for dispersing pigments, see the article by M. C. Schuster and E. F. Fullam, *Ind. Eng. Chem., Anal. Ed.*, **18**, 653-57 (1946); cf. also, Zworykin, and *The Practice of Electron Microscopy*, D. G. Drummond, Editor, The Royal Microscopical Society, London, 1950, especially pp. 31-44.

<sup>47</sup> M. L. Fuller, D. G. Brubaker, and R. W. Berger, *J. Applied Phys.*, **15**, 201 (1944).

<sup>48</sup> C. H. Gerould, *J. Applied Phys.*, **18**, 333-43 (1947).

formulated as follows: 2 percent ethyl cellulose, 70 percent amyl acetate, and 30 percent ethyl alcohol. The mulling is continued until a "thick paste" is formed, and additional amyl acetate is then mixed in slowly until the dispersion is diluted to an extent suitable for addition to the silica substrate. This procedure is stated to have no effect on the size and shape of particles of less than 5 microns.

Techniques using mechanical vibrators (about 15,000 cycles per second) and ultrasonic radiation have been used to disintegrate air floccules when the powdered material is placed on a film cast on a microscope slide. A vibrating muller has been described by O'Brien.<sup>49</sup>

A spark discharge has proved useful for carbon black dispersions.<sup>50</sup> Filmless mounts have also been used,<sup>51</sup> and particles may be "captured" from a smoke or by atomizing a solution.<sup>52</sup> A replica method for vulcanized rubber dispersions of carbon black has been used by Ladd,<sup>53</sup> but definition is inferior to other methods.

The material forming the film must meet several requirements: it must have sufficient strength to withstand handling and to retain its shape in the electron beam; it must be thin enough to transmit electrons without forming an image by itself; it must be inherently a poor electron scatterer. Nitrocellulose, ethyl cellulose, polyvinyl formal polymer, polystyrene, and cellulose acetate meet these requirements when properly formulated. In order to obtain a thin film, a solvent cut of the dispersion in the resin is spread on a water surface which has been cleaned of surface contamination by sweeping with paraffin-covered rods. A portion of the film is removed and placed on the supporting screen. After drying the specimen is introduced into the column of the electron microscope.

There are, of course, problems of specimen preparation which investigators using the electron microscope need to consider. For particle-size studies, it is necessary that several preparations be examined, for the field of the electron microscope is necessarily small and sampling errors can occur. By working with the optical microscope and scanning each preparation before electron microscopy, such errors can be reduced. There remains, however, the possibility that only the finer particles are observed in the field if any segregation occurred in forming the mount. The aggregates observable in many electron micrographs have an unknown character, and the question of whether or not such clusters are

<sup>49</sup> H. C. O'Brien, *Science*, **103**, 429 (1946).

<sup>50</sup> W. A. Ladd and W. B. Wiegand, *Rubber Age* (N. Y.), **57**, 299-307 (1945).

<sup>51</sup> J. H. L. Watson, *J. Applied Phys.*, **17**, 121-27 (1946).

<sup>52</sup> E. F. Burton, *Nature*, **152**, 540 (1943); A. M. Gravath, A. E. Smith, J. R. Vinograd, and J. N. Wilson, *J. Applied Phys.*, **17**, 309-10 (1946).

<sup>53</sup> W. A. Ladd, *Ind. Eng. Chem., Anal. Ed.*, **16**, 642-44 (1944).

ultimate working particles or impermanent aggregations caused by the mounting technique can be answered only by systematic variations in the preparation of the specimen. Some investigators consider particle-size distribution counts from electron micrographs to be uncertain unless several thousand particles are counted from electron micrographs made with different mounts.

One source of error in particle-size data obtained from electron micrographs has been noted by Watson.<sup>54</sup> This error arises from an increase in the mean size of the acetylene carbon black as a result of the electron bombardment. The change is appreciable, amounting to 70 percent in 5 minutes. The appearance of the particles changes also. The crystalline character of the particles is lost after a few minutes' bombardment, changing from straight-edged to rounded or oval. At the same time the over-all contrast of the image is lost, and the chains of particles merge into clumps.

This effect is most prominent in filmless mounts of the carbon-black pigments and can be diminished in pigment samples mounted on a supporting film. There is no assurance that the artifact is eliminated by the latter method, however, and the possibility of other effects, due to shrinkage and evaporation, remains.<sup>55</sup>

To operate the electron microscope with a minimum of change in the specimen, Watson suggests the following rules: (1) maintain minimum electron-beam intensity; (2) focus on a part of the specimen field that is not to be photographed; (3) take micrographs as rapidly as possible; and (4) avoid fields near the supporting grid. Further discussion of the "growth" of particles in the electron beam has been given by Cosslett,<sup>56</sup> and the pseudostructures that may appear have been described by Watson.<sup>57</sup> The heating effect of the electron beam is the primary cause of the changes which include melting, evaporation, sublimation, alteration in crystalline state, and movement of the material.

Changes in organic pigments during irradiation in the electron microscope have been described by Hamm and Van Norman.<sup>58</sup> Both indanthrene blue and copper phthalocyanine were transformed to stable forms, and evidence was obtained that the pigments existed in different crystalline structures. Variations in hue, usually ascribed to differences in particle size, are attributed by these authors to such polymorphism.

<sup>54</sup> J. H. L. Watson, *J. Applied Phys.*, **18**, 153-61 (1947).

<sup>55</sup> J. H. L. Watson, *J. Applied Phys.*, **17**, 121-27 (1946); L. Marton, N. N. Das Gupta, and C. Marton, *Science*, **104**, 35-36 (1946).

<sup>56</sup> V. E. Cosslett, *J. Applied Phys.*, **18**, 844-45 (1947).

<sup>57</sup> J. H. L. Watson, *ibid.*, **19**, 713-20 (1948).

<sup>58</sup> F. A. Hamm and E. Van Norman, *ibid.*, **19**, 1097-1109 (1948).

### Adsorption of gases and vapors

The adsorption method for particle-size determination has been extensively exploited only since about 1938, although the study of adsorption of gases by solids is one of the oldest research topics of physical chemistry. Adsorption (from the Latin, *ad* and *sorbere*, "to suck in") refers to the concentration of a substance at a surface or interface, whereas absorption refers to penetration of the mass of a substance. Generically, *sorption* is used to designate the phenomena of both adsorption and absorption. The substance on which an adsorption occurs is termed the adsorbent, and the gas (or other material) that enriches the interface is designated the *adsorbate*.

The literature on the subject is extensive as shown by the comprehensive bibliography prepared by Dietz<sup>60</sup> and by the monographs by McBain,<sup>60</sup> Brunauer,<sup>61</sup> and Mantell.<sup>62</sup> Extensive industrial applications of adsorption make it one of the most important subjects in chemistry and engineering. For our purposes we shall have occasion to refer only to the procedure for the calculation of particle sizes.

The experimental measurement of adsorption requires some means for measuring the amount of gas adsorbed as a function of pressure. The volume is expressed, usually, in cc. of gas per gram of the powdered solid, and the resulting data are plotted to show the amount of gas adsorbed as the pressure is varied with the temperature remaining constant. An isotherm of this type is reproduced in Figure 6.

Numerous measurements by many investigators on all types of solids led to a general mathematical expression which is usually known as the Freundlich adsorption equation. This equation is of wide applicability for both vapor-phase and liquid-phase adsorptions: it has the form,

$$\frac{x}{m} = Kp^{1/n} \text{ or } Kc^{1/n} \quad (1)$$

where  $x$  is the total amount of gas adsorbed on  $m$  weight of adsorbent,  $p$  is the pressure of the gas,  $c$  the concentration of a dissolved substance, and  $K$  and  $n$  are constants.<sup>63</sup> The value of  $n$  varies between 1 and 5. When adsorption data for many classical systems are plotted as  $\log x/m$

<sup>60</sup> V. R. Dietz, *Bibliography of Solid Adsorbents*, United States Cane Sugar Refiners and the National Bureau of Standards, Washington, D. C., 1944.

<sup>60</sup> J. W. McBain, *The Sorption of Gases and Vapours by Solids*, G. Routledge & Sons, Ltd., London, 1932.

<sup>61</sup> S. Brunauer, *Physical Adsorption*, Princeton University Press, Princeton, N. J., 1943.

<sup>62</sup> C. L. Mantell, *Adsorption*, McGraw-Hill Book Co., Inc., New York, 1945.

<sup>63</sup> H. Freundlich, *Colloid and Capillary Chemistry*, H. S. Hatfield translator, Methuen & Co., Ltd., London, 1926; pp. 110-2.

vs.  $\log p$ , straight lines result. Although this equation has proved of considerable utility, it is largely empirical, and the desire to explain adsorption mechanisms in terms of molecular properties of the adsorbate made other approaches, theoretical in character, more attractive. Of these the Langmuir adsorption isotherm is perhaps the most important. This equation was based on the idea of a monomolecular layer of gas molecules adsorbed on the solid and was derived from the kinetics of condensation and evaporation of gases at the surface of the solid.<sup>64, 65</sup> Certain assumptions are involved in the equation: the surface of a solid is considered a space lattice of atoms, and the vacant areas above and between atoms offer a place for a "condensed" gas molecule; at equilibrium, the rates of evaporation and condensation are equal; adsorbed molecules are assumed to have no influence on adjacent molecules, their effect being confined to the portion of the lattice occupied; further, the surface is considered homogeneous. The Langmuir adsorption equation may be expressed as follows:

$$A = \frac{aBp}{1 + ap} \quad (2)$$

where  $A$  is the fraction of the surface covered,  $p$  is the equilibrium pressure and  $a$  and  $B$  are constants.

The Langmuir equation has several advantages. The constants have a theoretical basis, and it accords well with experimental values, although over a narrower pressure or concentration range than the Freundlich isotherm, being especially useful at low pressures. Some isotherms, however, indicate an increased adsorption at higher pressures, and for these isotherms the Langmuir relationship is inapplicable. Further, the concept of a monomolecular layer of adsorbate molecules becomes untenable in light of considerable experimental evidence. A notable advance was made, beginning in 1935, by Brunauer, Emmett, and Teller (now abbreviated BET) for the practical application of adsorption methods and data to finely powdered as well as porous materials. The idea of multi-layer adsorption formed the basis for the departure from the Langmuir treatment.<sup>66, 67</sup>

<sup>64</sup> I. Langmuir, *Phys. Rev.*, **8**, 149 (1916); *J. Am. Chem. Soc.*, **37**, 1139 (1915); *ibid.*, **40**, 1361 (1938).

<sup>65</sup> For an analysis of the theory underlying the Langmuir equation, see E. K. Rideal, *An Introduction to Surface Chemistry*, Cambridge University Press, 1930, pp. 182-202; and H. Freundlich, *Colloid and Capillary Chemistry*, pp. 130-2.

<sup>66</sup> An important contribution was made by A. F. Benton and T. A. White, *J. Am. Chem. Soc.*, **54**, 1820-30 (1932). These investigators attributed discontinuities in their adsorption isotherms to the formation of single and double layers of molecules on the adsorbent.

<sup>67</sup> S. Brunauer and P. H. Emmett, *ibid.*, **57**, 1754 (1935); *ibid.*, **59**, 2682-89 (1937).



In the conventional plot of volume of adsorbed gas vs. pressure, an S-shaped curve frequently results. Initially at low pressures the uptake of adsorbate is large, then as the pressure is increased an approximately linear relationship is reached, and finally at high pressures an enhanced adsorption is observed. If the discontinuity in the curve is taken as indicating the completion of a monomolecular layer of molecules adsorbed on the solid surface, then means are at hand for estimating quantitatively the surface area of the adsorbate. The principle of the method may be outlined as follows: (1) an adsorption curve is obtained experimentally and the point at which a monomolecular layer of the adsorbate is completed is estimated; (2) the average cross-sectional area of the molecules of the adsorbate is calculated independently from the density of the liquefied or solidified adsorbate, assuming close packing; (3) the specific surface of the solid is computed from the number of adsorbed molecules and their total area.

In the first work, the linear part of the curve was extrapolated to the pressure axis; the intercept was designated "Point A." Other investigators have also used a similar extrapolation of the isotherm to indicate the volume of gas corresponding to a monomolecular layer. Further work with different gases as adsorbates led to the conclusion that the beginning of the linear part of the isotherm, designated "Point B," was a better selection for an empirical point for this computation.<sup>66,67</sup> (See Figure 6.) Data for surface-area computations could thus be obtained merely by inspection of the adsorption curve. In 1938, the theory was developed mathematically and a third method for plotting and computing the volume of gas corresponding to a monomolecular film was described.<sup>68</sup>

The BET equation follows:

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m c} + \frac{(c - 1)p}{V_m c p_0} \quad (3)$$

In this equation  $V$  is the volume of gas adsorbed at  $p$  pressure,  $p_0$  is the saturation pressure at the temperature at which the measurement is made;  $V_m$  is the volume of gas forming a monolayer; and  $c$  is a constant. The constant  $c$  is related to the heat of adsorption of the adsorbate. When  $p/V(p_0 - p)$  is plotted as the ordinate and  $p/p_0$  as the abscissa, the straight line resulting permits easy computation of the terms in the equation. From the slope and intercept,  $V_m$  and  $c$  can be calculated (Figure 7). The usual range of the ratio  $p/p_0$  is 0.05 to about 0.35.

Experimental measurements are made in a standard way at temperatures near the boiling point of the adsorbate. The powdered solid is

<sup>68</sup> S. Brunauer, P. H. Emmett, and E. Teller, *ibid.*, **60**, 309-19 (1938).

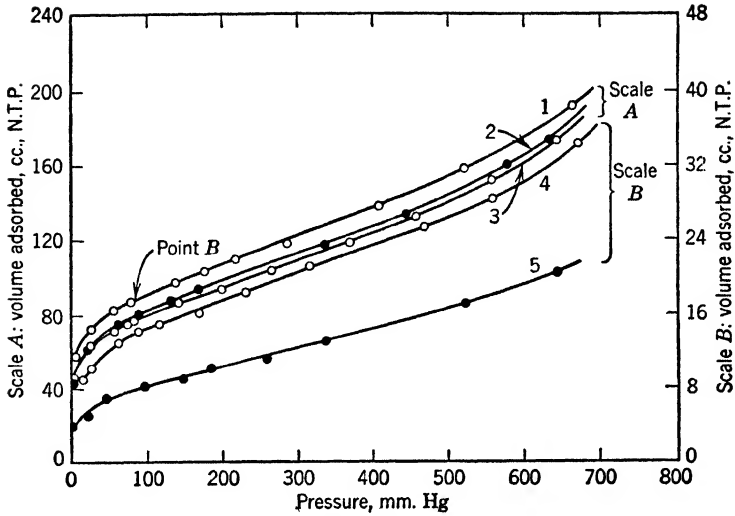


FIGURE 6. Adsorption of nitrogen on carbon blacks at liquid nitrogen temperatures. (Legend: (1) 3.29 g. Arrow Black; (2) 3.09 g. Micronex; (3) 2.95 g. Wyex; (4) 2.86 g. P-33; (5) 5.50 g. Thermatomic.) (After P. H. Emmett, with permission.)

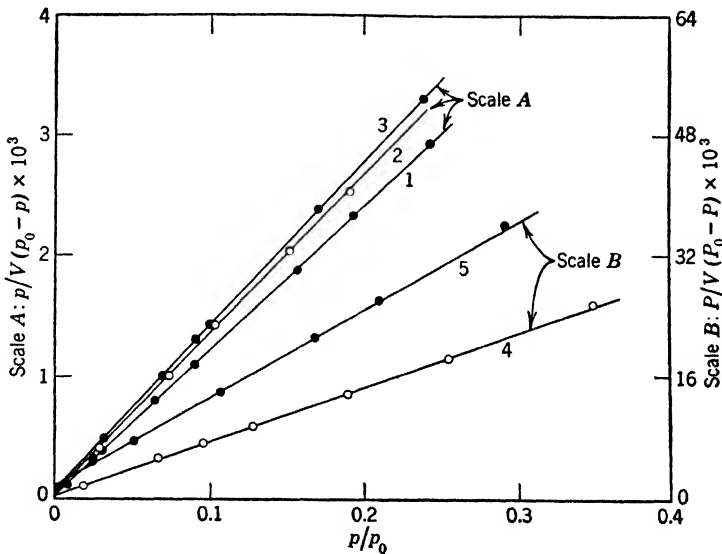


FIGURE 7. Adsorption data for nitrogen on carbon blacks plotted according to the BET equation. (Legend, same as Figure 6.) (After P. H. Emmett, with permission.)

placed in a glass bulb, sealed into a vacuum system, and the "dead space" around the adsorbent and in connecting tubes is measured with helium (which is not adsorbed). The volume of nitrogen, butane, or other gas taken up by the powder is then measured at a series of pressures, and correction for the dead space is made from the calibration with helium. When nitrogen is used as the adsorbate, a bath of liquid nitrogen is used to provide a temperature of  $-195.8^{\circ}\text{C}$ . during the adsorption run. Details on the experimental procedures will be found in the original papers.<sup>69</sup>

The actual values obtained for specific surface by adsorption methods depend on the value selected for the adsorbate molecule. The molecular areas are computed on the assumption that the molecules are in hexagonal, two-dimensional close packing. From the densities in the liquid and solid states, the molecular weight, and Avogadro's number the area for the nitrogen molecule was calculated as  $16.2 \text{ \AA}^2$  (liquid) and  $13.8 \text{ \AA}^2$  (solid). For butane the two areas are given as  $32.1 \text{ \AA}^2$  (liquid) and  $32.0 \text{ \AA}^2$  (solid). Areas for adsorbates are listed by Emmett and other investigators.<sup>70,71</sup> There is some uncertainty in the validity of these values, and further work may necessitate revision: further, as Emmett points out, the molecular areas of the adsorbate may differ for various solids because of differences in lattice spacing.

A fourth method for computing specific surface from adsorption data has been described by Harkins and Jura.<sup>72</sup> This method is based on the idea of a condensed film on the solid, entirely analogous to the surface films formed on a water surface by an insoluble material, e.g., stearic acid on dilute hydrochloric acid solution. It is not necessary to assume a given area for the adsorbate molecule, for a constant is obtained for different gaseous adsorbates by means of calorimetry. The method includes the following steps: (1) exposing a powdered solid (e.g., titanium dioxide) to the vapors of the adsorbate until the saturation pressure is reached; (2) immersing the solid in the liquid and measuring the heat of immersion. The surface energy of the liquid is known, and the adsorbate

<sup>69</sup> P. H. Emmett, *Advances in Colloid Science*, Vol. I, pp. 1-36, Interscience Publishers, Inc., New York, 1942; American Society for Testing Materials, "Symposium on New Methods for Particle Size Determination in the Subsieve Range," pp. 95-105, Philadelphia, 1941. See also the papers by Harkins and Jura in the next section. A simplified apparatus has been described by K. A. Krieger, *Ind. Eng. Chem., Anal. Ed.*, **16**, 398-99 (1944).

<sup>70</sup> H. K. Livingston, *J. Am. Chem. Soc.*, **66**, 569-73 (1944); *J. Colloid Sci.*, **4**, 447-58 (1949).

<sup>71</sup> W. D. Harkins and G. Jura, *J. Chem. Phys.*, **11**, 431-32 (1943).

<sup>72</sup> W. D. Harkins and G. Jura, *J. Am. Chem. Soc.*, **66**, 919-27; 1356-62; 1362-66; 1366-73 (1944).

is considered as an envelope of the same liquid on the particles of solid. The energy change on immersion is then associated with the extent of surface over which the liquid has been spread. If the liquid is water, the total heat evolved in ergs is divided by the surface energy of water (118.5 ergs per sq. cm.); the quotient then is the area of the particles with the adsorbed film of water. A small correction for the thickness of this film is made.

The Harkins-Jura (HJ) method has provided a remarkable confirmation of the BET method. For a sample of titanium dioxide the HJ value for specific surface was 13.8 sq. m. per gram and the BET value, using  $16.2 \text{ \AA}^2$  for the area of the nitrogen molecule, was 13.9 sq. m. per gram.

Harkins and Jura have developed the method to provide independent values for specific surface. They plot adsorption data according to the equation

$$\log \frac{p}{p_0} = B - A \frac{1}{V^2} \quad (4)$$

where  $A$  and  $B$  are constants and the other symbols have the same meaning as in equations previously given. The curve of  $\log p/p_0$  vs.  $1/V^2$  is a straight line. The surface area then is equal to

$$S = KC^{1/2} \quad (5)$$

where  $C$  is the slope of the plot and  $k$  is a constant obtained from surface area measurements by the calorimetric procedure mentioned above. The value of  $K$  is assumed to be characteristic of the adsorbate and unchanged for different adsorbents. The relative pressure in these plots may go as high as 0.7, in contrast to 0.35 for the BET plots.

The accuracy of gas-adsorption methods for specific surface is estimated as 10 percent.

A relatively simple method for measuring specific surface by adsorption of water vapor has been described by Smith and Green<sup>78</sup> with data on a variety of pigments. Measurements were made at atmospheric pressure at 25° C., and in an atmosphere approximately 50 percent saturated with water vapor. The assumption is that a monomolecular layer forms and that no condensation occurs. The water molecule is assumed to have a cross-sectional area of  $10 \text{ \AA}^2$ . No attempt was made to adjust the final relative pressure of water vapor for different samples, and, lacking such control, a large variable error could enter into the computations. Such an error is inevitable if the adsorption isotherms are S-shaped. The experimental method is of great interest because of its simplicity.

<sup>78</sup> D. Smith and H. Green, *Ind. Eng. Chem., Anal. Ed.*, **14**, 382-86 (1942).

Further information on the adsorption of other vapors is provided by Gans, Brooks, and Boyd<sup>74</sup> who measured adsorption of water vapor, propyl alcohol, and benzene on several crystalline powders at 25° C. Molecular areas in Å<sup>2</sup> used in the computation were as follows: water, 10.6; propyl alcohol, 20.0; benzene, 30.5. Comparable specific surface values for the different vapors were obtained; comparison was also made with nitrogen adsorption data and an electron micrograph particle-size count on two titanium dioxides. In general the agreement of the different methods was remarkably good.

Further discussion of this interesting subject is beyond the scope of this book. A comparison of the BET and HJ methods has been made,<sup>75</sup> and a large volume of current research is appearing in the literature. Actual values for different solids obtained by adsorption methods are given later in this chapter (Tables VII, VIII, IX, X).

### Adsorption from solution

A powdered solid introduced into a dilute solution of an adsorbable substance removes the solute in proportion to its surface area. In order to use this method for the determination of specific surface, it is necessary to determine the conditions under which a monomolecular film is formed on the solid surface, and to obtain a valid molecular area for the adsorbed substance. Then from the quantity of material removed from solution, as determined by analysis, the area may be computed.

Although adsorption from solution is a technique long used in colloid chemistry, it was not until 1932 that Harkins and Gans<sup>76</sup> were able to use the data quantitatively. Titanium dioxide was dried by heating under vacuum and then immersed in a solution of oleic acid in dry benzene; the suspension was shaken until equilibrium was reached, and then allowed to settle. The supernatant liquid was analyzed to determine the change in concentration brought about by adsorption on the powdered solid. By assuming a molecular area for the adsorbed oleic acid molecule, specific surface values were computed which are of the correct magnitude, as shown by subsequent work on the same samples. The actual values are somewhat low, probably because the value of 20.0 Å<sup>2</sup> assumed for the area of the oleic acid molecule is incorrect for this molecule on the adsorbent. Adsorption from liquid solution has been studied

<sup>74</sup> D. M. Gans, V. S. Brooks, and G. E. Boyd, *Ind. Eng. Chem., Anal. Ed.*, **14**, 396-99 (1942).

<sup>75</sup> P. H. Emmett, *J. Am. Chem. Soc.*, **68**, 1784-89 (1946); *Ind. Eng. Chem.*, **37**, 639-44 (1945); H. K. Livingston, *J. Chem. Phys.*, **12**, 466 (1944).

<sup>76</sup> W. D. Harkins and D. M. Gans, *J. Phys. Chem.*, **36**, 86-97 (1932).

also by Ewing<sup>77</sup> for five zinc oxides. Methyl stearate and glycol dipalmitate in benzene solution were adsorbed in monomolecular films (or some multiple film) on the zinc oxide. Specific surfaces computed from the adsorption were in fair agreement with values computed from optical photomicrographs. Saunders<sup>78</sup> used heptioic acid in aqueous solution for measurement of the specific surface of calcined and hydrated alumina powders.

Adsorption from solution presents several experimental difficulties. When the experiments are performed with hydrocarbon solvents, the presence of trace quantities of water vitiate the results. As a consequence, it is necessary to take precautions to eliminate moisture from the reagents and glassware, and to perform the necessary operations under the driest possible conditions. The material adsorbed should not, of course, react with the solid. The area of the adsorbed molecule is also uncertain; the area per molecule obtained from film-balance studies of the fatty material spread on a water surface is often used with the assumption that orientation on the solid surface is the same. The method is thus of limited accuracy, but it is useful for comparative values since the measurements are simple to make.

## Sedimentation

Methods that depend on the settling of a dispersed solid have been developed to the point where they cover the entire subsieve range. The simplest procedures depend on sedimentation under gravity; these methods are suitable in the range from about 100 microns to about 0.5 micron. When a centrifugal field is used to augment the force on the settling particle, the range is extended to a lower limit of about 0.02 micron. Size-distribution curves are obtained, and the sizes computed are those of sphere of "effective" diameter,  $d_e$ .

*Gravitational sedimentation.* The well-known Stokes' law, the basis for all sedimentation measurements, may be expressed as

$$F = 3\pi\eta dv \quad (6)$$

where  $F$  is the applied force,  $\eta$  the coefficient of viscosity of the suspending liquid,  $d$  the diameter of a sphere, and  $v$  the terminal or constant velocity of the particle moving through the liquid. This equation, derived theoretically, is based on the following conditions: (1) the fluid is of infinitely large volume compared to the particles; (2) the particles are

<sup>77</sup> W. W. Ewing, *J. Am. Chem. Soc.*, **61**, 1317-21 (1939); cf. also American Society for Testing Materials, "Symposium on New Methods for Particle Size in the Sub-sieve Range," pp. 107-10.

<sup>78</sup> L. Saunders, *J. Chem. Soc.*, 1948, 869-73.

true spheres and are smooth and rigid; (3) the particles are independent and not associated into flocules; (4) the velocity of the particles is small; (5) there is no slip between the particle and the liquid; (6) the particle is of sufficient size to be unaffected by the kinetic motion of the molecules of the suspending liquid; and (7) electrical effects between particles and the liquid can be neglected. It is apparent that for most particulate substances of industrial origin, many of these conditions are not realized; since most of the particles are not true spheres, shape factors need consideration. Some uncertainty in computed values is introduced by these factors.

For a suspension in which the particles are settling under gravity, Stokes' law may be expressed as

$$d_e = \sqrt{\frac{18\eta h}{(\rho - \rho')gt}} \quad (7)$$

where  $(\rho - \rho')$  represents the difference in specific gravity between the solid  $\rho$  and the suspending liquid  $\rho'$ ,  $h$  is the sedimentation height,  $g$  is the gravitational constant, and  $t$  is the sedimentation time.

For gravitational sedimentation the experimental procedure is relatively simple. A quantity of a dilute suspension is placed in stoppered glass graduates. The suspension is allowed to settle for a time sufficient to bring down the largest particles; the supernatant liquid is decanted, the sediment is reslurried with an additional quantity of the suspending liquid, and settling is allowed to take place again. A series of cuts is made in this way, with the sediment after a series of settlings and decantations reserved as the first sample. The decanted liquids are used to reslurry the intermediate sediments. The chart shown in Figure 8 shows the sequence. Any practicable number of fractions may be made in this way. For a relatively coarse powder with particles in the range of 5 to 50 microns the maximum settling time is about 2 hours; for particles to 1 micron, the settling time is about 20 hours (overnight). In using data obtained by this method, the time interval for the sedimentation establishes the size group as computed from Stokes' law.

This method is simple and requires only inexpensive apparatus. It provides a series of fractions of the material which can be used for other studies. For routine measurements, however, several modifications are of advantage.

One of the sedimentation techniques that has received considerable attention is Odén's balance method.<sup>79</sup> A suspension of particles settles

<sup>79</sup> S. Odén, chapter in *Colloid Chemistry*, Vol. I, J. Alexander, Editor, pp. 861-909. This article includes an extensive bibliography of earlier work. See also, *Trans. Faraday Soc.*, **17**, 327-48 (1921-22).

into a balance pan and the weight accumulated after different time intervals is easily determined. The experimental data are usually plotted as sedimentation weight vs. time, and, from this, a cumulative size-frequency curve is derived.

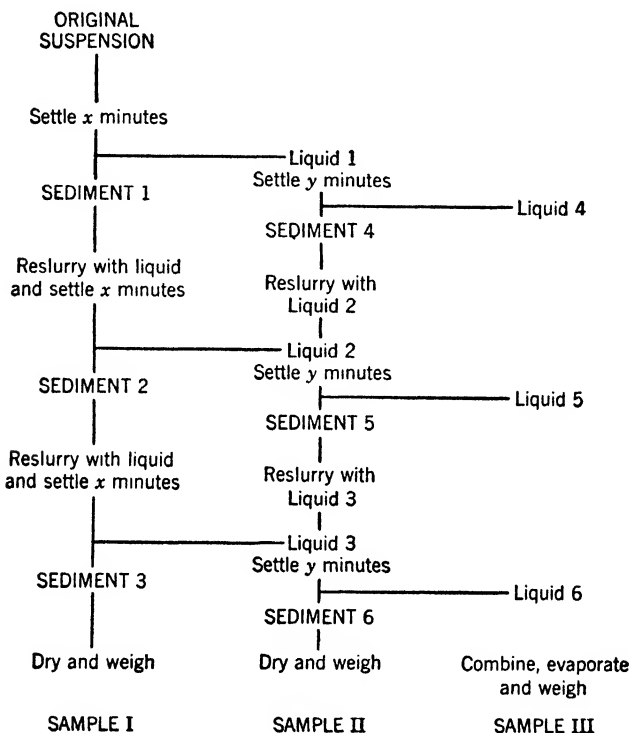


FIGURE 8. Chart showing a series of three fractionations for particle-size analysis by gravitational sedimentation.

The sedimentation balance method has been extensively used in several modifications. Calbeck and Harner<sup>80</sup> describe an experimental arrangement in which the suspension is placed in a vacuum flask on a regular beam balance; Sumner<sup>81</sup> devised an automatically recording balance system. Various other improvements have been described.<sup>82, 83</sup>

<sup>80</sup> J. H. Calbeck and H. R. Harner, *Ind. Eng. Chem.*, **19**, 58-61 (1927).

<sup>81</sup> G. G. Sumner, *Trans. Faraday Soc.*, **28**, 20-7 (1932).

<sup>82</sup> For a bibliography of pertinent papers see S. W. Martin, American Society for Testing Materials, "Symposium on New Methods for Particle Size Determination in the Subsieve Range," pp. 66-89.

<sup>83</sup> A. E. Jacobsen and W. F. Sullivan, *Ind. Eng. Chem., Anal. Ed.*, **19**, 855-60 (1947).



Several sedimentation procedures are considered, in Martin's terms, "approximate incremental" methods. These include the pipette and hydrometer methods. In the former, a sample of the suspension is withdrawn from a fixed position in the settling vessel after settling for a predetermined time, and, after evaporation of the liquid, the residue is weighed. This method was described by Andreasen<sup>84</sup> and is frequently known by his name. Hinkley<sup>85</sup> has given a description of the procedure with a method for computation. Schweyer<sup>86</sup> has modified the Andreasen method slightly and finds it to be rapid and precise. The pipette designed by Schweyer provides a means for sampling at different distances for fall: the finer particles have a short distance, whereas the large particles fall the full length of the containing vessel. The time for the measurement is thus reduced to one-fourth the time ordinarily required.

The hydrometer method depends on the difference in specific gravity of the medium and the suspension; measurement of the apparent specific gravity of the suspension is accomplished by a specially designed float. The method has been severely criticized: introduction and removal of the hydrometer from a suspension agitates the suspension, interfering with free settling; further a density gradient in the suspension exists, and the hydrometer measures some average specific gravity. Although some controversy exists over the value of the hydrometer method, a number of investigators report satisfactory results and agreement with the pipette methods,<sup>87</sup> and it provides a standardized test.<sup>88</sup> It is undoubtedly one of the most rapid test methods providing a size-distribution curve. A paper by Klein<sup>89</sup> covers in considerable detail the experimental procedures and calculations for the hydrometer method.

The particle shape affects the rate of fall. This aspect of Stokes' settling has been frequently studied, and the observations of Kunkel<sup>90</sup> are pertinent. Using "model" particles of different shapes, Kunkel found that any departure from sphericity resulted in a smaller velocity. For thin plates and needles, which may be considered extreme cases, the error introduced is greater than 50 percent. When falling freely, plates

<sup>84</sup> A. H. M. Andreasen, *Kolloid-Beihfte*, **27**, 349-458 (1928); *Kolloid-Z.*, **82**, 37-42 (1938); *Angew. Chem.*, **20**, 283-85 (1935).

<sup>85</sup> W. O. Hinkley, *Ind. Eng. Chem., Anal. Ed.*, **14**, 10-13 (1942).

<sup>86</sup> H. E. Schweyer, *Ind. Eng. Chem., Anal. Ed.*, **14**, 622-32 (1942).

<sup>87</sup> Cf. H. E. Schweyer, *loc. cit.*

<sup>88</sup> American Society for Testing Materials, D 422-38T.

<sup>89</sup> A. Klein, American Society for Testing Materials, "Symposium on New Methods for Particle Size Determination in the Subsieve Range," pp. 52-65. Theoretical aspects of the method are given by S. B. Biddle, Jr., and A. Klein, *Am. Soc. Testing Materials, Proc.*, **36** (Part II), 310-31 (1936).

<sup>90</sup> W. H. Kunkel, *J. Applied Phys.*, **19**, 1056-58 (1948).

and needles turned the long axis in a horizontal direction (perpendicular to the direction of movement). When spherical particles flocculate the velocity is intermediate: thus a linear arrangement of four spheres resulted in a difference from Stokes' law of 20 percent which was equivalent to a planar arrangement of six spheres. A three-dimensional packing of six spheres resulted in a 13 percent departure from Stokes' law.

All the sedimentation procedures are based on the equivalent settling diameter of the particle. Note has already been made of the assumptions in the application of Stokes' law, and further discussion of some of these conditions is required. The dispersion must be deflocculated if the sedimentation results are to be valid. This requirement cannot be overlooked. For many suspensions, a surface-active agent is indicated, and some aid in selection may be obtained from Chapter 6. Where the suspending medium is water and the solid is an inorganic material, sodium hexametaphosphate is frequently a useful deflocculant; this reagent may be used with a synthetic wetting agent or a protective colloid such as gum arabic or sodium lignin sulfonate. If the particles are appreciably flocculated, results will not, of course, give a reliable estimate of the size of the primary particle.<sup>91</sup> The concentration of the suspension should be less than 5 percent; some investigators prefer even lower concentrations to prevent "hindered" settling. Temperature control is necessary to avoid convection currents in the system.

*Centrifugal sedimentation.* It has been noted that particles with sizes less than 1 micron cannot be studied by gravity separation, but when the settling force is augmented by centrifuging, an analysis of particles very much smaller becomes possible. If the centrifuge is of the ordinary laboratory type, equipped with tubes and cups (beaker-type centrifuge), the size region between 0.1 and 2.0 microns can be studied with acceptable accuracy.

The theoretical basis for this method is the same as that for gravity sedimentation, the Stokes' equation being used with an appropriate change for the increased magnitude of the force acting on the particle during centrifuging. Analysis is based on Odén's intercept method. The mathematical analysis given by Romwalter and Vendl,<sup>92</sup> has been used by several investigators. Martin<sup>93</sup> elaborated a technique suitable

<sup>91</sup> Sedimentation properties of flocculated and deflocculated suspensions have been studied by H. H. Steinour, *Ind. Eng. Chem.*, **36**, 618-24; 901-7 (1944).

<sup>92</sup> A. Romwalter and M. Vendl, *Kolloid-Z.*, **72**, 1-3 (1935).

<sup>93</sup> S. W. Martin, *Ind. Eng. Chem., Anal. Ed.*, **11**, 471-75 (1939); American Society for Testing Materials, "Symposium on New Methods for Particle Size Determination in the Subsieve Range," pp. 74-89; *Paint Industry Magazine*, August, 1942, pp. 262, 264, 266, 268, 270, 272, 273, 275, 277, 279.

for typical white pigments such as titanium dioxide. A pigment concentration of less than 3 percent was found to give results implying free settling; this concentration allowed a minimum separation of 0.9 micron between particles in the suspension, approximately 3 times the particle diameter. Higher concentrations resulted in hindered settling which was reflected in an apparent increase in surface area of the particles. Sedimentation was performed in water, glycerine, and typical paint vehicles. In making the measurement, the centrifuge was operated at a known speed for a selected time; a sample was then taken either by decanting the liquid above the sediment or by withdrawing with a pipette. The quantity settled was determined for a series of sedimentations, and a curve showing percent of total solid in sediment vs. time of centrifuging was derived. Size analysis by centrifuging for pigments has been described also by Jacobsen and Sullivan.<sup>94</sup>

The experimental results of several investigators clearly indicated the presence of aggregates of the primary particles: appreciable quantities of the titanium dioxide were in size groups above 1 micron, when dispersion was accomplished by stirring or comparable means. On the other hand, when this pigment was dispersed on a two-roll mill in crepe rubber and then isolated again by dissolving the rubber in toluene, no particles above 1 micron were recorded and the majority of particles were in size groups less than 0.3 micron.

The validity of the analysis of centrifugal separation given by Romwalter and Vendl has been questioned by Brown.<sup>95</sup> Extension of the theory has been made by Robison and Martin.<sup>96</sup>

Other types of centrifuges have been used for size analyses and fractionation. Hauser and co-workers<sup>97</sup> describe the use of the so-called supercentrifuge.<sup>98</sup> This instrument has a balanced cylindrical rotor driven at high speed, and the suspension is fed into the bottom of the bowl where it is subject to one force parallel and another perpendicular to the axis of the rotor. The mathematical relations of the process are complex and require a number of assumptions. The procedure described by these authors is very useful, and, by a series of fractionations, a narrow "cut" in the size group can be made. Quantities of the different samples can be produced for other tests.

<sup>94</sup> A. E. Jacobsen and W. F. Sullivan, *Ind. Eng. Chem., Anal. Ed.*, **18**, 360-4 (1946); *ibid.*, **19**, 855-60 (1947).

<sup>95</sup> C. Brown, *J. Phys. Chem.*, **48**, 246-58 (1944).

<sup>96</sup> H. E. Robison and S. W. Martin, *J. Phys. & Colloid Chem.*, **52**, 854-81 (1948).

<sup>97</sup> E. A. Hauser and J. E. Lynn, *Ind. Eng. Chem.*, **32**, 659-62 (1940); E. A. Hauser and H. K. Schachman, *J. Phys. Chem.*, **44**, 584-600 (1940).

<sup>98</sup> Made by the Sharples Corp., Philadelphia, Pa.

The ultracentrifuge produces centrifugal fields of very high magnitude. In the first instrument described by Svedberg and his co-workers, forces about 5,000 times that of gravity were used to effect separation of colloidal particles<sup>99</sup> in a size range of 20 to 70 millimicrons. It is, of course, possible to separate smaller particles, and one example given by Svedberg and Nichols reached 1 millimicron. For most pigment-type materials, however, it is not necessary to employ the ultracentrifuge.<sup>100</sup>

## Elutriation

The principles of sedimentation methods apply to the techniques used in elutriation with this essential difference: a countercurrent of fluid is used to increase the effective path traversed by the particle. Since large volumes of the medium are necessary, elutriation procedures are designed to use air or water. A powdered material may be fractionated in this way. The laws describing sedimentation apply in elutriation.

Air elutriation has been extensively studied by Roller.<sup>101</sup> The apparatus consists of a series of four specially shaped cylindrical columns with conical ends. The cylindrical portion of the settling chambers are 1.125, 2.25, 4.5, and 9.0 inches in diameter. Air centers a U-shaped sample holder and carries the powder into the selected chamber; the fraction that is carried out of the chamber has a settling rate slower than the velocity of the air in the chamber. By changing to a chamber with smaller diameter, retaining the same volume-rate of air flow, the next larger fraction is carried over. A commercial model of the Roller instrument is available.<sup>102</sup>

Roller used this instrument for analysis of cements. It is suitable for a wide variety of other powders. The lower limit is approximately 1.0 micron, but the method is usually used on powders of considerably larger size.

<sup>99</sup> T. Svedberg and J. B. Nichols, *J. Am. Chem. Soc.*, **45**, 2910 (1923).

<sup>100</sup> An extensive literature has been built up on the ultracentrifuge. The following references are excellent sources of information on the instrument and its fields of application: T. Svedberg, *Colloid Chemistry*, Second Ed., Chemical Catalog Co. (Reinhold Publishing Corp.), New York, 1928; T. Svedberg and K. O. Pedersen, *The Ultracentrifuge*, Clarendon Press, Oxford, 1940; Conference on "The Ultracentrifuge" by D. A. MacInnes, W. J. Archibald, J. W. Beams, W. B. Bridgman, A. Rothen, and J. W. Williams, *Annals N. Y. Acad. Sci.*, **43** (Article 5), pp. 173-252 (1942); T. Svedberg, *Ind. Eng. Chem., Anal. Ed.*, **30**, 113-29 (1938).

<sup>101</sup> P. S. Roller, *Am. Soc. Testing Materials, Proc.*, **32**, Part II, 607-28 (1932); "Symposium on New Methods for Particle Size Determination in the Subsieve Range" (with P. V. Roundy, Jr.), pp. 36-49; *J. Phys. Chem.*, **45**, 41 (1941).

<sup>102</sup> American Instrument Co., Silver Spring, Maryland.

Liquid elutriation methods are also used. One type suitable for laboratory purposes consists of a long glass tube through which water rises at a rate adjusted to conform to the settling rate of the suspended solid. A series of elutriations makes possible separation into the desired number of fractions.<sup>103</sup>

### Permeability

When a gas or liquid is allowed to stream through a porous mass the resistance to the flow is established by the pore space, the pressure differential, viscosity of the fluid, and various dimensional factors such as thickness and area of the bed.

From these quantities the specific surface of the solid and a  $d_3$  diameter can be computed. The method does not, of course, provide a size-distribution analysis. The theory for permeability is complicated. Present investigations are based on an equation derived theoretically by Kozeny in 1927.<sup>104</sup>

A series of experimental investigations, starting with Carman,<sup>105</sup> have shown that the method has considerable utility. Carman used liquids for most of his experiments, but other investigators have preferred the measurement of gas flow. Lea and Nurse<sup>106</sup> using different gases found that the method gave consistent results for surface areas to about 0.4 sq. m. per gram. The values obtained were in accord with sedimentation analysis. The experimental apparatus described by Carman and by Lea and Nurse has been modified by other investigators, and the value of the method for rapid industrial testing seems fairly well established. Blaine<sup>107</sup> described a simple instrument and a calibration procedure for measurements on cement and lime which require only about 3 minutes for the test. Gooden and Smith<sup>108</sup> used the method for measurements on powdered silica; they found that measurements on the more finely divided fractions did not accord with microscopic data. To simplify computation, their instrument was arranged with an automatic calculat-

<sup>103</sup> A. M. Gaudin, J. O. Groh, and H. B. Henderson, *Ind. Eng. Chem.*, **22**, 1363-66 (1930).

<sup>104</sup> For mathematical details the reader is referred to a critical review by R. R. Sullivan and K. L. Hertel, Chapter 2 in *Advances in Colloid Science*, Vol. I, pp. 37-80, Interscience Publishers, Inc., New York, 1942. The subject is also discussed by Dalla Valle, *Micrometrics*, Chapters 10, p. 194 ff., and 13, p. 260 ff.

<sup>105</sup> P. C. Carman, *J. Soc. Chem. Ind.*, **57**, 225-34 (1938); **58**, 1-7 (1939); American Society for Testing Materials, "Symposium on New Methods for Particle Size Determination in the Subsieve Range," pp. 24-33.

<sup>106</sup> F. M. Lea and R. W. Nurse, *J. Soc. Chem. Ind.*, **58**, 277-83 (1939).

<sup>107</sup> R. L. Blaine, *A.S.T.M. Bull.*, **108**, 17-20 (June 1941); *ibid.*, **123**, 51-55 (1943).

<sup>108</sup> E. L. Gooden and C. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, **12**, 479-82 (1940).

ing feature. Rigden<sup>109</sup> studied the air and liquid permeability methods for a variety of powdered solids with specific surface ranging from 0.4 to about 5 sq. m. per gram. Considerable discrepancy was noted between the two methods, and Rigden attributes the differences to "slip" of air at the surface of the pores in the beds. Modifications in the Kozeny equation were made to account for this factor: the "corrected" equation provided results that were in good agreement. Rigden states that the beds should be compacted as tightly as possible; this is considered essential when liquids that cause the powder to flocculate are used.

The permeability method appears of greatest value for particles above 1 micron in size. For powdered materials, such as pulverized coal, cement, sand, lime, and fibrous materials, it offers a rapid and convenient procedure especially suitable for industrial control measurements. For particles below 1 micron, several complications appear. The packing of the powdered material in the bed is one variable difficult to control. With close packing, the pressure necessary to force gas or liquid through the bed becomes very high. The possibility of turbulent flow also arises. When liquids are used, adsorption on the surface alters the effective porosity. In addition, modifications in the equations appear necessary. Permeability measurements on very fine particles can be made, nevertheless, and the results of Carman<sup>105</sup> for zinc oxide particles are in fair agreement with other methods. Pechukas and Gage<sup>110</sup> surmounted some of the difficulties by using highly compressed plugs of the powdered material to reduce turbulent flow in the bed and pressure differentials up to one atmosphere. Inorganic pigments were used in the investigation of Arnell.<sup>111</sup> Gas permeabilities were determined, and the specific surface computed by means of a modified Kozeny equation. The pressure range was from 2.6 cm. to atmospheric. Good agreement with electron micrograph particle-size counts was observed in selected instances. The author concludes that the greatest source of error in the method is packing of the bed: small variations in packing are magnified in computed specific surface values.<sup>112</sup> Low gas pressures seem preferable.

Carman considers the method valid to 0.1 micron, and Pechukas and Gage conclude that their technique is suitable to this limit. Arnell's results for small particles indicate acceptable agreement for particles

<sup>109</sup> P. J. Rigden, *J. Soc. Chem. Ind.*, **62**, 1-4 (1943); **66**, 130-36 (1947).

<sup>110</sup> A. Pechukas and F. W. Gage, *Ind. Eng. Chem., Anal. Ed.*, **18**, 370-6 (1946).

<sup>111</sup> J. C. Arnell, *Canadian J. Res.*, **24A**, 103-16 (1946); **25A**, 191-209 (1947); J. C. Arnell and G. O. Henneberry, *ibid.*, **26A**, 29-38 (1948); P. C. Carman and J. C. Arnell, *ibid.*, **26A**, 126-36 (1948).

<sup>112</sup> Cf. also W. F. Keyes, *Ind. Eng. Chem., Anal. Ed.*, **18**, 33-34 (1946).

below 1.0 micron. A conservative limit of 0.5 micron seems justified, however. It may be noted that this last figure places the method in the range of the optical microscope.

### Diffusion

The rate of diffusion of a particle of colloidal size from a solution into water is established by the size of the particle, viscosity of the medium, and physical constants as given in the Einstein equation <sup>113</sup>

$$D_f = \frac{RT}{N} \cdot \frac{1}{6\pi r\eta} \quad (8)$$

where  $D_f$  is the diffusion constant (sq. cm. per sec.);  $R$ , the gas constant;  $T$ , the absolute temperature;  $N$ , Avogadro's number;  $\eta$ , the coefficient of viscosity of the liquid; and  $r$ , the radius of the particle (cm.). This equation was derived for spherical particles. It is assumed that the suspended particles are large in comparison to the molecules of the solvent and that they are electrically neutral.

A microdiffusion cell, designed by Fürth and Ullmann,<sup>114</sup> is simple to make and convenient to use for these measurements. Details on construction are also given by Lenher and Smith,<sup>115</sup> as used for the measurement of the particle size of dyes. The cell is about 1 mm. deep and is so arranged that a portion of the original dye solution, diluted a known amount, is adjacent to the solution diffusing into clear solvent; this is a reference standard for color. Observation of the diffusion is accomplished with a microscope, and the distance is measured by means of a filar micrometer.

A porous plate was used in the diffusion measurements reported by Valko.<sup>116</sup> The cell containing the solution and diffusion disc requires a larger volume of solution than the microscopic method, but it is relatively free from disturbances of vibration and temperature fluctuations. Because it is sealed, measurements on oxidizable materials (e.g., leuco bases) can be made.

Measurements with the diffusion cells are said to be reproducible to  $\pm 5$  percent. The diffusion method has been criticized, since the charge on the dye particle is not included in the Einstein equation and the diffusion coefficients as calculated may be in error by an indeterminate

<sup>113</sup> H. Freundlich, *Colloid and Capillary Chemistry*, pp. 350, 546-50.

<sup>114</sup> R. Fürth, *Kolloid-Z.*, **41**, 300-4; (1927); R. Fürth and E. Ullmann, *ibid.*, **41**, 304-10 (1927).

<sup>115</sup> S. Lenher and J. E. Smith, *Ind. Eng. Chem.*, **27**, 20-25 (1935); *J. Am. Chem. Soc.*, **57**, 497-503; 504-8 (1935).

<sup>116</sup> E. I. Valko, *Trans. Faraday Soc.*, **31**, 230-45 (1935).

amount. The error can be minimized, however, by adding a relatively large amount of an electrolyte, such as sodium chloride, to both the dye solution and the water into which the dye is diffusing; the possibility that a potential gradient will be established in a highly conducting medium is small.

The particle size of a dye in colloidal solution is actually an aggregate size. Lenher and Smith calculated the micellar radius of 12 dyes from diffusion data and found the range to be 6 to 40 Å (0.6 millimicron to 4 millimicrons). Corresponding molecular weights were found to be 935 to 200,000, and formula-molecular weights from 610 to 935. The results indicated that some dyes were present in the molecular state, but generally the aggregation was between 10 and 100 molecular units per micelle, with a maximum of about 225. The diffusion method was checked with a measurement by means of an ultracentrifuge. Excellent agreement was found in the test case.

Salts present in commercial dyes or added to dye baths usually promote aggregation. As an example, solutions of commercial dyes contained aggregates with radii averaging less than 17 Å, but on the addition of salt the size was increased by 50 percent.

Valko<sup>117</sup> has summarized data for a considerable number of dyes and expresses the extent of aggregation as "degree of association." The degree of association increases with dye concentration and electrolyte concentration and, for most dyes, decreases at high temperatures. Valko concludes that, under the conditions of application for commercial dyeing processes, numerous wool dyes and some direct cotton dyes are dispersed as single ions.

Surface-active agents do not disperse the aggregates of dyes in solution, and their utility in dyeing can be attributed to accessory effects.<sup>118</sup>

These observations are of considerable interest in dyeing processes. Lenher and Smith found that an optimum particle-size range exists; above this limit absorption of the dye by cotton does not take place effectively. This limit is given as about 17 Å, which is somewhat smaller than the dimensions of the submicroscopic pores in the cotton fiber (20 to 40 Å). An attractive hypothesis can be devised to explain the mechanism of dyeing on this basis: diffusion of the dye molecule or small aggregate into pores in the fiber occurs during the dyeing process; selection of the dye and formulation of the dye bath is adjusted empirically to ensure such diffusion; aftertreatments result in growth of the dye particle, the dye being thus fixed within the colloidal structure of the fiber.

<sup>117</sup> E. I. Valko, Chapter 29, pp. 594-619 in *Colloid Chemistry*, Vol. VI, J. Alexander, Editor, Reinhold Publishing Corp., New York, 1946.

<sup>118</sup> J. E. Smith, *Ind. Eng. Chem.*, **31**, 40-3 (1939).



Such an explanation, however, does not account for many of the complexities of the physical chemistry of the dyeing process.

### X-ray measurements

The size of colloidal particles can be deduced from x-ray diffraction data. When x-rays are diffracted by a powdered substance, a series of rings is formed on a photographic plate. If the particles are less than  $10^{-5}$  cm. (0.1 micron), the rings are broadened; from the width the particle size can be computed. According to Clark<sup>119</sup> the range is from  $10^{-6}$  to  $10^{-8}$  cm. For particles between  $10^{-3}$  and  $10^{-5}$  cm., the diffraction lines are sharp and the effect of size is indistinguishable. With larger particles, greater than  $10^{-3}$  cm., the rings appear "peppered" with spots. There are thus two ranges in which x-ray diffraction data can be utilized. In the microscopic range, Clark notes that the x-ray measurements give an average of only the largest particles.

The method of x-ray diffraction has special uses. For example, an indication of grain size in a composite mass is possible. Thus the extent of aggregation of particles can be estimated. The lower size limit, less than 1 millimicron, extends the instrumental means for analysis below the practical limit of the electron microscope. The x-ray methods have not been extensively used, however, partly because of the complexity of experimental work and partly because of the difficulty of interpretation.<sup>120</sup>

Clark and Rhodes<sup>121</sup> studied 18 carbon blacks, using the x-ray diffraction method. The computed sizes were in the approximate range of 15 to 25 Å, far lower than microscopic values, as would be expected. These investigators suggest that, since the x-ray method measures only primary particles and the microscopic method measures aggregates, a computation can be made of the number of primary particles forming the aggregate. On this basis the carbon-black aggregates contain from  $10^2$  to  $10^4$  primary particles. These studies were considerably extended in a more recent examination of 60 commercial and experimental blacks.<sup>122</sup> Some conception of the structure of carbon-black particles is afforded by the work of Warren<sup>123</sup> who concluded that the particles

<sup>119</sup> G. L. Clark, *Applied X-Rays*, McGraw-Hill Book Co., Inc., New York, 1940, pp. 489-510.

<sup>120</sup> In addition to the monograph by G. L. Clark, the reader may find the following reviews useful: R. Brill, *Kolloid-Z.*, **69**, 301-12 (1934); A. Guinier, *J. chim. phys.*, **40**, 133-50 (1943).

<sup>121</sup> G. L. Clark and H. D. Rhodes, *Ind. Eng. Chem., Anal. Ed.*, **12**, 66-71 (1940).

<sup>122</sup> G. L. Clark, A. C. Eckert, Jr., and R. L. Burton, *Ind. Eng. Chem.*, **41**, 201-8 (1949).

<sup>123</sup> B. E. Warren, *J. Chem. Phys.*, **2**, 551-55 (1934).

represent a heterogeneous mixture with some single graphite layers and groupings of the layers to form an elementary graphite crystal. Birks and Friedman<sup>124</sup> studied magnesium oxide particles. By controlled heating of magnesium carbonate at different temperatures, magnesium oxide particles were formed which ranged from 50 to 1000 Å. For particles larger than 100 Å, agreement within 10 percent was obtained with electron micrographs.

An interesting application of the x-ray diffraction method has been made by Valko<sup>125</sup> to elucidate the nature of the dye particle affixed to cellulose fibers. Ordinarily a dye present on a fiber cannot be observed with an optical microscope until it has been "developed" by steaming, boiling, or other aftertreatment, and many dyes remain so finely divided that their presence as discrete particles cannot be established by microscopy. Using a cellulosic substrate and dyeing heavily with several vat dyes, Valko observed that some vat dyes formed crystallites 5 to  $10 \times 10^{-6}$  cm. in radius. Changes in particle size corresponding to variation in hue with aftertreatment could be correlated with crystallization of the dye.

Small angle scattering of x-rays provides a separate means for estimating particle size.<sup>126,127</sup> The scattering is especially evident with a material in the form of clusters with spaces between the primary particles. Carbon black is in this category, and the clusters observed by Biscoe and Warren were judged to be several hundred angstroms in size. Particle-size data obtained in this way, however, are only approximate.

### Tinting strength

The control test used extensively in the manufacture of pigments and colors is designed to show up variations from a standard sample by diluting a colored material with a white pigment. As it is usually employed, the test measures a composite of properties: hue and "strength" differences, comparative breakdown of aggregates, consistency of dispersed paste, etc. The method can be calibrated, however, to give a simple means for estimating the specific surface of a powdered material.

Frith and Mott<sup>128</sup> used a series of carbon blacks, for which surface-area data had been published, as calibrating pigments. A standard mixing and mulling procedure was adopted, zinc oxide being used as the

<sup>124</sup> L. S. Birks and H. Friedman, *J. Applied Phys.*, **17**, 687-92 (1946).

<sup>125</sup> E. I. Valko, *J. Am. Chem. Soc.*, **63**, 1432-37 (1941).

<sup>126</sup> J. Biscoe and B. E. Warren, *J. Applied Phys.*, **13**, 364-71 (1942).

<sup>127</sup> M. H. Jellinek, E. Solomon, and I. Fankuchen, *Ind. Eng. Chem., Anal. Ed.*, **18**, 172-75 (1946).

<sup>128</sup> F. Frith and R. A. Mott, *J. Soc. Chem. Ind.*, **65**, 81-87 (1946).

tinting pigment and linseed oil as the vehicle. One of the carbon-black pigments was selected as standard. A plot of tinting strength vs. surface area of the carbon black resulted in a straight line, except for pigments with the highest surface areas in which the method for preparation caused some divergence. This curve thus served as a calibration chart from which the surface area of unknown samples, milled according to the standard procedure, could be interpolated. These investigators used the method for coal and coke analyses, but other black powders can be studied in the same way. Differences in hue of various black pigments will affect the accuracy of the initial calibration, however, and the method is essentially an approximate one. The method can be used also with white pigments, such as titanium dioxide and zinc oxide. For white pigments, a tinting color of comparable particle size should be used (e.g., lamp-black). Estimation of specific surface for the standards can be made by methods described previously; for example, different commercial grades of a white pigment can be fractionated by sedimentation and centrifugation, and these fractions can be used for calibration.

### Turbidimetry

The turbidity of dilute suspensions offers a means for estimating particle sizes. Numerous methods have been devised to measure the light transmitted, scattered, or absorbed by a dispersion. Potential advantages are apparent: equilibrium of the system is not disturbed; the sample is unchanged and may be used for other studies; measurements by optical instruments can be quickly made. These advantages are offset by several complicating factors: the light that enters the suspension is subject to reflection, absorption, polarization, and scattering; and the relative magnitude and interdependence of these effects vary with the wavelength of light and the relative particle size. A simple measurement of light transmitted by a sample thus does not uniquely define the size characteristics of a finely divided solid. Because of the complexity of these relationships a complete theoretical analysis has not been elaborated. Instead, certain empirical adjustments have been made by different investigators, and a variety of instruments has resulted. These have names associated with optical phenomena as tyndallometer, nephelometer, dispersimeter, diaphanometer, and turbidimeter.

Theory for turbidimetric analysis may be classified roughly into two parts: when the particle size of the suspended substance is very small in relation to the wavelength of incident light, Rayleigh scattering predominates; as the particle size increases and becomes larger than the wavelength of light, the light transmitted is no longer critically determined by the wavelength, and the opacity is a function of the optical

constants of the system (including the refractive index difference) and the particle size. A good review of the theory has been given by Wells.<sup>129</sup>

Most of the experimental studies of turbidimetry for particle-size measurement have been made with white pigments and some with black pigments; the complications of color are thus avoided. Stutz and Pfund<sup>130</sup> examined suspensions of zinc oxide and found minimum transmission at a particle size around 0.24 micron, with filtered light with a dominant wavelength of approximately 0.54 micron. Correlation with  $d_1$  values could be made. Evidently this is in a region where both scattering and reflection occur. Gamble and Barnett<sup>131</sup> used radiation in the region 0.5 micron to 4 microns. This range includes part of the visible spectrum and extends into the infrared. Measurements were made with a rock salt infrared spectrometer. Curves of transmission (percent) vs. wavelength were of characteristic shapes: a sharp break occurs in the wavelength region where the particles become reflecting, and differences in size distribution are shown by the position of the wave. More recent work was done by Bailey<sup>132</sup> who extended this technique, using titanium dioxide and bentonite, and found fair agreement with ultracentrifuge measurements. The complexity of theory in its current form is shown by the equations developed by Clewell<sup>133</sup> and Duntley.<sup>134</sup>

Of the several instruments that have been described, Wagner's turbidimeter has received considerable attention.<sup>135</sup> This instrument utilizes a glass cell 8 inches long and 1.5 inches square. A light source and photo-cell pickup are arranged to move vertically and allow measurements on different positions of the cell. Sedimentation of the suspension can be studied optically in this way. Wagner used the instrument for analysis of Portland cement particle sizes. Traxler and Baum<sup>136</sup> compared the Wagner turbidimeter with the Roller air elutriator for various powdered substances. They decided that this turbidimetric method was unreliable. A further study was made by Schweyer<sup>137</sup> who concluded that, except for cement, silica, and comparable materials, the Wagner turbidimeter gives results of questionable certainty.

<sup>129</sup> P. V. Wells, *Chem. Revs.*, **3**, 331-82 (1927).

<sup>130</sup> G. F. A. Stutz and A. H. Pfund, *Ind. Eng. Chem.*, **19**, 51-53 (1927).

<sup>131</sup> D. L. Gamble and C. E. Barnett, *Ind. Eng. Chem., Anal. Ed.*, **9**, 310-4 (1937).

<sup>132</sup> E. D. Bailey, *Ind. Eng. Chem., Anal. Ed.*, **18**, 365-69 (1946).

<sup>133</sup> D. H. Clewell, *J. Optical Soc. Am.*, **31**, 521-27 (1941).

<sup>134</sup> S. Q. Duntley, *ibid.*, **32**, 61-70 (1942).

<sup>135</sup> L. A. Wagner, *Am. Soc. Testing Materials, Proc.*, **33**, 553-70 (1933).

<sup>136</sup> R. N. Traxler and L. A. H. Baum, *ibid.*, **35**, 457-71 (1935).

<sup>137</sup> H. E. Schweyer, *Ind. Eng. Chem., Anal. Ed.*, **14**, 622-32 (1942).

Methods based on turbidimetry continue to appear in technical journals.<sup>138,139</sup>

There seems little doubt that the method should not, in its present state, be considered an absolute one. For practical purposes, however, the rapidity and ease of making a measurement commend it for control measurements. Several instruments on the market are suitable, or an instrument can readily be contrived. Calibration is necessary in terms of a specific material.

### Estimation of Oversize Particles

For many purposes information on the particle-size distribution of the pigment particles is of little importance, but an estimation of the size and relative quantity of particles exceeding some limit becomes essential. As an example, consider a high-gloss lacquer or enamel film containing 10 percent by volume of a dispersed pigment whose ultimate particle size is of the order of 0.1 micron. If the film contains 0.1 percent of this pigment in the form of aggregates 30 microns in diameter, then on the average 10 of these aggregates will protrude through each square centimeter of the surface. The blemishes so introduced are readily apparent and seriously detract from the quality of the finish. This is an extreme case, but it can be seen that a lower content of even smaller aggregates will also affect the surface appearance.

The ultimate particles of commercial pigments when properly comminuted are too small to cause difficulties of the kind described. Consequently rating the quality of a dispersion frequently resolves into a technique for viewing a pigment dispersion in such a way that the presence of oversize particles may be seen. This is sometimes referred to as a texture or grit test.

One of the simplest tests, which is widely used, is performed as follows: a small portion (about 2 cc.) of the pigment dispersion is placed on a glass plate and spread by means of a spatula; as the spatula is drawn over the dispersion the smoothness and gloss are noted at the edge of the receding blade. The presence of aggregates is indicated by a roughness and lack of gloss. When performed by a skilled operator and in conjunction with a standard dispersion, this test method is surprisingly reliable.

The microscope may be used for an estimation of aggregate size. A very small quantity of the dispersion is introduced into a drop of the vehicle used in formulating the composition and gently mixed on a microscope slide with a small stirring rod. A cover glass is then placed over

<sup>138</sup> Cf. H. E. Rose and H. B. Lloyd, *J. Soc. Chem. Ind.*, **65**, 52-58, 65-74 (1946).

<sup>139</sup> E. Sharratt, H. S. Vansomeren, and E. C. Rollason, *ibid.*, **64**, 73-75 (1945).

the diluted dispersion and carefully pressed to a thickness suitable for observation. Usually the field contains a background of particles comminuted to their ultimate fineness together with some large aggregates. By scanning several fields, a general idea of the number of such oversize particles may be obtained, and, if the microscope is equipped with a calibrated eyepiece scale, it is possible to note the dimensions of these particles. The writer has employed this method of examination to follow the progressive reduction in aggregate size during mill operation and to estimate the number of passes required on a roll mill or the number of hours required in a ball mill to obtain the requisite fineness.

Several other relatively simple techniques are useful. The dispersion may be diluted with an appropriate solvent and flowed over the surface of a glass plate when the presence of aggregates becomes apparent. Viewing by transmitted light from the back of the panel is of assistance. Another procedure is to strain the diluted composition through a 325-mesh sieve; a rough quantitative measure of the quantity of aggregates may be obtained in this way.<sup>140</sup>

A refinement of this test was described by North<sup>141</sup> in which portions of graded Aloxite abrasives from 600 to 280 mesh are added to a dispersion of 73 parts of zinc oxide ground into 27 parts of refined linseed oil. The abrasive is merely stirred into the pigment paste. Comparison is made by drawing down the dispersion for examination against one of the zinc oxide dispersions containing the graded large particles. It is apparent that this procedure can be adapted for specific purposes by adding known quantities of graded particles to a portion of an acceptable dispersion which can then be used as a standard.

More refined methods employ devices designed to provide a numerical grading scale. In the wedge-grit method described by Craig,<sup>142</sup> the dispersion is drawn down on a piece of plate glass by means of a wide scraper blade, one end of which slides on the glass and the other on a strip of metal 0.003 inch thick. The wedge of the dispersion so formed is examined for the location of aggregates. Lateral positions are indicated on an arbitrary scale from 0 to 20. On this scale a rating of 19 represents virtual freedom from oversize particles and lower numbers indicate progressively larger aggregates.

<sup>140</sup> American Society for Testing Materials, Standard Test Method D 185-45, *A.S.T.M. Standards on Paint, Varnish, Lacquer and Related Products*, Philadelphia, Pa., 1946.

<sup>141</sup> W. B. North, *Nat. Paint, Varnish Lacquer Assoc., Sci. Sect., Circ. 423* (1932); H. A. Gardner, and G. G. Sward, *Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors*, Eleventh edition, Henry A. Gardner Laboratory, Bethesda, Md., 1950, p. 277.

<sup>142</sup> T. J. Craig, *Am. Ink Maker*, **16**, No. 10, pp. 27, 29, 31; No. 11, pp. 21-23, 39 (1938).

The idea of a wedge to indicate approximate dimensions of oversize particles is used in the Hegman fineness gauge.<sup>143</sup> This instrument consists of two channels, cut into a steel block, 0.004 inch in depth at one end and flush with the surface of the block at the other. The channels are 5 inches long and 0.5 inch wide and are marked at intervals of 0.0005 inch (12.7 micron) with numbers from 0 to 8. A special scraper blade, with 30° half angle and rounded edge, is used to reduce the effect of varying position angle as the drawdown is made by different operators. With this gauge, typical readings on commercial paints were found to be as follows: high-gloss enamel, 7; semi-gloss wall paint, 4; flat wall paint, 2; outside house paint, 1.

A comparison of the several methods of estimating aggregate size has been reported.<sup>144</sup> Methods that would be suitable for production control, of good reproducibility, ease of manipulation, and low instrument cost, were considered essential. For one set of comparisons, arbitrary standards were prepared and the dispersions were rated from coarse to fine. Drawdowns made with these standards were dried, rated in a series of steps from 1 (coarsest) to 10 (finest). This procedure was rejected because reproducibility was poor and tests could not be made readily. Tapered and cylindrical drawdown blades were tested. These, too, were rejected because of poor reproducibility and considerable variation with different operators. The principle of the fineness gauge described above, however, was found free from these objections. The committee recommended two gauges of different dimensions: (1) tapered paths 5 inches long, 0.004 inch deep at the end; and (2) tapered paths 5 inches long, 0.002 inch deep at the end. The former is suitable for various types of paints, and the latter is intended for finely ground enamels, printing inks, and lacquers. An applicator knife with a double round edge was recommended.

In use, 2 to 4 drops of the dispersion are placed in the deep end of each trough of the gauge, and the knife is then drawn down the length of the gauge block at a uniform rate. The blade should be held in a position vertical to the surface and at right angles to the edges. The dispersion is examined immediately after drawing down by viewing at a grazing angle, and the point where surface irregularities are visible is noted; the rating of the dispersion is then read directly from the calibration on the gauge block.

<sup>143</sup> J. M. Purdy, *Paint, Oil, Chem. Rev.*, **109**, No. 17, pp. 14, 16 (Aug. 22, 1946). This gauge is made by the Precision Gage and Tool Co., 320 E. 3rd St., Dayton, Ohio.

<sup>144</sup> New York Club, Federation Paint & Varnish Prod. Clubs, *Paint, Oil, Chem. Rev.*, **109**, No. 23, pp. 76-81 (November 14, 1946); *Am. Paint J.*, **31**, No. 6A, pp. 10-7 (November 5, 1946).

Refinements in the design of a gauge and methods for reading the dispersion index of printing ink were described by Walker and Zettlemoyer.<sup>146</sup> This gauge, called a Grindometer, has grooves 1 inch wide and 0.001 inch in maximum depth. It has been successfully used for production control of printing ink dispersions. Bernstein,<sup>146a</sup> reporting on a cooperative testing program, noted a qualitative correlation between photomicrographs and gauge readings. The gauge was useful in showing differences in the dispersing qualities of different vehicles.

Evidently some skill is necessary in the performance of this test, especially in judging the end point. Dispersions containing highly volatile solvents are difficult to evaluate; further, high-viscosity compositions are reported to give variable ratings.<sup>146</sup>

Several methods for determining the quality of the dispersion of carbon black and other pigments in rubber are used. The simplest test, but one which is quite apt to be misleading, is visual comparison of the surface gloss of the stock during milling. At the initial stages of milling, when the carbon black is being mixed into the compound, the surface appears rough and dull, but, as mixing proceeds and the pigment aggregates are comminuted and wetting takes place, the stock assumes a high gloss. Mill operators, lacking other means of evaluation, have relied on this test from the early days of the industry. The surface sheen may conceal undispersed aggregates within the sheet, however, and the rating will be quite faulty. It is for this reason that other test methods are preferred.

A simple improvement is observation of a cut or torn section of the stock. Grenquist<sup>147</sup> cut samples with scissors and examined the edges by means of a microscope at a magnification of 300 times. Aggregates of carbon black appear as black masses lacking homogeneity. This method was refined somewhat by Allen and Schoenfeld.<sup>148</sup> The stock is torn, rather than cut, when in sheet form 6 to 8 mm. thick, and the edges are examined either by eye or with a low-power microscope. Standard samples are used for comparison. Two types of aggregates were observed: one, a soft aggregate which is in the process of comminution, shows as an irregular mass with the rubber covering the separate particles in the aggregate; the other, a hard aggregate, which is comminuted

<sup>146</sup> W. C. Walker and A. C. Zettlemoyer, *Am. Ink Maker*, **27**, No. 9, pp. 67-69, 93 (September, 1949).

<sup>146a</sup> I. M. Bernstein, *ibid.*, **27**, No. 10, pp. 29-33, 59 (November, 1949).

<sup>146</sup> Baltimore Club, *Am. Paint J.*, **31**, No. 6-E, pp. 22-23 (November 9, 1946).

<sup>147</sup> E. A. Grenquist, *Ind. Eng. Chem.*, **20**, 1073-78 (1928); *ibid.*, **21**, 665-69 (1929).

<sup>148</sup> R. P. Allen, *Ind. Eng. Chem., Anal. Ed.*, **2**, 311 (1930); R. P. Allen, and R. K. Schoenfeld, *ibid.*, **25**, 994-97 (1933).



with difficulty, has sharp edges and remains unwetted by the rubber hydrocarbon.

Microsections, despite the difficulties of preparation, provide useful information, but a number of sections have to be scanned to obtain information on the frequency and character of oversize aggregates.

### Data for Various Solids

Comments on particle size and shape have already been given in the descriptions of measuring methods. There are additional items of interest and importance that deserve mention in connection with well-defined classes of compounds. Numerical data on various powdered substances have been gathered in the several accompanying tables. Observations on the characteristics of different pigments and powders as given here were drawn from the references, as well as from personal examination of numerous original electron micrographs.

TABLE IV. CHECK LIST OF ARTICLES CONTAINING ELECTRON MICROGRAPHS OF POWDERED MATERIALS

Carbon blacks—Micronex	<i>Columbian Colloidal Carbons</i> , Vol. II, Columbian Carbon Co., New York, 1940; pp. 34-40.
Carbon blacks—Thermax, lampblack, Furnex, P-33, acetylene, Stat-ex, Micronex, Super Spectra	<i>Ibid.</i> , Vol. III, 1942; pp. 34-50.
Carbon blacks	W. A. Ladd, <i>Ind. Eng. Chem., Anal. Ed.</i> , <b>16</b> , 642-44 (1944).
Clays—dickite, kaolinite, halloysite, montmorillonite, bentonite, beidelite, attapulgite; others	A. F. Prebus, Chapter 7, <i>Colloid Chemistry</i> , Vol. V, J. Alexander, Editor, Reinhold Publishing Corp., New York, 1944; pp. 194-205; R. P. Humbert, <i>Bull. Am. Ceram. Soc.</i> , <b>21</b> , 260-3 (1942).
Chrome yellows and orange; iron oxides; ochre; zinc oxide	D. L. Tilleard and N. D. P. Smith, <i>J. Soc. Chem. Ind.</i> , <b>65</b> , 261-64 (Plates 1, 2) (1946).
Clays—China, bentonite; lithopone; iron blue; phthalocyanine blue; titanium dioxide-anatase, rutile; titanium dioxide-calcium sulfate composite; ultramarine; white lead; zinc sulfide	D. L. Tilleard and N. D. P. Smith, <i>ibid.</i> , <b>65</b> , 305-8 (Plates 5, 6) (1946).
Clays—montmorillonite, kaolinite, bentonite, other varieties	B. T. Shaw, <i>J. Phys. Chem.</i> , <b>46</b> , 1032-43 (1942).
Clays—attapulgus, China; ferric oxide, hydrated; iron blue; zinc oxides	H. Green and E. F. Fullam, <i>J. Applied Phys.</i> , <b>14</b> , 332-40 (1943).

TABLE IV. CHECK LIST OF ARTICLES CONTAINING ELECTRON MICROGRAPHS OF POWDERED MATERIALS (*Continued*)

Calcium carbonate	A. R. Lukens, C. G. Landis, and T. G. Rochow, <i>Paper Trade J.</i> , <b>112</b> , 31-38 (April 10, 1941).
Calcium carbonate; carbon black—high color; chrome yellow, medium; iron oxide yellow; iron blue; lithopone; titanium dioxide; zinc sulfide	E. F. Fullam, <i>Interchem. Rev.</i> , <b>1</b> , 20-1 (1942).
Chrome yellow, medium; chrome green; carbon black, high color; lithopone	E. K. Fischer and D. M. Gans, <i>Colloid Chemistry</i> , Chapter 14, Vol. VI, J. Alexander, Editor, Reinhold Publishing Corp., New York, 1946; pp. 292-93.
Iron oxides—yellow, black	K. E. Burgess, <i>Protective and Decorative Coatings</i> , J. J. Mattiello, Editor, Office of Quartermaster General, U. S. Govt. Printing Office, Washington, D. C., 1945; pp. 208-11. (N.B. This is not one of the volumes of the same title published by John Wiley & Sons, Inc.)
Diatoms, diatomaceous earth, kieselguhr	<i>Interchem. Rev.</i> , <b>2</b> , 34-36 (1943); R. B. Anderson, J. T. McCartney, W. K. Hall, and L. J. E. Hofer, <i>Ind. Eng. Chem.</i> , <b>34</b> , 1618-28 (1947).
Carbon black; clay diatoms; magnesium, aluminum, zinc smokes; zinc oxide	V. K. Zworykin, et al., <i>Electron Optics and the Electron Microscope</i> , John Wiley & Sons, Inc., New York, 1945; pp. 309-19.
Zinc oxides	D. G. Brubaker, <i>Ind. Eng. Chem., Anal. Ed.</i> , <b>17</b> , 184-87 (1945).
Carbon black, titanium dioxide, zinc oxide	J. Hillier, <i>Symposium on New Methods for Particle Size Determination in the Subsieve Range</i> , ASTM, Philadelphia, March, 1941; pp. 90-4.
Antimony oxide; calcium carbonate clay—attapulgis; chromium oxide; iron blue; iron oxide; phthalocyanine green; ultramarine; zinc oxide	M. C. Schuster and E. F. Fullam, <i>Ind. Eng. Chem., Anal. Ed.</i> , <b>18</b> , 653-57 (1946).
Antimony oxide; carbon black; clay—kieselguhr; chrome yellow; iron blue; white lead; titanium dioxide; zinc oxide	P. G. Meerman, <i>Verfkroniek</i> , <b>20</b> , 160-5 (1947).
Titanium dioxide	A. E. Jacobsen and W. F. Sullivan, <i>Ind. Eng. Chem., Anal. Ed.</i> , <b>18</b> , 360-64 (1946).
Aluminum, iron, and vanadium oxides; colloidal gold	J. Turkevich and J. Hillier, <i>Anal. Chem.</i> , <b>21</b> , 475-85 (1949).

TABLE V. SURFACE AREAS AND PARTICLE SIZES OF WHITE PIGMENTS AND EXTENDERS BY WATER VAPOR ADSORPTION AND MICROSCOPY \*

Pigment	Specific Surface (sq.m./g.)	$d_3$ Adsorption ( $\mu$ )	$d_3$ Microscopy ( $\mu$ )
Titanium dioxide	8.2	0.19	0.43
Asbestine	4.1	0.51	....
Whiting	2.6	0.85	....
Zinc oxide (Green Seal)	2.4	0.45	0.44
Blanc fixe	2.2	0.62	....
Lithopone	2.3	0.61	0.43
White lead, basic carbonate	1.1	0.80	0.66
Antimony oxide	0.61	1.7	0.61
Barytes	0.59	2.3	....

\* D. Smith and H. Green, *Ind. Eng. Chem., Anal. Ed.*, **14**, 382-86 (1942).

TABLE VI. PARTICLE SIZE OF ZINC OXIDES BY DIFFERENT METHODS \*

Method	Kadox Black	XX Red	XX Red	Reheated
	Label 15	Label 72	Label 78	
	$d_3$	$d_3$	$d_3$	$d_3$
	( $\mu$ )	( $\mu$ )	( $\mu$ )	( $\mu$ )
Microscopic measurement	0.28	0.34	0.79	1.86
Adsorption of methyl stearate	0.19	0.24	0.55	4.5
Liquid permeability	0.12	0.15	0.25	1.3
Nitrogen adsorption	0.115	0.124	0.28	1.7

\* P. H. Emmett and T. DeWitt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 28-33 (1941).

TABLE VII. SURFACE AREAS AND PARTICLE SIZES OF INORGANIC PIGMENTS BY ADSORPTION METHODS

Color	Area (sq.m./g.)	$d_3$ ( $\mu$ )	Adsorbate	Reference
Chrome yellow, primrose	7.14	0.166	Nitrogen	H
Chrome yellow, light	8.41	0.126	Nitrogen	H
Chrome yellow, medium	7.03	0.138	Nitrogen	H
Chrome orange, dark	0.62	1.43	Nitrogen	H
Iron oxide, lemon yellow	16.6	0.096	Nitrogen	H
Iron oxide, red	15.4	0.078	Nitrogen	H
Iron oxide, black magnetic	6.83	0.173	Nitrogen	H
Burnt sienna	110.	0.017	Nitrogen	H
Vermilion, English	3.24	0.241	Nitrogen	H
Orange mineral	1.60	0.401	Nitrogen	H
Iron blue	43.8	0.0721	Nitrogen	H
Iron blue	32.9	0.093	Butane	II
Ultramarine	13.1	0.20	Nitrogen	H
Iron blue	26.	0.13	Water	SG
Orange mineral	0.76	1.3	Water	SG
Chrome yellow, medium	3.9	0.26	Water	SG
Ultramarine	13.	0.20	Water	SG

References: H—E. N. Harvey, Jr., "Symposium on Paint and Paint Products," *Am. Soc. Testing Materials, Special Tech. Pub.*, **75**, pp. 60-84; SG—D. Smith and H. Green, *Ind. Eng. Chem., Anal. Ed.*, **14**, 382-86 (1942).

Note: The surface areas by nitrogen and butane adsorption are BET values; the  $d_3$  values are based on an average surface area computed by three different methods.

TABLE VIII. SURFACE AREAS AND PARTICLE SIZES OF COLLOIDAL CARBONS BY NITROGEN ADSORPTION

Black	$S$ (sq.m./g.)	$d_3$ ( $\mu$ )	Reference
Royal Spectra	1040	0.0032	H
Carbolac 1	936	0.0036	EC
Carbolac 1	947	0.0035	STB
Carbolac 2	772	0.0043	EC
Super Spectra	552	0.0060	H
Mogul	475	0.0070	EC
Mogul	346	0.0096	H
Mogul	350	0.0095	STB
Monarch 71	398	0.0084	EC
Monarch 71	330	0.010	STB
Super Carbovar	391	0.0085	STB
No. 140	238	0.014	H
Peerless, Standard	223	0.015	H
Elf 20	110	0.030	STB
Elf 4	112	0.030	EC
Miconex	106	0.031	E
Molacco	62	0.054	
Acetylene	64	0.052	STB
Lampblack	28	0.12	STB
Gastex	26	0.13	AST
P-33	15	0.22	E

References: AST—F. H. Amon, W. R. Smith, and F. S. Thornhill, *Ind. Eng. Chem., Anal. Ed.*, **15**, 256-58 (1943); E—P. H. Emmett, *ibid.*, **13**, 28-33 (1941); EC—P. H. Emmett and M. Cines, *J. Phys. & Colloid Chem.*, **51**, 1329-41 (1947); H—E. N. Harvey, Jr., *Am. Soc. Testing Materials, Special Tech. Pub.*, **75**, p. 76 (1947); STB—W. R. Smith, F. S. Thornhill, and R. I. Bray, *Ind. Eng. Chem.*, **33**, 1303-7 (1941).

TABLE IX. SURFACE AREAS OF COLLOIDAL CARBONS BY NITROGEN ADSORPTION AND ELECTRON MICROSCOPY

Black	Adsorption (sq.m./g.)	Electron Microscope * (sq.m./g.)
Lampblack	25.5	23.5
Lampblack (activated)	208.	27.4
P-33	20.7	20.9
Acetylene black	64.5	55.9
Grade 6 Channel	110.	74.8

\* Density of 2.00 assumed for computation. P. H. Emmett, *Ind. Eng. Chem., Anal. Ed.*, **13**, 28-33 (1941).

TABLE X. SURFACE AREAS AND PARTICLE SIZES OF ORGANIC PIGMENTS BY ADSORPTION METHODS

Color	Area (sq.m./g.)	$d_3$ ( $\mu$ )	Adsorbate	Reference
Hansa yellow, G	24.3	0.18	Nitrogen	H
Hansa yellow, G	13.6	0.50	Butane	H
Hansa yellow, 10G	14.9	0.36	Nitrogen	H
Benzidine yellow	22.2	0.16	Nitrogen	H
Phthalocyanine blue	78.9	0.054	Nitrogen	H
Phthalocyanine green	57.1	0.049	Nitrogen	H
Eosine toner	80.3	0.027	Nitrogen	H
Toluidine toner	16.3	0.26	Nitrogen	H
Victoria blue, PTA lake	58.5	0.055	Nitrogen	H
Eosine toner	41	0.073	Water	SG
Rhodamine toner	12	0.18	Water	SG
Madder lake	53	0.073	Water	SG
Red lake C (barium lake)	15	0.23	Water	SG
Lithol red	36	0.083	Water	SG
Peacock blue (aluminum hydroxide lake)	83	0.036	Water	SG
Lithol rubine	26	0.12	Water	SG

References: same as Table VII.

## Titanium dioxide

Several varieties of titanium dioxide have assumed the lead as important white pigments. Two crystalline types, anatase and rutile, are in commercial production, but most of the particle-size measurements reported are for anatase. The pigment is prepared by hydrolysis of titanium sulfate or titanium tetrachloride solutions; the initial precipitate is extremely fine and gelatinous in character with a specific surface approximately 300 sq. m. per gram.<sup>149</sup> On calcination, the crystals grow until a practical pigment size is reached with a specific surface of approximately 10 sq. m. per gram. A number of size measurements of titanium dioxide pigments have been made by various methods. Tilleard and Smith<sup>150</sup> state that both anatase and rutile are observed as spherical in form of sizes less than 0.1 micron. Electron micrographs have been published which show the particles as masses of extremely small crystals that are deformed, presumably, during calcination. It will be recalled that particle sizes obtained by centrifugation showed the presence of aggregates not entirely disrupted even by the severe shearing stresses on a two-roll mill. Adsorption data for typical commercial pig-

<sup>149</sup> E. N. Harvey, Jr., *Interchem. Rev.*, **4**, 103 (1945).

<sup>150</sup> D. L. Tilleard and N.D.P. Smith, *J. Soc. Chem. Ind.*, **65**, 261-64; 305-8 (1946).

ments reveal areas of 8 to 14 sq. m. per gram, with corresponding  $d_3$  values of 0.2 to 0.11 micron.

In some composite pigments (calcium sulfate-titanium dioxide) the separate components were observable in specimens described. In highly calcined, products, however, the identity of the separate components was not evident.

### Zinc oxide

Numerous measurements have been made on zinc oxides. This pigment is commercially available in a range of particle sizes and crystal shapes. One of the finest, intended for rubber compounding, has a  $d_3$  value of 0.10 to 0.12 micron. The commercial zinc oxides that are definitely acicular have particles with a mean length of 1 micron and a width of 0.12 to 0.20 micron. Tilleard and Smith<sup>150</sup> found considerable variation in the sizes of zinc oxide particles made by different processes: the product of the direct process (from ore) contained prisms  $1.5 \times 0.5$  micron, whereas the French process (from metallic zinc) produced smaller particles, 0.3 to 0.5 micron long and 0.12 micron wide. The acicular grade contained prisms with lengths varying from 0.25 micron to 5 microns.

One series of zinc oxides has been the subject of considerable investigation, providing a comparison of four different measuring methods (Table VI). The nitrogen adsorption method yields values somewhat smaller than the other methods. In general, particle sizes obtained by both adsorption and electron-microscope studies accord well with the older values estimated by the optical microscope and other methods.

### White lead

Microscopy of white lead pigments has been reasonably successful because the particles are, for the most part, above the lower limit of resolution of the light microscope. The presence of small particles was shown by electron microscopy. Tilleard and Smith<sup>150</sup> observe differences between products from the chamber, electrolytic, and stack processes. Small spherical particles between 0.07 and 0.1 micron with many aggregates from 0.5 to 1.0 micron were observed in the chamber-process white lead. Particles of approximately 0.5 micron were noted for the stack process. The electrolytic process appears to result in finer particles than the other two processes with many particles of less than 0.05 micron. The measured  $d_3$  value of basic carbonate white lead of 0.8 micron appears somewhat high in comparison with the electron-micrograph observations, but it is comparable to the  $d_3$  value of 0.66 micron, reported by Smith and Green by optical microscopy. Older values obtained by optical microscopy are in the range of 0.6 to 1.2 micron.

## Clays

Unlike pigments, clays are likely to represent mixtures of compounds, and interpretation of electron micrographs is more difficult. Humbert<sup>151</sup> presents electron micrographs of a variety of clays. The montmorillonites show structures that range from a fluffy, amorphous-type material to clearly defined, thin plates. Tilleard and Smith<sup>150</sup> observed that the sheets or flakes of bentonite were about 20 to 100 Å in thickness and in the thinner areas were quite "transparent" to the electron beam. This structure corresponds with evidence from x-ray diffraction data indicating that bentonite has a layer structure; on imbibition of water, swelling occurs, and, when the particles are deposited from a dilute suspension in water, a sheet or film is formed. China clay contains hexagonal plates 0.1 to 5 microns in diameter; <sup>151a</sup> the thickness is about the same as that of bentonite specimens, noted above. Some varieties of magnesium clays are fibrous. Diatomaceous earths are formed from the siliceous skeletons of microscopic marine forms and are characterized by an intricately fine structure. Because of the varied nature and complex structure of clays, it is difficult to express the particle size in terms of an equivalent geometrical shape. Shaw<sup>152</sup> states that the particle size of montmorillonite merely reflects the degree of dispersion and that ultimate dispersion breaks the mineral down to unit crystals or plates with a thickness of approximately 1 millimicron.

An important investigation of the properties of diatomaceous earth has been reported by Anderson and co-workers.<sup>153</sup> The diatom skeletons that form the deposits have a lace-like structure with innumerable pores. The crude deposit is dried, calcined, and classified into size fractions by screening or by settling in air or water. The commercial product, also known as kieselguhr, diatomite, or infusorial earth, has a large surface area as a consequence of the porous structure. Areas ranging from 15 to 37 square meters per gram were found by nitrogen adsorption for the natural earth. After calcination, the surface area decreased, reaching 2 to 6 square meters per gram. The over-all dimensions of the diatom particles vary considerably: some are plates averaging about  $5 \times 10$  microns; others are rod-shaped,  $1.5 \times 30$  microns in size. The pore diameter also varies, but many species have holes ranging from about 0.2 to 1.0 micron in diameter and a few specimens have holes as large as 5

<sup>151</sup> R. P. Humbert, *Bull. Am. Ceramic Soc.*, **21**, 260-3 (1942).

<sup>151a</sup> Size estimates from electron micrographs by M. Swerdlow and L. Brama of the National Bureau of Standards.

<sup>152</sup> B. T. Shaw, *J. Phys. Chem.*, **46**, 1032-43 (1942).

<sup>153</sup> R. B. Anderson, J. T. McCartney, W. K. Hall, and L. J. E. Hofer, *Ind. Eng. Chem.*, **39**, 1618-28 (1947).



microns in diameter. Computation of a diameter for this material would be meaningless.

### Iron oxides

Natural iron oxides were found by Tillcard and Smith<sup>160</sup> to have a very wide range in particle size. Some components appeared translucent, a property attributed to the clay admixed with the colorant. None of the colors was observed to have a definite crystalline form. Synthetic iron oxides, on the other hand, had fairly definite crystalline form and were free from particles inferred to be clays. The yellow iron oxide appeared definitely acicular, and the majority of particles were very small and rod-shaped, approximately 0.03 micron in width, the larger particles being approximately 0.1 micron wide and 0.5 micron long. The red oxide showed particles mostly below 0.1 micron in diameter and many around 0.05 micron. Stable aggregates of the primary particles were observed. In one well-characterized line of iron oxide pigments<sup>161</sup> electron micrographs show the yellow and red pigments in the form of elongated crystals, whereas the brown and black are rounded aggregates. Differences in manufacture are reflected in the shape: one red oxide made by calcination has spheroidal particles, another oxide, made by a precipitation process, has acicular crystals. The former is about 0.06 micron in diameter; the latter, extensively used in paint formulation, has "ultimate" crystals approximately 0.03 micron in width and 0.15 to 0.3 micron in length. There is, however, considerable variation in size. Nitrogen adsorption gave  $d_3$  values ranging from 0.1 to 0.17 micron.

### Iron blue

Commercial varieties of iron blue have particles of very fine size, in the class of carbon blacks. Electron micrographs confirm the  $d_3$  values obtained by nitrogen adsorption and show particles as small as 0.05 micron. There is some evidence that the particle is formed by fracture of a dried gel, and as a consequence the particles are of irregular shape. Some varieties produce transparent dispersions, and this fact can be adduced as further evidence for the small particle size. Harvey<sup>8</sup> reports a particle-size count made on an electron micrograph that gave a  $d_3$  value of 0.062 micron, slightly lower than the adsorption measurement 0.072 micron.

<sup>164</sup> Columbian Carbon Co., New York, *Mapico Pigments*, 1944; *Red Oxide of Iron*, 1941 (booklets).

### Ultramarine blue

In comparison with other pigments, ultramarine has a rather large particle size, of the order 0.6 to 1.0 micron. This pigment is manufactured by heating a mixture of sulfur, soda ash, charcoal, and clay. There is some evidence that clay particles persist through the processing, and a porous structure can be inferred from the relatively smaller diameters computed from adsorption data. The particles ordinarily do not have a regular form and appear to be fractured pieces of a larger magma. The specific surface for one type has been reported as 13 sq. m. per gram ( $d_3 = 0.2$  micron) which suggests a somewhat porous structure.

### Lead chromate

Chrome yellow medium, which corresponds fairly closely to a normal lead chromate, forms definite crystals. Prisms 1 micron long and 0.2 micron wide were observed by Tilleard and Smith. Considerable variation in the chrome-yellow pigments is associated with chemical composition: the light hues are admixed with lead sulfate; the orange varieties are basic lead chromate. Primrose-yellow particles were described by Tilleard and Smith as rounded particles ranging from 0.1 to 0.3 micron, lemon-yellow as elongated crystals about 0.5 micron in width and 2 to 3 microns long, and chrome oranges, as clusters of rounded particles 0.3 to 0.5 micron in size. Differences in particle shape can be related to some extent to characteristic crystal form; and, since both orthorhombic and monoclinic crystals are formed, a commercial pigment may contain mixtures, depending on the chemical conditions existing during precipitation and subsequent treatment. The writer has observed one type of light chrome yellow that regularly formed large acicular crystals; the mass of crystals produced by allowing the slurry to stand overnight entrained all the mother liquor and gave, in effect, a pseudo gel structure from the interlacing crystals. Subsequent drying and pulverizing broke the crystals into short lengths, and their original structure would be hard to deduce from the resulting array of fragments. Generally, the chrome-yellow pigments can be studied to advantage with the optical microscope, but fine structure is revealed only by the electron microscope.

### Fluorescent and phosphorescent pigments

Fluorescent pigments are activated by ultraviolet light, and, when the activating source of energy is turned off, the fluorescence ceases. Phosphorescence, on the other hand, continues for many hours after the exciting source of energy is removed. The most brilliant fluorescent compounds are dyes such as eosin, rhodamine, auramine, as well as a

group of special compounds that are substantially colorless in white light. Metallo-organic compounds are also used.<sup>155</sup> The particle size of these materials is, of course, very small, well below visibility in the optical microscope.

Inorganic fluorescent compounds, however, are of larger particle size. Sulfides of zinc or cadmium or mixtures are used; their particle size is approximately 1 micron.<sup>156</sup> Phosphorescent pigments composed of sulfides of zinc, cadmium, calcium, and strontium are very coarse, ranging from 5 to 20 microns. These materials cannot be ground to finer sizes without losing some of the brilliance of their phosphorescence.

### Carbon pigments

Colloidal black pigments proved the most perplexing of all pigments before the electron microscope became available. The methods of optical microscopy provided data that suggested particles less than 0.2 micron in diameter, but all results were held suspect, despite the most skillful technique, in view of the lower values intimated by other measuring methods. Ultramicroscopy indicated a range from 15 millimicrons upwards, and 50 or 60 millimicrons was considered a probable approximate size for standard rubber black. Adsorption, centrifugal sedimentation, and x-ray diffraction supported these lower estimates, but the methods did not supply information sufficiently definitive to be more than a confirmation of the ultramicroscopic values and the inferences from optical microscopy. The industrial importance of carbon black and related materials (acetylene black, lampblack, bone black) impelled many investigators to refine existing means for more satisfactory information, but their attempts had small reward. In 1940 a series of electron micrographs was published,<sup>157</sup> and work in Germany at the same time brought a new insight to the subject.

The carbon-black particle was revealed by the electron microscope as spheroidal in form, in contrast to the older idea, maintained by some investigators, that the primary particles were hexagonal platelets. The particle size was shown to be a fraction of that apparent in the optical microscope, and the disposition to form aggregates was clearly manifested. Research on the carbon pigments has proceeded apace since that

<sup>155</sup> G. T. Schmidling, Chapter 22A, pp. 655-711, *Protective and Decorative Coatings*, J. Mattiello, Editor, John Wiley & Sons, Inc., New York, 1943; cf. also Chapter 22B in the same volume.

<sup>156</sup> G. F. A. Stutz, American Society for Testing Materials, "Symposium on Paint," Philadelphia, Pa., 1943; pp. 57-60.

<sup>157</sup> Columbian Carbon Co., New York, *The Particle Size and Shape of Colloidal Carbon as Revealed by the Electron Microscope* (1940); *The Surface Area of Colloidal Carbons* (1942). A summary of earlier work on the measurement of particle size of carbon black is included in these books.

time, so that now the colloidal carbons represent a class of particulate materials that has been more thoroughly investigated than any other.

Two size-distribution curves for carbon black are shown in Figure 9. The mean particle diameter (presumably  $d_{med}$ ) for Super Spectra is given as 0.013 micron and for lampblack as 0.097 micron.

Surface areas and  $d_3$  values for a series of well-characterized colloidal carbons are given in Table VIII. The areas were determined by nitrogen adsorption; the diameters were computed from the equation  $d_3 = 6/(\text{Density} \times \text{specific surface})$ . The density was taken as 1.8.<sup>158</sup> Sev-

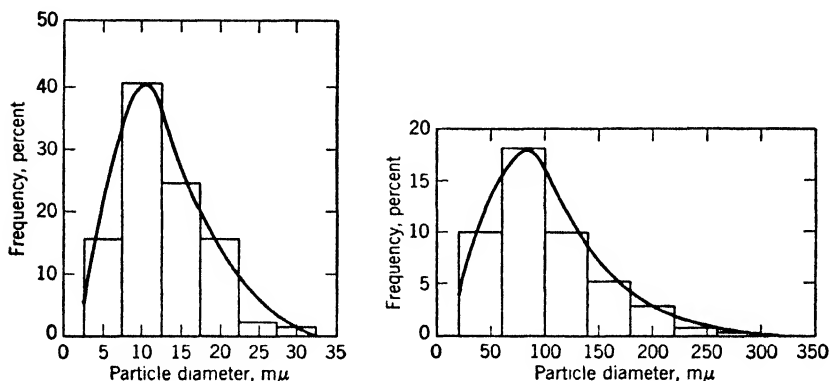


FIGURE 9. Size-distribution curves for Super Spectra carbon black (left) and lampblack (right). (Courtesy Columbian Carbon Co. and Binney and Smith Co.)

eral of the carbon pigments were studied by different investigators, and attention is drawn to the data for Carbolac 1 and Mogul blacks. The agreement is quite satisfactory. In addition, Harvey<sup>8</sup> found  $d_3$  for Carbolac 1 by butane adsorption to be 0.0037 micron.

The correspondence between adsorption and electron microscope data is shown in Table IX. When the blacks are non-porous, the agreement is good, but for porous materials the surface area from adsorption is much greater.

Formation of pellets of carbon black has no detectable effect on the surface area available to adsorbents. Emmett and Cines<sup>159</sup> formed pellets of three types of carbon blacks by means of the "Spheron" process<sup>160</sup> and measured surface areas by low-temperature nitrogen adsorption. The areas of the pelletized samples were found to be the same

<sup>158</sup> This density, obtained by the water and oil displacement methods, is usually employed. Higher densities of about 2.0 are found by helium displacement and may be preferred for computation of  $d_3$  values from adsorption data. Cf. R. P. Rossman and W. R. Smith, *Ind. Eng. Chem.*, **35**, 972-76 (1943).

<sup>159</sup> P. H. Emmett and M. Cines, *J. Phys. and Colloid Chem.*, **51**, 1329-41 (1948).

<sup>160</sup> E. Billings and H. H. Offutt, U. S. Patent 2,120,541 (June 14, 1938).

as those of samples of the original powder black within experimental error. Emmett and Cines computed that about 3 percent of the area would be "blocked" if each carbon-black particle were in contact at a single point with another particle of equal size. The assumption for this computation was that the particles were 4 millimicrons in diameter and that the surface closer than 0.4 millimicron to the adjacent particle would be unavailable to the adsorbent. Actually the particles would be expected to be in contact at more points, and the actual decrease in available surface should be about 10 percent. These investigators offer the explanation that the particles are sufficiently mobile to allow the separate particles to adsorb the full complement of nitrogen.

### Organic pigments

The images formed by organic pigments in the electron microscope generally show less contrast than inorganic powders, and, as a consequence, the micrographs reveal less detail. For many pigments, the primary particles are, moreover, quite small and they tax the resolving power of the instrument. A resinated calcium lithol toner was observed with the largest particles about 0.1 micron and the smallest approximately 0.005 micron. Considerable variation in shape was observed—from rounded particles to others that appeared to be prismatic. Many of them were evidently fragments of larger particles. One benzidine yellow had extremely small particles which were associated in string-like complexes (perhaps floccules). Peacock blue, a representative aluminum hydrate base product, had an extremely irregular form with great variation in size. This pigment is actually a pulverized gel, and a regular shape could hardly be anticipated. Phthalocyanine blue appeared as very fine particles, in appearance similar to a high-color carbon black, and of fairly uniform size. Adsorption data lead to a  $d_3$  value of about 0.05 micron. This pigment varies chemically, and some species readily form beautiful bunches of acicular crystals when suspended in aromatic hydrocarbons. These bundles are of such size that they can easily be seen under low-power optical magnification.<sup>161</sup> This crystal habit could persist through different dispersion procedures and result finally in minute acicular particles not easily detected even by electron microscopy. The disposition to crystallize in this form is reduced by chlorination and appears to be completely lost in the polychlor compound which is a brilliant green.

<sup>161</sup> S. A. Scully, *Interchem. Rev.*, **3**, 39-44 (1944); a photomicrograph of phthalocyanine crystals appears on the cover of this issue. Formulation adjustments using aliphatic hydrocarbon solvents to avoid crystallization are described by A. E. Gessler and D. M. Gans, U. S. Patent 2,317,371 (April 27, 1943).

Adsorption data, collected in Table X, supplement this information. Harvey notes  $d_3$  values for a few organic colors, of which a phloxine toner was the smallest. Hansa yellow has comparatively large particles, in accord with other properties grossly observed, such as the opacity of pigment dispersions. Toluidine toner is in a similar category.

Considerable work remains to be done on the electron microscopy of organic pigments.

### Optical Properties and Particle Size

The optical properties of pigment dispersions are frequently the attributes that establish their utility in consumer products. Protective coatings for all except the meanest uses are necessarily decorative as well as protective in function, and the manufacturer is pressed to obtain exact color matches and to maintain decreasingly smaller tolerances from batch to batch. Where white coatings are used, the maximum opacity consonant with durability and cost is the usual objective. As in so many other branches of applied science, remarkable progress has been achieved by empirical methods. Elaboration of the theory for the optical properties of dispersions is not germane to the central thesis of this monograph, but several topics relating to particle size deserve brief mention.<sup>162</sup>

Elementary principles of optics teach that the optical characteristics of pigmenting substances are established by (1) the index of refraction difference between that of the dispersed solid and the suspending medium, (2) the absorption of light by the solid, and (3) the particle size. Only the particle size is subject to control.

Massive crystals of many substances are often transparent. A white pigment is essentially a transparent substance which absorbs an inappreciable amount of radiant energy of wavelengths in the visible spectrum (approximately 400 to 700 millimicrons). When a crystal is pulverized, the powder appears white because the light that strikes it is reflected at all possible angles at the air-solid interfaces. Some light goes through the particles and is refracted on emerging, only to meet additional reflecting interfaces. If some of the wavelengths are absorbed, then the powder is colored.<sup>163</sup>

<sup>162</sup> The effect of flocculation on opacity is noted in Chapter 4. The relation of particle size to flow properties of dispersions is discussed in Chapter 5.

<sup>163</sup> A general summary of this subject is by H. E. Merwin, *Am. Soc. Testing Materials, Proc.*, **22**, Part II, 1946 (1917). A readable general treatise by R. M. Evans is to be recommended: *An Introduction to Color*, John Wiley & Sons, Inc., New York, 1948; see Chapter XVIII, pp. 278-94.

The reference point in any function relating particle size to optical properties is the wavelength  $\lambda$  of the light impinging on the particles. When the particle size is very small in relation to the wavelength the dispersion appears translucent or transparent, for no scattering occurs at the interface between the particle and the surrounding medium. As the particle size increases, scattering becomes progressively greater until an optimum size is reached, which for most pigments dispersed in conventional paint vehicles is of the same magnitude as  $\lambda$ .

These are general statements. Adequate data to establish various limits are at present not available. Barnett<sup>164</sup> in a review touching briefly on the optical properties of dispersions observes that particle-size information is meager and thus far has been of small help in assessing the practical value of pigments for their optical properties. There are, nevertheless, some data of interest. The measurements of Stutz and Pfund<sup>165</sup> have already been noted. Their value 0.24 micron as the optimum size for an aqueous zinc oxide dispersion holds only under the conditions of their experiment (transmission measurements with light of dominant  $\lambda = 0.54$  micron). More recent data cited by Clewell<sup>166</sup> for a similar suspension gave a slightly larger size, 0.29 micron. Merwin<sup>168</sup> gives the optimum particle size for white pigments as the range of 0.5 to 1 micron, but his estimate was made on early particle-size measurements and can be rated, accordingly, as high. A theoretical analysis by Shoulejkin<sup>167</sup> showed that particles of approximately the same size as  $\lambda$  produced the highest scattering in the direction of the incident light.

The optimum size for a white pigment cannot be specified without consideration of the size distribution. A typical dispersion of titanium dioxide in a paint vehicle contained 38 percent of the particles in the size group 0.3 to 0.4 micron; the largest particles were greater than 0.5 micron (3 percent) and the smallest, 0.15 to 0.2 micron (16 percent).<sup>168</sup> In addition, particle shape needs consideration. Acicular zinc oxide dispersed in oil has a higher opacifying effect than would be expected. Depew and Eide<sup>169</sup> state that needle-shaped crystals act as though they had been cut into sections of the optimum length for maximum opacity. The diameter of the crystals is then the important dimension.

<sup>164</sup> C. E. Barnett, *Ind. Eng. Chem.*, **41**, 272-79 (1949).

<sup>165</sup> See discussion on turbidimetry.

<sup>166</sup> D. H. Clewell, *J. Optical Soc. Am.*, **31**, 521-27 (1941).

<sup>167</sup> W. Shoulejkin, *Phil. Mag.* (Series 6), **48**, 307-20 (1924).

<sup>168</sup> J. Barksdale, J. L. Turner, and W. W. Plechner, Chapter 15, pp. 389-417 in Vol. 2, *Protective and Decorative Coatings*, J. Mattiello, Editor, John Wiley & Sons, Inc., New York, 1942.

<sup>169</sup> H. A. Depew and A. C. Eide, *Ind. Eng. Chem.*, **32**, 537-40 (1940).

Because of the complexity of these optical relationships, empirical testing methods are essential for practical evaluation of pigment-hiding power. One procedure is to coat a white card printed with a geometrical design in black and to rate visually the relative obscuring qualities of different dispersions. An improvement on this method is by means of reflectometer measurements on the coating spread over a white and black surface; contrast ratios can be computed, and a more quantitative assay is then possible.<sup>170</sup>

The tinting-strength method is frequently used to rate pigments. When a colored pigment is mixed with white, the resulting tint provides a quantitative measure of the effectiveness of either the color or the white, depending on the purpose of the test. As already noted, the method can be used to estimate particle size when suitable calibration standards are prepared. There is some controversy over the relationship between tinting strength and the hiding power of the white pigment, but the writer has found an exponential curve to fit data obtained by standardized techniques for tinting strength and hiding power. Using fractionated samples of anatase titanium dioxide, the maximum tinting strength was found at  $d_3$  values from 0.4 to 0.6 micron.

With colored pigments Barrick<sup>171</sup> found the maximum in tinting strength of molybdate orange at 0.5 micron and iron blue at 0.3 micron. Size fractions were obtained by centrifuging.

The intensity of blackness or "jetness" of carbon black dispersed in bodied linseed oil (as well as other vehicles) is directly related to particle size: with the finer carbon-black particles greater "blackness" results.<sup>172</sup> This relationship is shown in Figure 10, taken from the experimental results of Smith and co-workers. The "nigrometer" is a reflectometer designed to measure differences in reflectance at very low levels. As the particle size decreases the appearance of "blackness" increases, and the nigrometer scale values decrease.

The effect of entrained air on the optical properties of dispersions deserves consideration. The ultraviolet reflectance of paints containing magnesium carbonate was found to decrease on prolonged grinding in a

<sup>170</sup> Methods for hiding-power determination have been reviewed by E. W. McMullen and E. J. Ritchie, Chapter 5, pp. 141-72 in Vol. IV of *Protective and Decorative Coatings*, J. Mattiello, Editor, John Wiley & Sons, Inc., New York, 1944. R. H. Sawyer has discussed various theoretical and practical features of this test: see American Society for Testing Materials, "Symposium on Color," Philadelphia, Pa., 1941, pp. 23-36; also, *J. Applied Phys.*, **13**, 596-601 (1942) and *Ind. Eng. Chem., Anal. Ed.*, **6**, 113 (1934).

<sup>171</sup> G. Barrick, *Paint, Oil & Chem. Rev.*, **104**, 7-10 (Jan. 1, 1942).

<sup>172</sup> W. R. Smith, F. S. Thornhill, and R. I. Bray, *Ind. Eng. Chem.*, **33**, 1303-7 (1941); O. J. Brown, Jr. and W. R. Smith, *ibid.*, **34**, 352-55 (1942).



pebble mill.<sup>173</sup> The effect was most noticeable when the refractive index difference between vehicle and pigment was small. A credible explanation advanced was as follows: the aggregates present entrained sufficient air to act as an interface for reflection, and, as the aggregate size was re-

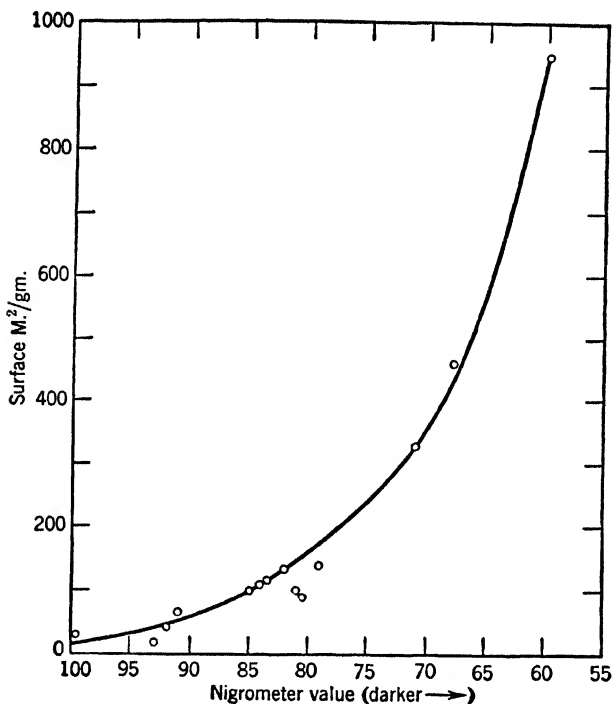


FIGURE 10. Relation between surface area of carbon blacks and color intensity. (Courtesy Godfrey L. Cabot, Inc.)

duced by extended grinding, the entrained air was displaced and the ultraviolet reflectance decreased.

### Resumé

The complexities of particle-size analysis, both experimental and mathematical, are such as to leave the industrial scientist in a quandary. Usually there is a specific question relating to the end-use properties of a given product, and the problem becomes one of deciding how to use published data or, if suitable information is not found in the literature,

<sup>173</sup> D. F. Wilcock, *Ind. Eng. Chem.*, **33**, 938-40 (1941).

to determine what course should be pursued in obtaining the necessary data.

The data assembled in Tables V–X will be of assistance in this quest. Since 1940 reproductions of electron micrographs of fine particles have been published in numerous journals. A check list to references for many of these photographs is given in Table IV. Unfortunately the quality of the printing in many papers is so poor that the detail present in the original is imperfectly reproduced. The illustrations have some value, nevertheless, in showing particle shapes and in providing a rough comparison of particle sizes.

The assumption underlying the listing of the numerical data and in the remarks on different materials is that commercial products are produced with some uniformity. This assumption does not allow for deductions regarding fine differences between products, but it is certainly valid for identifying classes of compounds. The empirical methods used for quality control in manufacturing effect automatically a measure of constancy in particle shape and size from lot to lot. With colorants in particular, the uniformity over a period of years is remarkable, and carbon black is perhaps the most uniform product of all.

What course to follow where information is not readily available depends on so many factors that a single answer is impossible. If the size is well above the lower limit of resolution of the optical microscope, the methods of visual examination or photomicrography should be adopted, since they are direct and offer a complete description of the particle. Particle-size counts are usually considered tedious, but actually they are no more so than many other analytical procedures. Sedimentation tests are easily performed if the essential condition of deflocculation of the particles can be realized. These methods may not provide sufficiently precise information, however, and other more involved procedures then become necessary. Among these are low-temperature nitrogen adsorption and electron microscopy. The remaining methods may be adopted for specific purposes, and for routine control purposes several procedures are of inestimable value. Comparison of different methods should be made whenever possible, not only to establish in the mind of the investigator some assurance for the validity of the adopted measuring procedure but also to provide a reference point or bench mark for the routinely accumulated data. The optical microscope used with ordinary skill is of great aid for this purpose.

Finally, in scanning the voluminous literature on the subject one is impressed by the infrequent cross-comparisons of methods. Measured values, sometimes undefined, often stand with little or no corroborating evidence. It is perhaps natural for one to take the view that the methods

and the data abound with seeming discrepancies, or at least that they are in a very imperfect state of development. But it is just as possible to gain quite the opposite impression: that despite formidable problems in definition and mathematical analysis and in the face of many variables that complicate particle-size measurements, the concordance of the reported values is indeed remarkable.

### 3. The Solid-Liquid Interface and Wetting

When a powdered solid has been dispersed in a liquid medium, the physical properties of the system can be related to the extent and character of the interface between solid and liquid. Wetting may be defined as the process by which a liquid comes into contact with a solid to form a solid-liquid interface. There are at least two and perhaps three possible cases: (1) the liquid spreads over the solid, displacing any adsorbed gases, wetting the solid completely; (2) the liquid does not spread, remaining as a lens; and (3) the liquid spreads partially, forming a junction at the solid with a finite contact angle. The first case is considered to represent complete wetting and the second, non-wetting. The third case is variously described as incomplete or partial wetting, poor wetting, etc., but neither the measurement nor interpretation can be made with certainty at present.

In examining the process of wetting and the physical properties of the solid-liquid system formed, it will be desirable to arrange our discussion in the following sequence: surface properties of liquids and solids, theory and methods for studying the solid-liquid system based on the contact angle concept, and, finally, the more recent experimental methods which offer a measure of the attraction of the solid surface for a liquid. In many respects these topics contain the essential problems of surface and colloid chemistry, and they form the key to our understanding of the properties of pigment dispersions.

#### Interfacial Tension and Surface Energy

When any two phases are in contact, the submicroscopically thin region between them is termed, generally, an *interface*. Usage has ascribed to interface the connotation of the junction between two immiscible liquids or a solid and a liquid, and to *surface* the region of con-

tact of a gas and a solid. The interface, as a region of discontinuity, is the locus for physical effects which differ markedly from the properties of the separate phases.

### The air-liquid interface

When a liquid is subjected uniformly to pressure, as in air, it assumes the form of a sphere. The liquid acts *as if* it were surrounded with an elastic membrane which spontaneously causes the liquid to assume a minimum surface area for a given volume. The explanation for this property is based on the attractive forces of the molecules within the liquid and near the surface: a molecule within the liquid is subjected to an attractive force approximately equal in all directions, but a molecule near the surface is subjected to an attractive force greater in the direction of the body of the liquid than at the air-liquid or vapor-liquid surface. As a consequence work must be performed to increase the extent of interface. This work is equal to the free surface energy per unit area of the interface. The dimensions of surface tension  $\gamma$  are those of energy, ergs per sq. cm., an expression that reduces to dynes per cm., the usual units in which surface tension is expressed.

The term *surface tension* may convey a fictitious meaning if the surface phenomena are pictured as due to a kind of skin or membrane on the surface of a liquid. Actually, the unbalance of forces, noted above, which gives rise to a property measurable as surface tension, requires that we consider interfacial effects in terms of two media, liquid and vapor or liquid and gas in this instance, and that the extension of the interface merely brings an enlargement of the interface without change in kind or quality. Further, it is necessary to assume that the unbalance of forces is acting through a distance negligibly small in comparison with the range of our measuring tools.

The concept of surface tension has been extremely useful in explaining physical phenomena. An extensive tabulation of data by Young and Harkins<sup>1</sup> is easily accessible. In general the surface tension values for pure liquids are more reliable than those for solutions; difficulties and anomalies in the measurement for solutions, particularly those containing surface-active substances, have been discussed by several authors.<sup>2,3</sup> A review by Dorsey<sup>4</sup> is valuable for its critique of a large num-

<sup>1</sup> T. F. Young and W. D. Harkins, *International Critical Tables*, McGraw-Hill Book Co., New York, 1926-33; References as follows: Vol. I, pp. 42, 103; Vol. IV, pp. 434-77; Vol. V, pp. 449-50.

<sup>2</sup> E. A. Hauser, Chapter 12, pp. 391-415, in *Advances in Colloid Science*, Vol. 1, E. O. Kramer, Editor, Interscience Publishers, Inc., New York, 1942.

<sup>3</sup> E. K. Fischer and D. M. Gans, *Ann. N. Y. Acad. Sci.*, **46**, 371-402 (1946).

<sup>4</sup> N. E. Dorsey, "Measurement of Surface Tension," *Sci. Paper* 540, Nat. Bur. Standards, Washington, D. C., 1926.

ber of methods for measurement. Harkins<sup>5</sup> and Adam<sup>6</sup> have provided extended descriptions of experimental technique.

### The liquid-liquid interface

A liquid in contact with another liquid with which it is immiscible forms a physical system that also lends itself to satisfactory analysis. The interfacial tension at the junction of the two liquids can be measured, and from the surface tensions of the separate liquids the energy relations of the interface may be computed. The theory upon which the analysis is based was established by nineteenth century physicists, and in its varied modern expression it is associated chiefly with the investigations of Hardy, Harkins, Langmuir, Bartell, Adam, and Rideal.

If a liquid column or bar, 1 cm. in cross-sectional area, is broken, the work performed, known as the work of cohesion,  $W_C$  is numerically equal to  $2 \times$  the surface tension,

$$W_C = 2\gamma_A \quad (1)$$

When an interface is formed between two liquids, a comparable quantity, the work of adhesion  $W_A$ , represents the work necessary to separate the liquids. The equation connecting the several quantities, a classic of surface chemistry, was given by Dupré,<sup>7</sup> in a form equivalent to the following:

$$W_A = \gamma_L + \gamma_{L'} - \gamma_{LL'} \quad (2)$$

The work of adhesion  $W_A$  is the work necessary to separate 1 sq. cm. of interface;  $\gamma_L$  and  $\gamma_{L'}$  are the surface tensions of the two liquids and  $\gamma_{LL'}$  is the interfacial tension. The quantity  $W_A$  provides a measure of the attraction of the molecules of one liquid for another liquid. If one liquid is found to spread over the surface of a second liquid, it is evident that the spreading liquid has a greater attraction for it than for itself. A condition of spreading then requires that the work of adhesion be greater than the work of cohesion of the spreading liquid. These relations were elaborated by Hardy,<sup>8</sup> and Harkins and Feldman<sup>9</sup> who de-

<sup>5</sup> W. D. Harkins, Chap. VI, "Determination of Surface and Interfacial Tension," in Vol. I, *Physical Methods of Organic Chemistry*, A. Weissberger, Editor, Interscience Publishers, New York, 1945.

<sup>6</sup> N. K. Adam, *The Physics and Chemistry of Surfaces*, third edition, Oxford University Press, London, 1937.

<sup>7</sup> M. A. Dupré, *Théorie Mécanique de la Chaleur*, Gauthier-Villars, Paris, 1869; pp. 369-401.

<sup>8</sup> Sir W. B. Hardy, *Proc. Roy. Soc. (London)*, **A87**, 610 (1912); **A88**, 303 and 313 (1913); *Collected Scientific Papers of Sir William Bate Hardy*, Cambridge, 1936; pp. 508-31; 540-69.

<sup>9</sup> W. D. Harkins and A. Feldman, *J. Am. Chem. Soc.*, **44**, 2665-85 (1922).

fine  $S_{L/L'}$  the spreading coefficient, as

$$S_{L/L'} = W_A - W_C \quad (3)$$

and

$$S_{L/L'} = \gamma_L - (\gamma_{L'} + \gamma_{LL'}) \quad (4)$$

In this equation  $\gamma_L$  is the surface tension of the lower liquid on which spreading takes place. If  $S_{L/L'}$  is positive in value, spreading takes place, since  $W_C$  is less than  $W_A$ . On the other hand, if  $S_{L/L'}$  is negative, spreading does not occur.

It is evident that  $S_{L/L'}$  may be computed when data are available on the surface and interfacial tensions of the two liquids. Typical data are given in Table I. Many organic liquids spread on a clean water surface

TABLE I. SPREADING COEFFICIENTS OF LIQUIDS ON WATER

Liquid	Spreading Coefficient (dynes/cm.)
Spreading liquids	
Butyl alcohol	+48
Octyl alcohol	37
Zinc resinate in hydrocarbon solvent	32
Oleic acid	25
Ricinoleic acid	25
Mineral oil + 1% oleic acid	22
Linseed fatty acids	22
Linseed oil	21
Lithographic varnishes (bodied linseed oil)	20-25
Aniline	12
Benzene	8.9
Hexane	3.1
Chlorinated paraffin oil (40% chlorine)	1.2
Non-spreading liquids	
Monobrombenzene	-3.3
Carbon disulfide	-6.9
Paraffin oil (pharmaceutical grade)	-9.0

since the cohesion of the liquid is low, and the presence of polar groups, —OH, —COOH, —CONH, —CHO, increases the adhesion to water. The presence of such a group is not an essential requirement for spreading, for if  $W_C$  is sufficiently lower than  $W_A$ , then  $S_{L/L'}$  will be positive. Hexane is an example of this condition. Non-spreading liquids have low adhesion for water, and the halogen-substituted hydrocarbons are noteworthy in this respect. A non-spreading liquid, such as highly refined mineral oil, will spread if a very small quantity of fatty acid is first dissolved in it. The spreading coefficient is then little different from that of the fatty acid itself. When water is placed on an organic liquid, how-

ever, spreading rarely occurs. This result may be anticipated from Equation 4, where, by substituting values for  $\gamma_L$  (the surface tension of the liquid on which spreading is to occur, in this instance an organic liquid) and  $\gamma_{L'}$  (the surface tension of the spreading liquid, in this instance water),  $S_{L/L'}$  will be negative for all but exceptional liquid pairs.

### The solid-liquid interface

The energy relationships systematized by the idea of the spreading coefficient have been helpful in understanding the liquid-liquid system. The solid-liquid system with which we are primarily concerned presents a far more difficult case. It could be expected that an extension of the idea of the spreading coefficient to solids would be fruitful; indeed, Harkins and Feldman<sup>9</sup> (p. 2683) observe that the free surface energy of solids is in general much higher than that of liquids, and, since the interfacial tension also would be correspondingly greater, it could be expected that  $S$  in an expression comparable to Equation 4

$$S_{S/L} = \gamma_S - (\gamma_L + \gamma_{SL}) \quad (5)$$

would be positive for the majority of cases observed. Hence, it would be predicted that liquids would spread over most solid surfaces. The question of the actual magnitude of  $\gamma_S$  and  $\gamma_{SL}$  presents serious obstacles. For this reason, indirect methods for the measurement of the energy relations at the solid-air and solid-liquid interface have been employed.<sup>10</sup> In general, this measurement has been based on contact-angle relations, the direct measurement of heat effects when a liquid wets a solid, and the adsorption of vapors and gases.

### Surface energy of solids

That the surface of a solid should differ from the interior may be inferred by analogy with a liquid. Atoms in a plane at the surface are subjected to forces from the interior of the crystal, but not to equivalent forces above or at some sensible distance from the surface, and the consequent dissymmetry leads to a property analogous to the surface tension of liquids.<sup>11</sup> In a crystalline substance, the atoms are fixed in a lattice, and it is not possible to extend the analogy with liquids very far. By altering the extent of a solid surface, the lattice is disturbed, and energy associated with the crystal structure affects any measure of the surface

<sup>10</sup> A review with extensive citations to the literature has been given by A. O. Allen, A. Knoll, L. W. Ryan, C. Murray, Chapter 1, pp. 1-79, Vol. IV, in *Protective and Decorative Coatings*, J. Mattiello, Editor, John Wiley & Sons, Inc., New York, 1944.

<sup>11</sup> Cf. C. H. Desch, *The Chemistry of Solids*, Cornell University Press, Ithaca, N. Y., 1934.



energy. Gibbs<sup>12</sup> in commenting on this problem points out that there is no equivalence in stretching the surface of a solid and in forming new surface. However, for some amorphous substances (pitch, waxes, etc.), where the surface is formed by gradual transitions from the fluid, Gibbs admits the possibility of equivalence between a surface tension value and the work expended in forming a unit of surface. These materials are, in effect, viscous liquids although they exhibit rigidity and other properties associated with the solid state.

It is apparent that the questions raised are partly a matter of definition, relating particularly to our concepts of the solid state and the attributes of the surface which we evaluate in energy terms. Most investigators look upon the interfacial energy relations of a solid as directly comparable to those of a liquid, although entirely different methods must be employed to assess their value. It appears more consistent when all aspects of the subject are considered, to speak of surface energy, rather than surface tension, in relations involving solids. In the following section, data obtained by different investigators will be compared with the primary intent of establishing some idea of the magnitude of the surface energy of solids.

Edser<sup>13</sup> argues that, although the surface tension of a solid is not so clearly evident as that of a liquid, it can be demonstrated by consideration of the separation of a crystal along cleavage planes. When separation occurs, the cleavage planes, which are parallel to the faces of a crystal, represent minimal surface-tension values. Edser computed surface-tension values of crystalline solids from the coefficient of thermal expansion and density of the substance, using an equation based on the van der Waals' relationship. Surface tensions so computed are as follows (in dynes per cm.): potassium sulfate, 151; quartz, 920; pyrites, 1175.

Various other calculations have been made, especially by Born and Lennard-Jones, and the data for potassium and sodium halides have been compared by Saal and Blott<sup>14</sup> and Boyd.<sup>15</sup> For the alkali halides,  $\gamma$  at absolute zero is in the range of 74 to 150 dynes per cm. Only approximate correlation with experimental values on the fused salts was obtained. Saal and Blott conclude that none of the methods provides a reliable determination of surface tension.

<sup>12</sup> *The Collected Works of J. Willard Gibbs*, Longmans, Green and Co., New York, 1928; Vol. I, p. 315.

<sup>13</sup> E. Edser, *Fourth Report on Colloid Chemistry*, p. 281, British Association for the Advancement of Science, His Majesty's Stationery Office, London, 1922.

<sup>14</sup> R. N. J. Saal and J. F. T. Blott, *Physica*, **3**, 1099-110 (1936).

<sup>15</sup> G. E. Boyd, paper in "Surface Chemistry," pp. 128-40, *Pub. Am. Assoc. Advancement Sci.*, **21**, Washington, D. C., 1943.

The surface tension of the molten substance near the melting point can be taken as a kind of limiting lower value. Thus for metals, surface tensions in the range of 400 to about 1600 dynes per cm. have been found.<sup>16</sup>

Waxes are considered solids of low surface tension. Measurements by Bartell and Zuidema<sup>17</sup> on melted waxes, extrapolated to 25° C., indicated approximate surface tensions from 33 to 38 dynes per cm. The waxes measured were carnauba, opal, japan, and spermaceti. Paraffin is also in this range. Pitch as measured by Berggren<sup>18</sup> has a surface tension approximately 30 dynes per cm.

The surface tension of molten glass is around 300 dynes per cm. as determined by Parmelee and Harmon,<sup>19</sup> although lower values have been noted for soda lime and lead glasses. The diamond has the highest surface energy, according to the calculations of Harkins:<sup>20</sup> 111 crystal face, 5,400, and for the 100 face, 9,400 ergs per sq. cm.

All the values cited are approximations, and it is difficult to estimate the error in both the theoretically derived and experimental data. We can, however, assume that the surface energy of solids is generally higher than that of organic liquids and water (excluding, of course, solids of very low cohesion, such as waxes).

### Relations Based on a Contact Angle

Of the methods for studying the solid-liquid interface, the idea of a definite angle between a liquid and solid has been most frequently used. Despite certain fundamental limitations, the contact angle concept is plausible and in consequence has had a wide appeal. Basis for the theory also lies in the work of nineteenth century physicists and proceeds from the assumption that a measurable angle, characterizing the physical properties of the system, exists at the junction of a liquid and a solid under certain conditions.

If we recall the numerous instances in which a water drop appears to rest without spreading on some solid surface, the geometrical arrange-

<sup>16</sup> R. Fricke describes calculation of surface tension from heat of sublimation and comparison with surface tension on molten metals extrapolated to the melting point. For cubic face or space-centered crystals (aluminum, platinum, copper, silver, gold, lead, and iron) the surface tension of the liquid metal is 30 to 70 percent of the calculated value. *Naturwissenschaften*, **34**, 313-14 (1947), through *Chem. Abs.*, **43**, 5652-53 (1949).

<sup>17</sup> F. E. Bartell and H. H. Zuidema, *J. Am. Chem. Soc.*, **58**, 1449-54 (1936).

<sup>18</sup> B. Berggren, *Z. physik. Chemie*, **44**, 61-80 (1914).

<sup>19</sup> C. W. Parmelee and C. G. Harmon, Univ. Illinois, *Exp. Sta. Bull.* 311, Urbana, Ill., 1939.

<sup>20</sup> W. D. Harkins, *J. Chem. Phys.*, **10**, 268-72 (1942).

ment may be easily visualized as shown in Figure 1. In every instance the angle is measured through the liquid phase: values ranging from  $0^\circ$  to  $180^\circ$  may be imagined.

The point or line of contact of the liquid with the solid is taken as the resolution of the three interfacial tensions considered as vector quantities. This idea was first proposed by Thomas Young in 1805, and it has since been generally described as Young's equation.<sup>21</sup> The statement

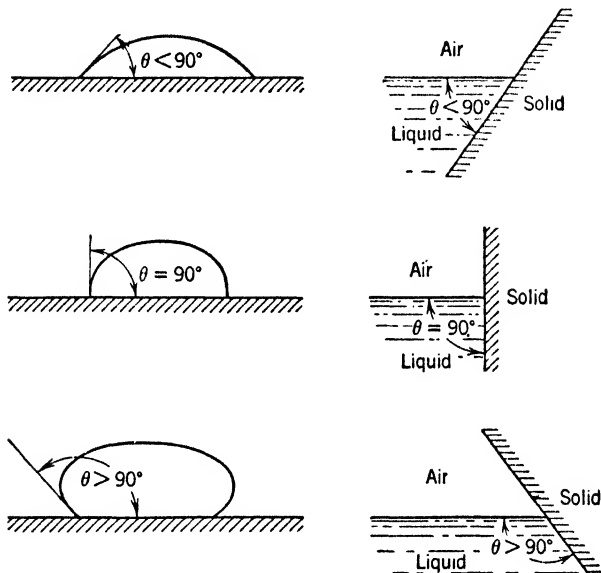


FIGURE 1. Conventional, idealized diagrams representing contact-angle relations.

by Young, however, is given in non-mathematical terms, and the uncertainty in meaning has been frequently noted. Since this statement is of considerable importance and the original paper is not easily accessible, the pertinent portion is quoted:

We may therefore inquire into the conditions of equilibrium of the three forces acting on the angular particles, one in the direction of the surface of the fluid only, a second in that of the common surface of the solid and fluid, and the third in that of the exposed surface of the solid. Now, supposing the angle of the fluid to be obtuse . . . the part which acts in the direction of the surface of the solid will be proportional to the cosine of the inclination . . . the same result follows when the angle of the fluid is acute. . . .

<sup>21</sup> T. Young, "An Essay on the Cohesion of Fluids," *Roy Soc. Phil. Trans.*, **1**, 65-87 (1805); reprinted with additions in *Miscellaneous Works of the Late Thomas Young*, George Peacock, Editor, J. Murray, London, 1855.

Although the whole of this reasoning, on the attraction of solids, is to be considered rather as an approximation than as a strict demonstration, yet we are amply justified in concluding that all the phenomena of capillary action may be accurately explained and mathematically demonstrated from the general law of the equable tension of the surface of contact appropriate to every combination of a fluid with a solid.

As it is usually stated in mathematical terms, Young's relationship is as follows:

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos \theta \quad (6)$$

where  $\gamma$  is the interfacial tension of the phase indicated by subscripts and  $\theta$  is the angle of contact of the liquid with the solid as measured through the liquid phase. Since  $\gamma_{SA}$  and  $\gamma_{SL}$  are indeterminate, Equation 6 is combined with Dupré's equation (Equation 2), rewritten for the solid-liquid system,

$$W_{A(SL)} = \gamma_{SA} + \gamma_{LA} - \gamma_{SL} \quad (7)$$

to give

$$W_{A(SL)} = \gamma_{LA} + \gamma_{LA} \cos \theta \quad (8)$$

The unknown quantities are eliminated in this manner, and the work of adhesion  $W_{A(SL)}$  should then be calculable when the contact angle is known.

Because of the apparent simplicity of this relationship and the necessity for an indirect experimental approach to the determination of the physical attributes of the solid-liquid interface, Equations 6-8 have provided the basis for considerable discussion and experimentation. When the contact angle is zero,  $\cos \theta = 1$ , and, accordingly, the work of adhesion becomes  $2\gamma_{LA}$ . There are, however, very serious complications in the use of Equation 8, and in its simple form it is not valid. The use of the relationship depends on the validity of contact-angle measurements, and it will be helpful to consider the difficulties inherent in such measurements.

### Methods for contact-angle measurements

Numerous methods have been devised for measuring contact angles, and for convenience these may be classified into two main groups: (1) angles measured by adjusting a surface to facilitate viewing and (2) angles measured by adapting the viewing conditions to the system as it is formed. In the former are well-known methods such as the tilting-plate and rotating-cylinder devices; in the latter are the sessile drop and pendant-bubble methods. A detailed description is beyond the scope of this book, but the principal methods will be noted briefly.

The tilting-plate method, as the name implies, depends on a plate immersed in a liquid and arranged to rotate so that the angle formed between the plate and the liquid surface can be measured. The contact angle is measured through the liquid, to the immersed portion of the plate. Readings are taken when no curvature of the junction of the liquid and the plate is visible at the liquid surface. A variation is the cylinder method in which the solid for testing is shaped into a cylinder and arranged for partial immersion in a liquid to various depths. The cylinder is raised or lowered until the liquid surface remains horizontal (i.e., does not form a meniscus) at the junction with the cylinder. By rotating the cylinder at the same time it is possible to estimate the so-called advancing and receding angles in which the measurement is made either as the liquid forms a new interface or as it retracts from a surface already covered. The sessile or pendant drop method is based on the contour of the drop either resting or hanging on a surface. Drops of known volume, usually small to minimize the effect of gravity in shaping a large mass of liquid, are placed in the path of a light beam, and the silhouette of the drop is recorded by photographing or tracing an enlarged image on a ground glass. A variation of this procedure is the use of a drop of such large volume that the curvature at the apex is negligible. In all instances the contact angle is measured between lines drawn tangent to the curved meniscus at the junction with the solid and the surface on which the drop is resting. The fixed-bubble method has found favor in studying ore-flotation processes. In making a measurement of this kind, a bubble of air is forced from a capillary tube to rest on the surface of the solid when immersed in the wetting liquid. The angle is measured between the bubble and solid through the liquid.

Several less direct methods are also employed. The rise of liquid in a capillary tube is determined by the surface tension and the angle at which the liquid meets the walls by the equation

$$\gamma_{LA} = \frac{1}{2}h\rho gr \cos \theta \quad (9)$$

where  $h$  is the height of rise,  $\rho$  is the density of the liquid,  $g$  is the gravitational constant, and  $r$  is the radius of the tube. It is rare, however, that any attempt is made to include the  $\cos \theta$  correction in surface-tension measurements, but this procedure has occasionally been used in estimating  $\theta$ .

These are, in brief, the principal methods by which data on contact angles have been obtained. We shall turn now to a consideration of some of the experimental results.

### Data on contact angles

An angle of contact represented as zero implies, in effect, that the liquid spreads over the surface or, as more commonly expressed, wets the solid perfectly and completely. Numerous measurements have been reported in which zero contact angles were observed.

The tabulation by Young and Harkins<sup>22</sup> includes a number of zero angles, and the statement is made that the literature includes over 100 observations in which the contact angle was reported as zero for liquids wetting glass. H. R. Adam<sup>23</sup> observed zero angles for water in contact with a variety of minerals when the surface was freshly prepared, but the behavior of the surface was easily modified, especially with sulfide minerals, when large angles were noted. Burwell,<sup>24</sup> after examining oils as lubricants, concluded that the contact angle for mineral oils with metallic surfaces is zero. Miller<sup>25</sup> observed zero or very small receding angles for a series of unsaturated esters on steel. Livingston<sup>26</sup> listed a number of instances from the literature in which the contact angle is zero if the solid is covered with the vapor of the liquid. An interesting experimental technique, employed by Irons,<sup>27</sup> provided data for  $\cos \theta$ . Irons found that, within experimental error,  $\cos \theta = 1$  for various liquids in contact with metals.

This record could be extended considerably. It appears, however, that a majority of observations fall into the category of zero contact angles.

An angle of contact greater than  $90^\circ$  means that the liquid does not spread over the solid surface. Perhaps the most frequently quoted example is mercury on glass. Young, in 1805, observed an angle of about  $140^\circ$ , and this value is still considered acceptable, since numerous subsequent measurements differ by only a few degrees. Other values have been noted: Bate,<sup>28</sup> for example, reported  $90^\circ$ . It is a matter of frequent observation that mercury appears to wet glass in a high-vacuum line; this condition would correspond to zero contact angle.

<sup>22</sup> T. F. Young and W. D. Harkins, "Tensile Strength and Angle of Contact," *International Critical Tables*, Vol. 4, p. 434, McGraw-Hill Book Co., New York, 1928.

<sup>23</sup> H. R. Adam, *J. Chem. Met. Mining Soc. S. Africa*, **21**, 17-24 (1920); cf. also pp. 670-84 in T. A. Rickard, *Concentration by Flotation*, John Wiley & Sons, Inc., New York, 1921.

<sup>24</sup> J. T. Burwell, *SAE Journal (Transactions)*, **50**, No. 10, 450-7 (1942).

<sup>25</sup> N. F. Miller, *J. Phys. Chem.*, **50**, 300-19 (1946).

<sup>26</sup> H. K. Livingston, *J. Phys. Chem.*, **48**, 120-4 (1944).

<sup>27</sup> E. J. Irons, *Phil. Mag.*, **34**, 614-25 (1943).

<sup>28</sup> A. E. Bate, *Proc. Phys. Soc.*, **53**, Part 4, 403-9 (1941).

A second system, frequently described, is that of water on paraffin. This measurement is often taken as a kind of reference standard for all contact-angle measurements, since it is, perhaps, the most reproducible system.<sup>29</sup> In all instances where distilled water is measured in contact with dry, refined paraffin, the value is greater than  $90^\circ$ . The values most frequently reported fall within the range of  $100^\circ$  to  $115^\circ$ . Differences in these values are attributed to variable composition of the paraffin.

Aside from these two instances there appears to be no liquid-solid combination in which angles greater than  $90^\circ$  can be considered reproducible with the precision necessary for physical significance. For the most part waxes, heavy metal soaps, and asphaltic compounds form the class in which large angles are observed with water as the wetting liquid.<sup>30</sup>

A contact angle of less than  $90^\circ$  but greater than  $0^\circ$  poses a difficult geometrical picture. It would be expected on a priori grounds that a liquid reposing at some small angle, such as  $20^\circ$ , would have a tendency to spread, but the constraints operating resolve to a theoretical equilibrium in which the liquid remains as a lens on the surface. The picture is not so simple, however, because the difficult problem of equilibrium, the difference between advancing and receding angles, the nature of the contaminant on the surface, and the method of measurement need consideration.

The most extensive and careful measurements have been reported by Bartell and his collaborators. This work has covered nearly every aspect of contact-angle measurement and theory, and it is especially pertinent in respect to the conditions for reproducibility. Bartell and Wooley,<sup>31</sup> for example, found that finite advancing angles were observed with  $\alpha$ -bromnaphthalene on silica and glass steamed with water vapor. When the surface was treated with benzene vapor for an hour, a zero angle was observed on glass, and silica gave finite advancing and receding angles ranging from  $5^\circ$  to  $24^\circ$ . The experiments reported by Bartell and Cardwell<sup>32</sup> were concerned with reproducible surfaces of gold and silver, obtained by vaporizing the metal onto glass in a high vacuum. Water and solutions of organic liquids were brought into contact with the metal surfaces, and the contact angles were then measured by means of a profile of a drop of liquid and a sessile bubble of air. Advancing

<sup>29</sup> W. D. Harkins and H. K. Livingston, *J. Chem. Phys.*, **10**, 342-56 (1942).

<sup>30</sup> R. N. Wenzel, *Ind. Eng. Chem.*, **28**, 988-94 (1936).

<sup>31</sup> F. B. Bartell and A. D. Wooley, *J. Am. Chem. Soc.*, **55**, 3518-27 (1933).

<sup>32</sup> F. E. Bartell and P. H. Cardwell, *J. Am. Chem. Soc.*, **64**, 494-97; 1530-34; 1641-33 (1942).

angles recorded after a few seconds' exposure to air were as follows: water on silver,  $40^{\circ}$  to  $46^{\circ}$ ; water on gold,  $37^{\circ}$  to  $43^{\circ}$ . Receding angles in both instances were zero. After six to seven hours the surfaces became hydrophobic and the angles measured above  $90^{\circ}$ ; receding angles then were of intermediate values,  $32^{\circ}$  to  $37^{\circ}$ . When organic liquids (isoamyl alcohol, butyl acetate, benzene, alpha-bromnaphthalene, and heptane) were dissolved in the water used in the same type of tests, the initial advancing angles ranged from  $36^{\circ}$  to  $91^{\circ}$  for silver and  $25^{\circ}$  to  $94.5^{\circ}$  on gold. Aging the system resulted generally in increased angles, reaching values above  $90^{\circ}$  for the solutions of organic liquids. It was noted that, when these solutions were made to advance in stages over the metal surfaces, different angles resulted. It was assumed that evaporation of the organic liquid occurred with adsorption of the vapor on the metal surface.

Numerous measurements of contact angles of water and solutions in contact with minerals have been reported. Sulman's classic paper<sup>33</sup> is frequently quoted. Angles intermediate between  $0^{\circ}$  and  $90^{\circ}$  were noted by Sulman, and the difference between the advancing and the receding angles was attributed to a "molecular interlocking" of the liquid and solid. Important investigations have been made in Wark's laboratory.<sup>34</sup> The conditions for ore flotation are extremely complex, and considerable experimental and theoretical effort has been expended in using the idea of a contact angle in understanding the large mass of empirical observations.

The nature of the surface can sometimes be controlled. One experiment reported by Harkins and Jura<sup>35</sup> for contact angles of water against built-up monolayers of egg albumin deposited on glass showed that the measured angles varied from  $24^{\circ}$  to  $56^{\circ}$  as the film pressure from which the film was deposited varied from 8.8 to 23 dynes per cm. The relationship was linear. The experiments on other built-up films are of interest in this connection.<sup>36</sup> Contact angles of barium, calcium, and magnesium soaps of long-chain fatty acids were found to be either  $0^{\circ}$  or greater than  $90^{\circ}$ , depending on the orientation of the soap molecule at the surface. The explanation is that a zero angle is observed when the polar groups are in contact with the water, and angles greater than  $90^{\circ}$  (approximating the value for pure paraffin) result when the hydrocarbon

<sup>33</sup> H. L. Sulman, *Bull. Inst. Mining Met. Trans. (London)*, **29**, 44-138 (1919).

<sup>34</sup> I. W. Wark, "Principles of Flotation," *Australasian Inst. Min. and Met.*, Melbourne, Australia, 1938; I. W. Wark and A. B. Cox, *Am. Inst. Mining Met. Engrs., Tech. Pub.* 461, pp. 1-48 (1932).

<sup>35</sup> W. O. Harkins and G. Jura, *J. Colloid Sci.*, **1**, 137-40 (1946).

<sup>36</sup> K. B. Blodgett, *J. Am. Chem. Soc.*, **57**, 1007-22 (1935).



groups are in contact with the water. The assumption has been made by some that intermediate angles would be observed if a mixture of polar and non-polar groups was present in the surface film.

The writer has attempted to measure contact angles for water and for solutions of surface-active agents against paraffin and various metal surfaces. When all conditions for the measurement were carefully standardized, one operator could obtain fairly reproducible readings, but there was considerable variation (as high as  $10^\circ$  to  $20^\circ$ ) when another operator tried to check the first readings. It was concluded that the values were relative, dependent on unresolved subjective factors, and represented non-equilibrium conditions.

### Adhesion tension

Freundlich<sup>37</sup> utilized the contact-angle relation to derive an expression for *adhesion tension* (German, "Haftspannung"), which is often taken as an indication of the degree of wetting,

$$\gamma_{SA} - \gamma_{SL} = A_{SL} = \gamma_{LA} \cos \theta \quad (10)$$

where  $\gamma_{SA}$  is the "surface tension" of the solid,  $\gamma_{SL}$  the interfacial tension of the solid and liquid, and  $\gamma_{LA}$  the surface tension of the liquid. The difference,  $\gamma_{SA} - \gamma_{SL}$ , is defined as the adhesion tension,  $A_{SL}$ , with the same dimensions as surface tension. If the angle of contact of the liquid with the solid is zero, then  $\cos \theta = 1$  and  $A_{SL}$  reduces to the value for the surface tension of the liquid. If a contact angle is finite, than  $A_{SL}$  assumes values that are less than the surface tension of the liquid.

The measurement of any angle comparable to  $\theta$  by direct means is impossible for a finely divided solid. Bartell and Osterhof<sup>38</sup> devised a method that depends on the pressure developed by a liquid penetrating into a mass of the powder compressed into a porous block. This device has come to be known as the pressure-displacement cell. The cell is made of metal, usually brass, and, in one design, is a cylinder with an internal diameter of one inch and a length of 12 inches. The ends are constructed to allow connection with a manometer and an air line on one side and a source of wetting liquid on the other. The powder, wetted with the liquid to be studied, is tamped into the cell and subjected to a pressure of about one ton per sq. in. under an hydraulic press; a quantity of the dry powder is then introduced, and, while the cell is still under pressure, the plungers are secured by clamps. The cell thus contains a

<sup>37</sup> H. Freundlich, *Colloid and Capillary Chemistry*, H. S. Hatfield, translator, Methuen & Co., Ltd., London, 1926; pp. 157-60.

<sup>38</sup> F. E. Bartell and H. J. Osterhof, *Colloid Symposium Monograph*, **5**, 113-34 (1927); *Ind. Eng. Chem.*, **19**, 1277-80 (1927).

plug of the powdered solid, part of which is dry and part wetted by the liquid, and it is then connected to the air line and manometer. Additional liquid is introduced into the wet end of the cell and the pressure required to prevent advance of the liquid through the plug is taken as the equilibrium displacement pressure  $P$ . The displacement pressure is related to a modification of the equation for capillary rise, as follows:

$$P = \frac{2\gamma \cos \theta}{r} \quad (11)$$

where  $r$  is the mean capillary pore size, determined by a separate experiment using the same powder and a liquid that is known to wet the solid ( $\cos \theta = 1$ ). The actual pressures observed range up to 10,000 grams per sq. cm.

Several investigators have endeavored to study wetting phenomena by means of the displacement cell. McMillen<sup>39</sup> studied the linseed oil-lithopone system and reported  $A_{SL}$  values ranging from 27 to 32 dynes per cm. Bell, Cutter, and Price<sup>40</sup> studied the same system and found comparable  $A_{SL}$  values. Water penetrating into various lithopones gave  $A_{SL}$  values in the range of 44 to 52 dynes per cm. Davies and Curtis<sup>41</sup> studied a number of liquids against powdered sulfur and found anomalies for which there was no explanation. They found the method tedious and the values difficult to reproduce. After considerable practice, reproducibility of the results obtained by the last two groups of investigators was reported as about 10 percent.

Since many of the liquids have zero angles against the solids studied, Bartell and Osterhof<sup>38</sup> used a differential system with two liquids against the solid and arrived at a relation that is intended to provide adhesion tension values despite the zero contact angle. This can be interpreted to mean that the adhesion between the liquid and the solid is greater than is necessary to bring the contact angle to a zero value.

Because of experimental difficulties, particularly with finely divided solids, and several questions on the validity of the equations, the wetting properties of pigments have not been evaluated by means of the displacement cell to any extent. It is evident that, if the liquid either spreads or does not spread over the solid, then the simple equations no longer hold and it is necessary to resort to more complicated expressions. Harkins and Livingston<sup>42</sup> have critically reviewed the concept of ad-

<sup>39</sup> E. L. McMillen, *Ind. Eng. Chem.*, **21**, 1237-39 (1929); **22**, 890-93 (1930).

<sup>40</sup> S. H. Bell, J. O. Cutter, and C. W. Price in *Wetting and Detergency*, A. Harvey, London, 1937; pp. 19-24.

<sup>41</sup> N. S. Davies and H. A. Curtis, *Ind. Eng. Chem.*, **24**, 1137-40 (1932).

<sup>42</sup> W. D. Harkins and H. K. Livingston, *J. Chem. Phys.*, **10**, 342-56 (1942).

hesion tension and suggest that the term *spreading pressure*  $\phi$  be used instead.

### Experimental difficulties in the measurement

All authorities agree that the measurement of contact angles is one of extraordinary difficulty, although it would seemingly be one of the simplest techniques. There are, however, certain postulates and assumptions that are usually overlooked. Some optical system is employed in an effort to determine the contour of the liquid surface as it approaches the solid. The assumption is made that the liquid approaches the solid in such a way that a definite edge can be observed and, further, that the profile of the liquid at the junction with the solid can be correctly represented by a line drawn from the solid and tangent to the curve of the liquid.

This situation may be illustrated with an example of water on any surface. Suppose that the observer can see the point of contact within three microns. The closest distinguishable point is then, roughly, equivalent to 10,000 water molecules from the solid. Any change in the actual slope of the water meniscus at the point of observation must be attributed to a change in the liquid meniscus which has a different slope at every point, according to the theories of capillarity. The slope at the point of observation cannot be the slope at the point of contact because the radius of curvature must change as the meniscus approaches the solid surface. (An exception to this statement is the case of a  $90^\circ$  contact angle). The viewing conditions presuppose, further, that the surface is molecularly smooth, an assumption that is quite untenable for polished surfaces but may be valid for a freshly cleaved crystal surface. It is evident that the shape of the meniscus a few molecular dimensions from the solid cannot be resolved by any lens system, so that the line is always drawn at a region considerably removed from the actual junction of liquid and solid.

The equations assume that equilibrium conditions are realized. Thus, if there are constraints of any kind (e.g., high viscosity of the liquid) the attainment of equilibrium would be greatly delayed, and, in the time allowable for a typical measurement, readings under non-equilibrium conditions would be made. In view of the well-known time effect in interfacial-tension measurements, it would appear a safe assumption that equilibrium is not instantaneously attained. It is entirely reasonable to assume that, if equilibrium has been reached, the measured angle should have an invariable value and that the junction of the three interfaces should be easily movable and should be established reversibly with the same value of the contact angle.

The divergence between advancing and receding angles is pertinent in this connection. When a liquid spreads over a solid surface, adsorbed gases or vapors (including water) are undoubtedly displaced or dissolved in the wetting liquid. It is of interest that the receding angles are always lower than the advancing angles and in many instances are zero. This could be expected. Indeed, the surface of a solid may be characterized almost entirely by the adsorbed substances, and the contact angle then ceases to have any significance as a measure of the properties of the interface unless the liquid displaces or dissolves the adsorbed gas. This process would be relatively slow, and the hysteresis in the measurement, as shown by advancing and receding angles, could be attributed to the delay experienced by a liquid advancing against such constraints.

Equilibrium conditions are difficult to achieve for other reasons. When measurements are made with volatile liquids, evaporation occurs from the surface, and the meniscus formed at the solid surface is certain to be disturbed. Moreover, if a film spreads with, let us assume, a small contact angle, the edge of the liquid is established by the rate of evaporation and the rate at which the film is replenished from the bulk of the liquid. As a consequence, the limit to which the liquid spreads is fixed by the competing processes of evaporation, spreading, and replenishment. Other constraints can operate also, and, although these may appear perfectly obvious, measurements have been made where a systematic error was involved. The factor of viscosity has been mentioned; with a highly viscous substance flowout, or penetration into a porous solid, requires many hours or days. A less evident error arises from the presence of structure (e.g., a flocculated suspension) within the liquid; any contact angle measured for such a material is entirely fictitious.

That none of the liquid (in the form of a film or condensed vapor) is present ahead of the junction of the bulk of the liquid seems also to be implied. The molecules of the liquid that are near the solid are thus considered to remain compactly associated with the main bulk of the liquid if a sharp demarcation is to be observed. Most liquids have an appreciable vapor pressure, and molecules in the surface can be pictured as leaving the bulk of the liquid and depositing in advance of the main body of liquid. In typical contact-angle measurements, the solid thus becomes contaminated, in a sense, with the wetting liquid and, after the time required for the attainment of equilibrium, it is inconceivable that the liquid would be entirely isolated. Instead, it would be associating with its own molecular species deposited in adjacent areas on the solid. In the derivation of the equations relating the contact angle to surface energy, the assumption is implicit that the solid is in contact with air (or other gas) or, in a more special case, is in a vacuum. On the other

hand, if the system is considered in equilibrium with the saturated vapor of the wetting liquid, then Doss and Rao<sup>43</sup> conclude that

$$\cos \theta = 2\alpha - 1 \quad (12)$$

where  $\alpha$  is the fraction of the solid surface covered by the adsorbed molecules. When the surface is completely covered,  $\cos \theta = 1$  and the contact angle is zero. Livingston<sup>26</sup> attempted to assess available data in light of this equation but concluded that no data exist where  $\theta > 0$  and  $\alpha < 1$ .

Perhaps the most difficult criterion to establish is the "cleanliness" of the solid surface. In every instance, of course, there is a layer of adsorbed gas or moisture that is tenaciously held. Desorption of gases on a solid surface requires heating under high vacuum for long periods, and then it is not entirely complete. Chance contamination from the air is expected, and such deposits are frequently oily in character. This aspect of the measurement defies both analysis and definition. Ferguson,<sup>44</sup> for example, remarks that the contact angles, as measured by some investigators, should be considered as representing a state of contamination, rather than the properties of the interface. The question can be asked: what criterion may be taken for cleanliness of the surface or, alternatively, is it possible to obtain a standard, reproducible state of contamination?

### Implications of the contact-angle concept

The idea of a contact angle is linked to several important matters concerning the equations introduced earlier and to definitions and concepts that are commonly used in various ways.

When the equation,  $W_{A(SL)} = \gamma_L + \gamma_L \cos \theta$  was mentioned as one of the standard formulations of surface chemistry, a precautionary note was added that the equation did not provide an adequate description of the energy relations at the solid-liquid interface. Harkins and Livingston<sup>29</sup> point out that this equation is a limiting one and that the correct equation is

$$W_{A(SL)} = \pi_e + \gamma_{LA}(1 + \cos \theta) \quad (13)$$

where  $\pi_e$  is the pressure of the film on the solid and represents the decrease in free energy of the solid when it is covered with an adsorbed

<sup>43</sup> K. S. Doss and B. S. Rao, *Proc. Indian Acad. Sci.*, **7A**, 113-17 (1938); *Chem. Abs.*, **32**, 4846. See also, H. K. Livingston, *J. Phys. Chem.*, **48**, 120-24 (1944).

<sup>44</sup> A. Ferguson, *Proc. Phys. Soc.*, **53**, Part 5, 554-68 (1941).

layer with a vapor pressure equal to that of the condensed adsorbate. The configuration of the system is shown in Figure 2. The value of  $\pi_e$  can be determined from adsorption data. It will be recalled that the original equation, lacking the term  $\pi_e$ , would hold only for an ideal system ( $\pi_e = 0$ ) when the solid surface adsorbs none of the liquid, and that the equation of Doss and Rao is another expression for this conception.<sup>44a</sup>

The terms *hydrophilic* and *hydrophobic* can be translated, loosely, as water-liking and water-hating. In an effort to obtain more precise definitions, these have been related to contact-angle data. Thus Harkins and Jura<sup>45</sup> define a hydrophobic solid as one on which water gives a con-

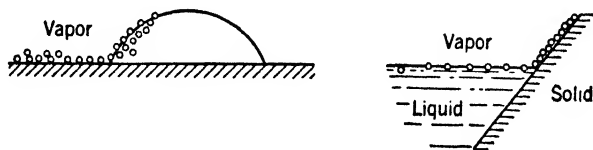


FIGURE 2. Liquid in contact with solid covered with a surface film.

tact angle greater than zero. Freundlich apparently takes the same view, for he refers to hydrophobic solid surfaces as those forming a contact angle with liquids in a binary system. If in such a mixture (e.g., water, organic liquid, and solid) the solid transfers preferentially to the water, it is considered hydrophilic. The inference is that a zero angle characterizes a hydrophilic substance. Bartell<sup>46</sup> considers three types of wetting of solids: (1) adhesional wetting occurs when the contact angle is less than  $180^\circ$ ; (2) immersional wetting is positive for angles less than  $90^\circ$  and negative for angles greater than  $90^\circ$ ; (3) spreading wetting is positive when the angle is zero. Spreading occurs, then, only when  $\theta = 0$ . Similarly, N. K. Adam<sup>47</sup> considers wetting complete if the contact angle is zero and incomplete if a finite contact angle exists. Complete "non-wettability" is considered impossible, and angles of  $180^\circ$  are considered impossible since there is always some attraction between the liquid and the solid. No qualitative distinction is noted for adhesion of a liquid to a solid for angles greater or less than  $90^\circ$ .

<sup>44a</sup> See also D. H. Bangham and Z. Saweris, *Trans. Faraday Soc.*, **34**, 554-70 (1938).

<sup>45</sup> W. D. Harkins and G. Jura, Chapter I, pp. 1-76, in *Colloid Chemistry*, Vol. VI, J. Alexander, Editor, Reinhold Publishing Corp., New York, 1946; the reference is to p. 61 of this article.

<sup>46</sup> F. E. Bartell, Chapter 3, pp. 41-60, in *Colloid Chemistry*, Vol. III, J. Alexander, Editor, Chemical Catalog Co. (Reinhold Publishing Corp.), New York, 1931.

<sup>47</sup> N. K. Adam, *Physics and Chemistry of Surfaces*, pp. 179-80.

The nomenclature of the subject has been criticized by Gans,<sup>48</sup> who contends that the designation zero contact angle is employed very loosely. A finite contact angle should represent an equilibrium between three forces along a line of contact, and the geometry of the contact of a liquid with a solid may be systematized as shown in Figure 3. The forces equivalent to the free energies of the system are drawn as vectors. The first drawing represents the condition where the liquid forms a finite contact angle with the solid. To the right of the lens the liquid will not spread in bulk, but only as a monolayer as, for example, a liquid-con-

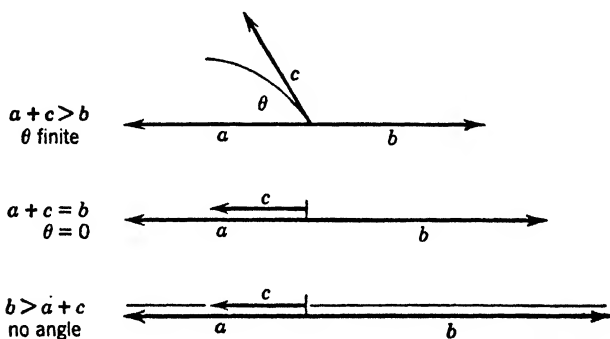


FIGURE 3. Vector diagrams for three possible conditions of wetting of a solid by a liquid. (After Gans, with permission.)

densed film. In the second condition the contact angle is actually zero, and equilibrium is represented by numerically balanced forces. It would be expected that such a configuration, with a contact angle precisely zero, is rare. The third condition is one for which there is no line of contact between liquid and solid, and, hence, no contact angle exists since spreading continues to form a duplex film on the solid. The last configuration would be the most common.

When one of these forces predominates, as shown in the third drawing, equilibrium cannot exist along any line of contact and spreading of the liquid occurs in the direction of that force. When spreading occurs, a contact angle of zero is a fiction. Assertions in the literature are based on the supposition that spreading of a liquid over a solid surface requires such a zero contact angle; there is, then, an implied equilibrium of forces that actually does not exist. A view somewhat similar to that described above appears implicit in the reasoning of Pease.<sup>49</sup>

The consequences of the geometrical configuration are significant. To speak of an angle of  $180^\circ$  means that there can be no contact between

<sup>48</sup> D. M. Gans, *J. Phys. Chem.*, **49**, 165-66 (1945).

<sup>49</sup> D. C. Pease, *J. Phys. Chem.*, **49**, 107-10 (1945).

liquid and solid, and the adhesion between the two would theoretically be nil. At the other limit of a zero angle, the idea of any angle, as noted by Gans, is superfluous. At intermediate values, where the measurements are admittedly unprecise, the adhesion of the liquid and the solid is reflected by the magnitude of the angle. At  $90^\circ$  there is an abrupt change in sign of  $\cos \theta$ ; at  $\theta < 90^\circ$ ,  $\cos \theta$  takes values up to  $+1$  at  $0^\circ$ ; at  $\theta > 90^\circ$ ,  $\cos \theta$  assumes values to  $-1$  at  $180^\circ$ . From the thermodynamic point of view, an angle of less than  $90^\circ$  leads to wetting, but no wetting occurs when  $\theta > 90^\circ$ . Some investigators would consider wetting to occur only for a zero contact angle with all higher values representing hydrophobic properties differing in degree. Another school considers wetting complete for a zero angle, corresponding to "complete wettability," with a gradual decrease in "wettability" as the angle becomes greater until it is nil at  $180^\circ$ .

Because of the uncertainties in this subject, it is impossible to resolve effectively the questions and problems raised. In theory, the concept of a measurable contact angle is acceptable, but the experimental evidence is far from convincing that any such angle measured presents a true picture of the physical relations at the solid-liquid interface. Unlike most other physical measurements, in which precision and accuracy improve as science progresses, the determination of contact angles has not been satisfactorily advanced despite ingenious experimentation. We are left with but two acceptable values: water on paraffin and mercury on glass, and both of these represent angles greater than  $90^\circ$ .<sup>50</sup>

There is, however, a practical point of view that circumvents the dilemma. Skepticism on the validity of contact-angle measurements will avoid wasted effort in further measurements unless some innovation in experimental procedure appears to surmount the recognized pitfalls. Measurements of other physical properties, where the contact angle enters as a factor, should be made only when the angle is known to be zero (or non-existent). This is the advice of Dorsey<sup>4</sup> on surface-tension measurements. In numerous other functions, conditions can sometimes be established for the same criterion, so that  $\cos \theta = 1$ , and the theory that includes this factor is then safely placated. In a general way, we can simplify the subject by noting merely whether or not a liquid spreads over a solid surface, and, if this criterion is accepted, the position at which a liquid appears to meet a surface can be designated, without physical implications, as an "angle of approach." A hydrophilic surface can be defined as one on which water spreads and an oleophilic sur-

<sup>50</sup> W. D. Bancroft remarks pointedly that the protagonists of the contact-angle concept do not have much success with the measurement. See *Applied Colloid Chemistry*, McGraw-Hill Book Co., New York, 1932; pp. 74-82.



face as one on which an oil spreads; hydrophobic or oleophobic surfaces are those on which water or oil does not spread.<sup>51</sup>

### Spreading of Liquids on Solids

In our thinking of the process of wetting, in which a liquid spreads over a solid surface, we are assisted by visualizing macroscopic surfaces. Observations made in the course of ordinary experience provide the prototypes on which we base our conception of surfaces that are of microscopic or submicroscopic extent. Thus much of the experimentation on spreading has been performed on a clean water surface of such area that the spreading phenomena can be observed instrumentally, and our picture of contact-angle relationships has been derived from the visual observation of drops or masses of liquid in contact with relatively large plane surfaces.

The spreading of liquids over other liquid surfaces has been especially fruitful. Hardy<sup>52</sup> recognized that, when a liquid such as benzene spread on a clean water surface, it formed initially a layer of sensible thickness (1 mm.) but that very shortly thereafter the benzene collected into lenses which were in equilibrium with a benzene layer of insensible thickness (monomolecular). Hardy termed the latter state a primary film and the former, a secondary film. This subject has been notably extended by Harkins<sup>53</sup> who has examined numerous experimental systems and has developed the thermodynamics of a general theory for the spreading of liquids. This theory applies not only to the most common examples of liquids on water but also to the spreading of liquids on solids and of solids on liquids. Three possible types of films are recognized: (1) monolayers, one molecule thick; (2) polymolecular layers; and (3) duplex films. A reduction in free surface energy occurs when a monolayer is formed. A duplex film, however, is thermodynamically unstable and transforms to a monolayer with the excess liquid gathering in the form of droplets or lenses. Films do not form on liquids or solids if an increase in free energy would be required.

Harkins considers the initial spreading coefficient for solids such as barium sulfate, titanium dioxide, zirconium silicate, and zirconium oxide to be positive, and the spreading of liquids is accordingly associated with

<sup>51</sup> It may be necessary to point out that colloid chemists use *hydrophilic* and, generally, *lyophilic* as designations for substances that have a high affinity for the liquid as shown by swelling of the substance and the formation of colloidal sols. With this nomenclature, a material like titanium dioxide is hydrophobic because it does not swell in water.

<sup>52</sup> W. B. Hardy, *Collected Papers*, pp. 711-17.

<sup>53</sup> W. D. Harkins, *J. Chem. Phys.*, **9**, 552-68 (1941).

a decrease in free energy. The actual experiments, however, present more complicated phenomena, for the water film present on all surfaces exposed to the atmosphere may effectively block or delay spreading by some liquids. Further, duplex spreading on a solid does not seem to occur readily, and monolayer formation by spreading may be at a rate slower than its rate of formation from the vapor of the liquid. Condensation of vapor on a solid surface may form a polymolecular film with such low mobility that spreading is appreciably impeded. These speculations are founded on both theoretical and experimental evidence and assist in some measure in interpreting the confusing subject of contact-angle measurements. If a duplex film is formed, the contact angle must be zero, but angles greater than zero could be established when either mono- or polymolecular films are formed. The equation connecting the "tensions" at the interface should, therefore, be corrected for the film pressure term,  $\pi$ , as noted previously.

When powdered solids, such as pigments, are immersed in liquids, a large volume of air and adsorbed moisture is associated with the surface. If the liquid wets (spreads) over the solid surface, the air and moisture are displaced; if wetting does not occur, the solid floats on the surface of the liquid or if the specific gravity is sufficiently high the mass settles, trapping air in the immersed mass.

Several simple experiments may be performed to illustrate these points. Lycopodium sprinkled on a clean water surface floats, and a finger may be pushed into the water and withdrawn without becoming wet. The lycopodium coats the skin and prevents spreading of the water. Extended mixing of the lycopodium will not cause it to be wetted by the water. A similar experiment may be performed with certain metallic powders that are coated with a fatty substance. Another experiment on a larger scale may be performed with a sphere pressed out of paraffin. When such a sphere is pushed below the surface of water, an air film forms around the paraffin as it is drawn into the water. Conversely, when hydrophilic solids are immersed in non-polar oils, the surface contains adsorbed moisture and is, in effect, analogous to a water surface. The oil will not spread, and the solid particles remain clumped together, rather than distributing or dispersing uniformly throughout the oil. Experiments demonstrating the effect of water and other hydrophilic liquids on the dispersion of titanium dioxide in an inert mineral oil have been reported.

The moisture adsorbed on the pigment may indeed be the main variable influencing the dispersion characteristics of commercial pigments. It must be emphasized that pigment stocks are only rarely given an oven drying immediately before use. Consequently, the pigment is generally

dispersed with an adsorbed film of moisture, the magnitude of which may be judged from data for the water content for various materials as given in Tables II and III. For titanium dioxide samples, water to the extent of 0.1 to 0.4 percent has been found adsorbed; for chrome yellow, 0.3

TABLE II. MOISTURE CONTENT OF COMMERCIAL PIGMENTS

Pigment	Water (Toluene Extraction) (wt. %)
Titanium dioxide (anatase, sample A)	0.1
Titanium dioxide (anatase, sample B)	0.3
Titanium dioxide (0.1% Al <sub>2</sub> O <sub>3</sub> )	0.4
Titanium dioxide-barium sulfate (composite pigment)	0.2
Chrome yellow (primrose)	0.8
Chrome yellow (medium)	0.5
Ultramarine blue	1.4
Toluidine toner	0.4
Hansa yellow	0.1
Iron blue (Milori-type)	4.0

TABLE III. MOISTURE CONTENT OF CARBON BLACKS

Carbon-Black Type	Initial		Water Content (%) at Relative				
	Oven-Dry		Humidity of				
	105° C.	12-					
	Water (%)	15%	36%	58%	74%	80%	95%
News ink (rubber) grade	0.0	1	1	2	3	3	9
Halftone ink ("flow") grade	0.0	3.5	7	7	8	8	12
High color (lacquer) A	0.0	1	6.5	15.5	16	18	20
High color (lacquer) B	1.0	1	8	11	13	14	15

percent is a representative average. Carbon black with greatly increased surface area and adsorptive capacity holds considerably larger quantities—to 10 percent under normal storage conditions. Water present to this extent actually acts as a diluent, and observed variations in strength of the pigment can be attributed to this factor alone. Certain other pigments contain water as part of the molecule; included in this group are iron blue and the lake colors which are prepared from a hydrous oxide base.

The quantity of water adsorbed is roughly equivalent to that necessary to form a monomolecular film on the solid surface. For example, assuming 10 sq. m. as the area per gram of titanium dioxide, and 10 Å<sup>2</sup> as the adsorbed area of the water molecule, a monomolecular film re-

quires 0.3 percent by weight on the pigment. Carbon black with a specific surface of 100 sq. m. per gram requires 3.0 percent water, and for high-color blacks, with surface areas reported as high as 800 to 900 sq. m. per gram, close to 30 percent adsorbed moisture corresponds to the dimensions of a monomolecular film. These computed quantities are in the range of the analytical values noted for commercial pigments.

### Measurement of Interfacial Energy

#### Heat of immersion

When a powdered solid is immersed in a liquid, the surface of the solid becomes an equal area of interface. This change is accompanied by an energy change manifested in the form of heat. The heat of wetting or heat of immersion of powdered solids has been known for many years. The magnitude, ranging from a fraction of a calorie to about 30 calories per gram for an activated silica gel, depends on the nature of the solid, its surface area, and the polarity of the wetting liquid. Although this method is conceded to be one of the most valid for the determination of important thermodynamic relations at the solid-liquid interface, comparatively few studies have been reported, and the fragmentary data available from the work of different investigators cannot at present be compared satisfactorily. This deficiency can be traced to the following factors: (1) methods of varying precision, (2) differences in sample preparation, (3) incomplete description of samples or the state of their surfaces, (4) incomplete particle-size information, and (5) limited surveys by each investigator. Thus comparisons within one set of measurements may be valid, but conclusions for other solid-liquid systems can be made only by inference.

The most thorough investigations for pigment-type materials have been made by Harkins and co-workers over a period of some twenty years. The method, which calls for precision calorimetry, has been described by Harkins and Dahlstrom.<sup>54</sup> The calorimeter consists of an 800-ml. silvered Dewar flask attached to a brass ring which serves as the support for a 36-junction copper-constantan thermopile, a stirrer, heater, and the mechanism for introducing the powder. The temperature change is measured potentiometrically to 0.00001° C. In order to remove moisture, the powders are heated initially in a high vacuum and at as high a temperature as is permissible without altering the surface of the solid. For titanium dioxide, a heating period of 24 hours at 500° C. and a vacuum of 10<sup>-5</sup> mm. (mercury) is used. After bringing the

<sup>54</sup> W. D. Harkins and R. Dahlstrom, *Ind. Eng. Chem.*, **22**, 897-902 (1930).

calorimetric system to thermal equilibrium, the powder is introduced into the calorimeter along with the wetting liquid.

Data obtained by Harkins, Dahlstrom, and Boyd<sup>54,55</sup> are given in Tables IV and V.

TABLE IV. HEAT OF IMMERSION OF POWDERED SOLIDS IN LIQUIDS

( $T = 25^{\circ} \text{C.}$ )

Liquid	TiO <sub>2</sub>	ZnO	SiO <sub>2</sub>	SnO <sub>2</sub>	BaSO <sub>4</sub>
	(heat of immersion, $h_{l(SL)}$ , in calories per gram)				
Water	1.24	1.18	0.334	0.345	0.517
Ethyl alcohol	1.20	....	0.291	....	
Butyric acid	0.880	....	....	....	
Ethyl acetate	0.850	0.737	0.259	0.267	0.395
Butyl alcohol	0.829	0.690	0.235	0.255	0.375
Nitrobenzene	0.666	0.660	....	0.239	....
Carbon tetrachloride	0.568	....	....	0.164	0.236
Benzene	0.351	0.300	0.084	0.111	0.147
Iso-octane	0.247	....	....	0.059	....

Data from W. D. Harkins and R. Dahlstrom, *Ind. Eng. Chem.*, **22**, 897-902 (1930), and G. E. Boyd and W. D. Harkins, *J. Am. Chem. Soc.*, **64**, 1190-4 (1942).

The data given are for rigorously purified systems. A suspension of titanium dioxide is remarkably sensitive to traces of surface-active materials. Harkins and Dahlstrom found that additions of various types of bodied oils to the benzene raised the heat of immersion from 0.31 to

TABLE V. EFFECT OF OILS ON HEAT OF IMMERSION OF TITANIUM DIOXIDE IN BENZENE

Reagent	Concentration (%)	Heat of Immersion (cal./g.)
Control	0.00	0.39
Blown linseed oil	0.10	0.78
Boiled linseed oil	0.85	0.75
Kettle-bodied linseed oil	0.10	0.74
Boiled linseed oil	0.10	0.71
Raw linseed oil	0.06	0.63

W. D. Harkins and R. Dahlstrom, *loc. cit.*, Table IV.

values from 0.71 to 0.78 calories per gram (Table V). Ewing<sup>56</sup> found greater than a threefold increase in the heat of immersion of zinc oxide in linseed oil over that in benzene, and additions of zinc oleate to the

<sup>55</sup> G. E. Boyd and W. D. Harkins, *J. Am. Chem. Soc.*, **64**, 1190-4 (1942).

<sup>56</sup> W. W. Ewing, *Ind. Eng. Chem.*, **23**, 427-29 (1931).

wetting liquid appreciably augmented the heat liberated. When water or butyric acid is introduced into the benzene in increasing quantities, the heat liberated finally approaches that for the immersion in the pure liquid itself (Figure 4).

Harkins observed that, if the heat of immersion for any polar solid for water is assigned the value 1.00 and the ratios are computed for other

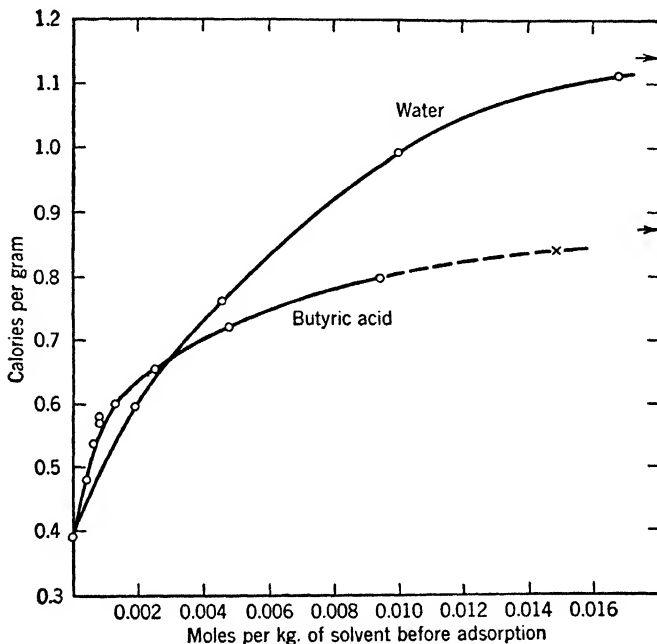


FIGURE 4. Energy of immersion of titanium dioxide in benzene which contains water or butyric acid. (The arrows at the right denote values for immersion in pure water or butyric acid; the cross represents the adsorption of a monomolecular film.) (After Harkins and Dahlstrom, with permission.)

liquids, then the relative value of the heat of immersion for any other liquid is dependent primarily on the characteristics of that liquid and is influenced only slightly by the nature of the solid. This generalization holds for a series of oxides, barium sulfate, and zirconium silicate.

The experimental results are of considerable interest qualitatively. When the specific surface of the solid is known, then calculation of the total energy of immersion and adhesion on the basis of unit area of surface becomes possible. The development of these ideas by Harkins follows. If a unit area (1 sq. cm.) of solid-liquid interface is formed by immersing a powdered solid in a liquid, the heat effect  $h_{I(SL)}$  is

$$h_{I(SL)} = E_S - E_{SL} \quad (14)$$

where  $E_S$  and  $E_{SL}$  represent the energy in the solid surface and solid-liquid interface, respectively. Within experimental error,

$$h_{I(SL)} = E_{I(SL)} \quad (15)$$

where  $E_{I(SL)}$  is the energy of immersion. These relations can be used to compute the total energy of adhesion  $E_{A(SL)}$ . If a unit area of the solid-liquid interface is destroyed by removing the liquid from the solid completely, then the energy in the solid surface  $E_S$  and that of the liquid surface  $E_L$  are related to the total energy of separation as follows:

$$E_{A(SL)} = E_S + E_L - E_{SL} \quad (16)$$

By combination,

$$E_{A(SL)} = E_{I(SL)} + E_L \quad (17)$$

or

$$E_{A(SL)} = h_{I(SL)} + E_L \quad (18)$$

It should be noted that  $E_L$  is the total energy of the liquid surface.

The energy of adhesion  $E_{A(SL)}$  is the increase in internal energy when a liquid is completely removed from a solid and can be determined by measurement of  $h_{I(SL)}$  and  $E_L$ . For the quartz-water system this energy is 720 ergs per sq. cm. Other values are given in Table VI. Solids of the

TABLE VI. ENERGY OF IMMERSION AND ADHESION

(Data in ergs/sq.cm. at 25° C.)

Liquid	Solid				
	BaSO <sub>4</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	SnO <sub>2</sub>	Graphite
	Energy of immersion ( $h_I$ or $E_I$ )				
Water	490	520	600	680	265
Ethyl acetate	370	360	460	530	...
Butyl alcohol	360	350	420	500	...
Carbon tetrachloride	220	240	...	320	195
Benzene	140	150	150	220	225
Iso-octane	...	105	...	120	...
	Energy of adhesion ( $E_A$ )				
Water	610	640	720	800	385
Ethyl acetate	430	420	520	590	...
Butyl alcohol	410	400	470	550	...
Carbon tetrachloride	280	300	...	380	255
Benzene	210	220	220	290	295
Iso-octane	...	155	...	170	...

type of titanium dioxide and barium sulfate are considered polar, whereas graphite is an example of a non-polar solid. With the former the energy associated with an interface becomes larger as the polarity of the molecules in the liquid becomes greater. Thus the highest energies of adhesion are obtained with water and alcohols and the lowest with benzene and octane. In general, values of adhesional energy for liquids in contact with polar solids are considerably greater than those for the same liquids in contact with water (a highly polar liquid).

### Adsorption

Data obtained from adsorption have been used with considerable success in evaluating the energy relations at the solid-liquid interface. Advances in this field came through a better understanding of the formation of films on the solid.

When a vapor is adsorbed on a solid surface, there is a free energy change accompanying the formation of the adsorbed layer. It will be recalled that the equation for the spreading coefficient of a liquid on a solid is

$$S_{S/L} = \gamma_S - (\gamma_L + \gamma_{SL}) \quad (5)$$

and that the work of adhesion for the same system is

$$W_{A(SL)} = \gamma_L + \gamma_S - \gamma_{SL} \quad (7)$$

When a contact angle can be shown as non-existent at the interface, thus representing theoretically no constraint to spreading,

$$S_{L/S} = \pi_e \quad (19)$$

where  $\pi_e$  is the film pressure of the liquid film on the solid. The work of adhesion is then

$$W_A = \pi_e + 2\gamma_L \quad (20)$$

by combination of these equations. Determination of  $\pi_e$  provides the necessary information, and this is accomplished by converting adsorption data to a decrease in surface-free energy.

The basis for this method is the well-known Gibbs adsorption equation.<sup>57</sup> The experimental data are provided by an adsorption isotherm in which the amount of vapor adsorbed by the solid is determined for a

<sup>57</sup> For details on this application and integration of the Gibbs equation see the following papers: D. H. Bangham, *Trans. Faraday Soc.*, **33**, 805-11 (1937) and D. H. Bangham and R. I. Razouk, *ibid.*, **33**, 1463-72 (1937); W. B. Innes and H. H. Rowley, *J. Phys. Chem.*, **45**, 158-65 (1941); M. H. Armbruster and J. B. Austin, *J. Am. Chem. Soc.*, **66**, 159-71 (1944); G. E. Boyd and H. K. Livingston, *ibid.*, **64**, 2383 (1942); G. Jura and W. D. Harkins, *ibid.*, **66**, 1356-62 (1944).



series of equilibrium pressures. The value of  $\pi$ , the lowering of free-surface energy, is obtained from the plot of the data for different values of  $v/p$  vs.  $p$ , where  $v$  is the volume adsorbed at the equilibrium pressure  $p$ , by graphical integration. The quantity  $\pi_e$  is derived from a curve of  $\pi$  vs.  $p$  and represents the film pressure at a saturation pressure.

Data in Table VII were obtained by Jura and Harkins for titanium dioxide. The method is extremely useful, but it is limited to liquids that

TABLE VII. SPREADING COEFFICIENT AND WORK OF ADHESION FOR TITANIUM DIOXIDE

(Data in ergs/sq. cm.)

Liquid	Spreading Coefficient	Work of Adhesion
Water	190	334
Nitrogen	56	72
<i>n</i> -Butane	43	73
<i>n</i> -Heptane	46	86

have an appreciable vapor pressure at temperatures feasible for experimental measurement.

An important series of measurements has been made by Harvey and McNesby<sup>58</sup> using this method for evaluation of the energy of adhesion to metal surfaces. Some of their results are collected in Table VIII. These investigators find that the work of adhesion of various liquids is

TABLE VIII. SPREADING COEFFICIENT AND WORK OF ADHESION METALS AND OXIDES<sup>58</sup>

	Iron				Zinc	Zinc	Zinc
	(SF)	Yellow Iron Oxide	Red Iron Oxide	Black Iron Oxide		Oxide (fine)	Oxide (coarse)
Specific surface (m <sup>2</sup> /g)	0.49	16.2	15.8	6.83	0.21	9.48	1.32
<i>Adsorbate</i>	<i>Spreading Coefficient (ergs/sq. cm.)</i>						
Nitrogen (-195.8° C.)	38.2	44.1	43.7	47.5	30.2	38.6	43.9
Ethyl chloride (0° C.)	51.0	65.5	62.2	50.5	38.0	51.6	....
Butadiene (0° C.)	58.9	56.7	49.1	46.4	47.6	52.2	54.5
	<i>Work of Adhesion (ergs/sq. cm.)</i>						
Nitrogen	54.2	60.1	59.7	63.5	46.2	54.6	59.9
Ethyl chloride	94.6	109.	106.	94.1	81.6	95.2	....
Butadiene-1,3	92.9	90.7	83.1	80.4	81.6	86.2	85.5

<sup>58</sup> E. N. Harvey, Jr. and J. R. McNesby, data quoted with permission from booklet, *Papers Presented at the Washington Meeting*, American Chemical Society, Division of Paint, Varnish, and Plastics Chemistry; pp. 109-26, August-September, 1948.

generally greater for the oxide surface than for the metal. With hydrocarbons, a tentative conclusion was that larger molecules within a homologous series and unsaturation in the hydrocarbon lead to higher values for the work of adhesion.

It is apparent that considerable experimental work remains to be performed on many other solid-liquid interfaces. At the present time it may be stated that only sufficient data are at hand to indicate trends and that correlation of surface-energy data with the surface properties of pigments and other powders and with adhesion of paint films to various surfaces (as examples of important commercial applications) can be more effectively made when experimental investigations now in progress are reported.

## 4. The State of the Dispersed Solid

After a finely divided solid has been dispersed in a liquid the separate particles are free to migrate in a measure determined by the viscosity of the liquid, the concentration of the suspension, and certain other factors. If the particles remain independent the suspension is characterized as peptized (in the colloidal sense), deflocculated, or well-dispersed. It is commonly observed, however, that the particles associate or flocculate and may form a complete network of interlacing structures. The importance of flocculation as a factor determining the physical properties of disperse systems has often been overlooked. Although the evaluation of flocculation is complicated by the lack of direct measuring methods, a sizeable store of information has accumulated from which a picture of the state of the dispersed solid may be drawn.

### Definitions

Flocculation may be defined as the formation of clusters of particles which are disturbed and broken by relatively weak mechanical forces or by a change in the physical forces at the interface between the solid and the suspending medium. The term flocculation derives from the Latin *floccus*, implying a woolly, soft massing of fibers or particles. An aggregate, on the other hand, is composed of a group of particles that are strongly adherent and can be broken by the application of relatively strong mechanical forces. (The term agglomerate is used frequently with the same meaning as aggregate.)

The distinction between flocculation and aggregation, as noted in previous chapters, depends primarily on the nature of the forces holding the particles together. An aggregate is usually formed during the manufacture of the powder and results from coagulation of the finely

divided particles initially suspended, as is the case with most synthetic pigments, in an aqueous slurry. The growth of crystals during processing and their subsequent massing during filtration and drying, result in the formation of a cake which is pulverized to aggregates in the range of sieve size. Such aggregates are not to be confused with floccules. In the vocabulary of industry, however, the term flocculation has unfortunately assumed a variable meaning, and it is often applied to any association of particles whether tightly adherent or loosely associated. Green<sup>1</sup> in pointing out this difference in nomenclature considers the term flocculation to have three implications: (1) the particles (units) composing a flocculate were originally separately dispersed in the continuous phase; (2) the flocculate is formed by movement of the particles within the dispersion medium by convection, stirring, or other means; and (3) "adherence" of the particles occurs.

The distinction between these terms is of considerable importance if confusion is to be avoided. Speaking generally, an aggregate when once dispersed into its component particles cannot form again with properties similar to those of the original. A flocculated mass, however, may be broken by stirring only to form again when the stirring stops. A convenient way to observe this phenomenon is to place a drop of a flocculated dispersion (e.g., titanium dioxide in mineral oil) on a microscope slide and press a cover glass over the dispersion. If the suspension is not too concentrated, the particles will be observed to move about in the liquid and to form clusters which gradually build up into a continuous network. The process may be repeated.

Deflocculation is the state of a dispersion of a solid in a liquid in which each solid particle remains geometrically independent and unassociated with adjacent particles.

This terminology has considerable justification and appears to be in accord with standard definitions.

### Particles Suspended in Air

Although our primary interest is the state of particles dispersed in a liquid medium, the comparable state of particles suspended in air is of considerable interest. To the colloid chemist these are designated as smokes and mists, depending on whether the suspended matter is a solid or liquid. It is common experience that these systems are sometimes extraordinarily stable, persisting for hours or weeks. The particles of smokes are electrically charged and can be deposited if they are passed between highly charged plates, as in the Cottrell precipitator.

<sup>1</sup> H. Green, *Ind. Eng. Chem.*, **15**, 122-26 (1923).

The flocculation of the particles of smokes has been studied in great detail by Whytlaw-Gray and co-workers.<sup>2</sup> In one series of experiments smokes of zinc, cadmium, and copper oxides were studied with a slit ultramicroscope.<sup>3</sup> The particles, after initial formation, showed a rapid growth in size with a decrease in Brownian motion, forming branching structures, string-like in shape. The size of the individual particles was of the order of  $5 \times 10^{-5}$  cm., and the length of the larger complexes was observed as 30 microns. The description in the original paper is vivid. The floccules twisted and curled about, indicating that the chain-like structures had extreme flexibility. Individual particles exhibited an independent vibration, analogous to Brownian movement, but more restricted. When viewed under an intense light, the chains appeared to be similar to a string of beads with each bead separated from its neighbor by a small space. Denser deposits had a similar structure, but there was considerable branching to form irregular masses. In an electrostatic field the chains were oriented parallel to the lines of force; on reversal of the field they rotated through  $180^\circ$ . When touched with a drop of oil the complexes broke up.

These investigators considered that particles forming the chains were separated by appreciable distances, since the images in an ultramicroscope are actually diffraction patterns. The means of attachment was not clearly evident from their observations. Strings of amicrons or invisible aggregates, the polar character of the particles, layers of sorbed air, and electrical charges on the particles were some of the factors with which aggregation was thought to be associated.

These formations can be compared with the fluffy masses of dust frequently observed in places where fine dust is allowed to accumulate undisturbed. The deposits assume a velvety appearance with strands standing out from the surface, as on a wall or ceiling, evidently due to the particles attaching themselves gradually to each other until the chains are long enough to be seen with the unaided eye. Flocculation of fine particles in air is connected also with their bulking or packing volumes.

### Particles Suspended in Liquids

When finely divided particles are suspended in liquids, the character of the dispersion may be observed by several methods including visual examination of "flowouts" on a glass plate, microscopic appearance, sedimentation, electrical conductivity, rheological properties, and sev-

<sup>2</sup> R. Whytlaw-Gray and H. S. Patterson, *Smoke: A Study of Aerial Disperse Systems*, Arnold & Co., London, 1932.

<sup>3</sup> R. Whytlaw-Gray, J. B. Speakman, and J. H. P. Campbell, *Proc. Roy. Soc. (London)*, **A102**, 600-15, 615-27 (1923).

eral miscellaneous techniques. These methods afford an insight into the mechanism and nature of flocculation, and the following discussion will present findings of various investigators.

### Visual observation of flocculation

When a small amount of a deflocculated dispersion is placed on an inclined glass plate, it will ordinarily flow out and present a uniform layer. A flocculated suspension, on the other hand, will form a streaky layer, comparable in some instances with a "Jack Frost" pattern. This uneven, lumpy appearance is often described as "poor dispersion."

An experiment that shows the effect of flocculation upon a mass of the dispersion has been described by Green.<sup>1</sup> A paste of zinc oxide and kerosene or mineral oil is prepared by stirring. The paste so formed is plastic and may be shaped into a conical heap. When a drop of heat-bodied poppyseed oil is added, the mass becomes fluid. Various other substances may be used in place of the heat-bodied oil which acts as a surface-active agent: zinc naphthenate, lecithin, or oleic acid.

The formation of a visible structure may be shown in quite another way. When powdered iron, nickel, or magnetic iron oxide is suspended in a vehicle, the effects of flocculation induced by a magnetic field may be studied by simple experiments. A few ml. of a dispersion of fine iron filings in mineral oil, prepared by stirring with a spatula on a glass slide, will be fluid until a horseshoe magnet is brought to the under side of the plate. The dispersion then assumes a stiff, pasty consistency. What has happened is evident: the particles under the magnetic field form a flocculated internal network possessing sufficient rigidity to prevent flow. When the magnet is removed the dispersion again flows out.

### Microscopic observation

The most convincing evidence is obtained from microscopic observation. A fully deflocculated dispersion shows independent units of the suspended particles usually in Brownian movement. The units may not necessarily be primary particles. On flocculation, however, the particles, initially separate, form into clusters until a network of these clusters extends throughout the dispersion. At the same time, Brownian movement appears to cease. Photomicrographs of flocculated and deflocculated pigment suspensions have been published.<sup>4</sup>

<sup>4</sup> See, for example, H. Green, reference 1; L. W. Ryan, W. D. Harkins, and D. M. Gans, *Ind. Eng. Chem.*, **24**, 1288-98 (1932); E. K. Fischer and C. W. Jerome, *ibid.*, **35**, 336-43 (1943). A special type of flocculation which may occur during preparation of mounts for light or electron microscopy, designated "sheet" or two-dimensional flocculation, has been described by H. Green, *Ind. Eng. Chem.*, **38**, 679-82 (1946).

Flocculation of the pigments used as reinforcing agents in rubber affects the physical properties of the dispersion. Depew and Ruby<sup>5</sup> examined microsections of various reinforcing materials dispersed in rubber. Their experiments were not definitive, but they pointed to the connection of physical properties of the compounded stock with the state of the dispersed pigment. For example, they ascribed the heating of tire treads highly loaded with carbon black to flocculation. Green<sup>6</sup> reasoned that the floccules formed during vulcanization when the rubber is least viscous and ascribed the reinforcing effects of carbon black to a flocculated structure. Grenquist<sup>7</sup> also used a microscopic technique for the study of the flocculation of carbon black and noted that the finest carbon blacks showed the most pronounced tendency toward this property. Park and Morris<sup>8</sup> associate "mill scorching" (hardening of the mixture during heating and milling) with flocculation of the carbon-black particles.

These early studies on the flocculation of carbon black dispersed in rubber were fully supported by evidence obtained from electron micrographs. Wiegand<sup>9</sup> referred to the association of particles as "structure," and the reticulum of flocculated particles (previously observed and described by other workers in paint and ink) suggested the designation "reticulate chain structure." Marked differences in the nature of the floccules can be seen in electron micrographs of different carbon blacks.<sup>10</sup> The paper by Ladd and Wiegand is of particular interest since stereo pictures are reproduced. In the flocculation of a thermal carbon (Thermax), a rod-like flocculate is formed, and the chains appear to radiate from a single particle at roughly 120° angles. Acetylene and lampblack exhibit a different structure in which long chains, with considerable branching, form the reticulate structure. On extended and severe shearing of the dispersion, the structures are broken, but the persistence of the floccules parallels, in approximate measure, the readiness with which they are formed. Acetylene black and lampblack floccules show the greatest persistence on shearing.

<sup>5</sup> H. A. Depew and I. R. Ruby, *Ind. Eng. Chem.*, **12**, 1156-59 (1920).

<sup>6</sup> H. Green, *Chem. Met. Eng.*, **28**, 53-57 (1923).

<sup>7</sup> E. A. Grenquist, *Ind. Eng. Chem.*, **20**, 1073-78 (1928); **21**, 665-69 (1929).

<sup>8</sup> C. R. Park and V. N. Morris, *Ind. Eng. Chem.*, **27**, 582-86 (1935); cf. also C. R. Park and P. P. McClellan, *ibid.*, **30**, 704-8 (1938).

<sup>9</sup> W. B. Wiegand, *Can. Chem. Process Inds.*, **25**, 579-81 (1941).

<sup>10</sup> W. A. Ladd and W. B. Wiegand, *Rubber Age*, **57**, 299-307 (1945); G. Benson, *ibid.*, **58**, 461 (1946); R. E. Dobbin and R. P. Rossman, *Ind. Eng. Chem.*, **38**, 1145-48 (1946).

### Sedimentation equilibria

A roughly quantitative measure of flocculation is obtained by suspending a powdered solid in different liquids and measuring the rate at which settling takes place and the final relative volumes of the suspended solid. This method has been used by a number of investigators, and the results are of considerable interest since differences in both solids and liquids may be examined and the influence of reagents may be studied. The results are of some practical importance also, since settling characteristics of a system, as in a paint, can be anticipated.

The technique for this work is essentially quite simple. A definite quantity of the solid is suspended in a liquid, placed in stoppered graduated, and the time necessary for the suspended phase to reach an equilibrium volume is determined. Sedimentation often proceeds in two stages: a rapid settling until a stage (the "critical point") is reached after which settling continues very slowly or ceases (the equilibrium volume). The "specific sedimentation volume" is the volume of the suspended solid (in ml.) per gram of solid.

The preparation of materials for the tests requires considerable care, however, if the results are intended to elucidate wetting relationships. This is particularly important with regard to adsorbed moisture. The technique of desorption of the solid under high vacuum and at elevated temperatures, together with precautions in handling, has been described by Ryan, Harkins, and Gans.<sup>11</sup>

Experimental data illustrating typical results are presented in Table I. One generalization from settling experiments is as follows: flocculated particles settle rapidly to high volumes, and deflocculated particles settle slowly to low relative volumes. The rate of settling is governed by the size of the floccule and may be predicted (in this case only as an approximation) by Stokes' law. For ideal systems, where the particles are settling under gravity in liquids of equal density and viscosity, the equation reduces to the following:

$$V = Kr^2 \quad (1)$$

where  $V$  is the velocity of settling,  $r$  is the effective floccule or particle radius, and  $K$  is a constant. It is evident that, since the velocity is related to the square of the radius, settling is greatly accelerated by par-

<sup>11</sup> L. W. Ryan, W. D. Harkins, and D. M. Gans, *Ind. Eng. Chem.*, **24**, 1288-98 (1932).



TABLE I. SEDIMENTATION EQUILIBRIA OF SOLIDS IN LIQUIDS

Liquid	Spreading Coefficient against Water	Solid					
		Titanium dioxide (Water-dispersible anatase)	Glass spheres	Ultra-marine	Iron blue (Milori)	Carbon black (News ink grade)	Carbon black (Flow black)
		Specific Packing Volume (cc. of sediment per gram of solid)					
Water	...	1.1	0.73	2.6	2.5	7.8	6.3
Ethyl alcohol	50	...	0.75	.	...	...	...
Propyl alcohol	49	...	0.78	.	...	...	...
Butyl alcohol	48	1.9	1.7	1.7	2.0	8.5	7.7
Amyl alcohol	44	..	2.6	...	...	...	...
Ethyl ether	45	...	2.0	.	...	...	...
Octyl alcohol	37	1.7	...	1.9	2.3	6.1	7.2
Oleic acid	25	1.6	...	.	...	...	...
Chloroform	13	3.3	...	6.2	4.1	8.5	8.5
Benzene	9	2.1	2.7	5.4	3.6	6.7	7.8
Toluene	7	2.0	3.6	.	.	...	...
Nitrobenzene	4	...	2.8	...	...	...	...
Chlorobenzene	2	2.0	.	.	.	...	...
Carbon tetrachloride	..	2.5	3.2	5.5	5.3	8.9	8.0
Carbon disulfide	-7	2.5	....	.	.	...	...
$\alpha$ -chloronaphthalene	-10	2.1	..	5.6	5.1	7.4	8.0

Note: Column 3, glass spheres, 15.2 micron radius; theoretical packing volume 0.60 cc. per gram. Data from Bloomquist and Shutt.<sup>19</sup>

ticles flocculating into units which then function as single particles of complex shape with greatly increased effective radius.<sup>12</sup>

The equilibrium sedimentation volumes are determined by the character of the solid, the polarity of the liquid, and the substances adsorbed at the interface. If the liquid is pure, the equilibrium volumes for a given solid have been correlated with the interfacial tensions of the liquids, measured against water, or with the corresponding spreading coefficient  $S$ . For pigments that could be described as "hydrophilic," i.e., on whose surface water will spread, the following observation may be made: in liquids of high  $S$ , the sedimentation volume is low; in liquids of low  $S$ , the volume is high. Mack<sup>13</sup> found a straight-line relationship between sedimentation volume and spreading coefficient for three hy-

<sup>12</sup> In aqueous suspensions a potential difference is observable between the top and the bottom of a suspension during settling. This sedimentation potential or Dorn Effect has not been extensively investigated.

<sup>13</sup> C. Mack, *Ind. Eng. Chem.*, **27**, 1500-5 (1935).

drophilic solids. Carbon black exhibited a negative slope, a result attributed to the hydrophobic characteristics of the surface. Ryan, Harkins, and Gans<sup>11</sup> correlated sedimentation volumes with polarity of the liquid. Bartell and Walton,<sup>14</sup> using the concept of adhesion tension, noted the greatest degree of settling of heat-treated stibnites in liquids against which the solid had the highest adhesion tension. In an extension of these experiments<sup>15</sup> various other pigment-grade materials were used. For solids that may be characterized by the term hydrophobic (certain carbon blacks and organic colors), low sedimentation volumes were noted in liquids with a high interfacial tension against water. With mixed liquids, rather complex properties were found.

Thomas and Soday<sup>16</sup> studied the settling of titanium dioxide in mineral spirits in which various resins had been dissolved. All of the resin solutions showed increased settling times.

Mardles<sup>17</sup> has studied the sedimentation equilibria of various solids in liquids correlating these data with viscosity measurements made on a capillary-tube plastometer. The suspensions that showed high anomalous viscosity (thixotropic flow characteristics) also exhibited high sedimentation volumes. The degree of flocculation determined the viscosity of the suspension as measured. The experimental technique used by Mardles did not clearly distinguish between viscosity and yield value of the suspensions, and the values reported for the viscosity ratio are thus some composite measure of the non-Newtonian flow factors. The evidence, nevertheless, amply supports the picture of a network of flocculated particles.

When rigorously dried solids are employed in sedimentation tests, the final volume is only slightly affected by the liquid. Gallay and Puddington<sup>18</sup> noted this result with starch, magnesium oxide, ferric oxide, and talc suspensions. Bloomquist and Shutt<sup>19</sup> found that the sedimentation volumes of dry glass spheres in a series of different liquids were, within experimental accuracy, nearly the same. The data of Ryan, Harkins, and Gans<sup>11</sup> show markedly smaller differences for dry solids in dry liquids in comparison with the same suspensions that were not kept

<sup>14</sup> F. E. Bartell and C. W. Walton, Jr., *J. Phys. Chem.*, **38**, 503-11 (1934).

<sup>15</sup> F. E. Bartell and N. F. Miller, *Nat. Paint, Varnish Lacquer Assoc., Sci. Sect., Circ.* 523, 303-14 (1936); C. A. Murray and F. E. Bartell, *ibid.*, *Circ.* 568, 251-59 (1938).

<sup>16</sup> C. A. Thomas and F. J. Soday, *Ind. Eng. Chem.*, **28**, 1174-76 (1936).

<sup>17</sup> E. W. J. Mardles, *Trans. Faraday Soc.*, **36**, 1007-17 (1940); **36**, 1189-98 (1940); **37**, 321-27 (1941); **38**, 222-27 (1942); **38**, 47-54 (1942); *J. Oil & Colour Chemists' Assoc.*, **25**, 194 (1942); **26**, 15 (1943); *Nature*, **153**, 746-47 (1944).

<sup>18</sup> W. Gallay and I. E. Puddington, *Can. J. Research*, **B21**, 171-78 (1943).

<sup>19</sup> C. R. Bloomquist and R. S. Shutt, *Ind. Eng. Chem.*, **32**, 827-31 (1940).

under anhydrous conditions. Because of the difficulties in dehydrating both solids and liquids and in maintaining anhydrous conditions during handling, it is likely that trace quantities of water remain in the suspensions.

The presence of water profoundly influences the final sedimentation volume of hydrophilic solids in liquids with low or negative spreading coefficients. The effect of water is to increase the volume of the suspension. Harkins and Gans<sup>20</sup> noted that the effect of water was far greater in suspensions of titanium dioxide, zinc oxide, and zinc sulfide in carbon tetrachloride than in ethyl acetate. When oleic acid was added to a suspension of dry titanium dioxide in benzene in a quantity sufficient to establish a monomolecular film around each particle, the suspension was deflocculated and low sedimentation volumes resulted. The addition of water, however, caused flocculation with high settling volumes, and it was deduced that the water preferentially displaced the oleic acid.

Correlation of sedimentation volumes with other physical properties of liquids has been observed. Ostwald and Haller<sup>21</sup> studied the settling of talc, fuller's earth, alumina, silica, magnesia, chalk, iron oxide, graphite, and activated carbon in a total of 50 different liquids. They found the trend toward the lowest volumes of the solid in liquids of highest dielectric constant. Blom<sup>22</sup> noted a straight-line relationship between the log of the molar heats of vaporization of the liquids and the sedimentation volume: liquids with high heats of vaporization gave the lowest volumes of solid.<sup>23</sup>

The experimental results of sedimentation equilibria studies are important, but the complexities of the experimental method render them of qualitative significance so far as "wetting" properties of the solids are concerned. The technique of shaking to effect dispersion does not result in any appreciable comminution of aggregates, so that a variable quantity of the solid remains in the sediment; the settling volume is determined to some extent by the dimensions of the graduate or cylinder used for the experiments; the time for equilibrium settling may extend to excessive time intervals (months) and readings taken before the final volume has been reached are, accordingly, high; preliminary desorption of the solid and maintenance of anhydrous conditions throughout require

<sup>20</sup> W. D. Harkins and D. M. Gans, *J. Phys. Chem.*, **36**, 86-97 (1932).

<sup>21</sup> W. Ostwald and W. Haller, *Kolloid-Beihfte*, **29**, 354-95 (1929).

<sup>22</sup> A. V. Blom, *Kolloid-Z.*, **51**, 186-90 (1930).

<sup>23</sup> The energy of vaporization is related to surface energy. For non-polar molecules, the energy required to lift a molecule from the interior of the liquid to the surface is approximately one-half the energy to lift it into the vapor (Stefan's rule). For details on this relationship and its dependence on molecular polarity and temperature, see W. D. Harkins and L. E. Roberts, *J. Am. Chem. Soc.*, **44**, 653-70 (1922).

extreme precautions and even under the best circumstances are subject to some doubt. As a consequence, it is necessary to interpret the results only in relative terms.

Sedimentation tests have practical value.<sup>24</sup> Settling characteristics of paints can be measured and probable storage properties predicted. Werthan, Wien, and Fatzinger<sup>25</sup> studied a variety of test procedures designed to simulate in some measure natural storage conditions. To accelerate the test, centrifuging alternated with shelf storage was studied. A four-day cycle with two one-hour centrifuging periods per day was found to approximate settling during one year of shelf storage for some paints, but the test could not be applied to all paints. Settling was measured by means of a penetrometer. A variation on this procedure has been described by Hancock and Brown<sup>26</sup> which is said to correlate satisfactorily with the settling that takes place during shelf storage. A considerable amount of test data on this subject has been published<sup>27</sup> but generalizations cannot be safely made. McMillen and Glaser<sup>28</sup> attempted to measure the rigidity of the settled pigment layer in paints. They found values from 10,000 to 100,000 dynes per sq. cm., depending on the depth of the container.

### Conductivity

Of the several properties connected with flocculation, that of electrical conductivity is of some direct significance. The experiments of McDowell and Usher<sup>29</sup> showed that a deflocculated suspension of carbon black in solvents (bromoform and tetrachloroethane) exhibited no measurable conductivity, but that flocculated suspensions when undisturbed allowed appreciable currents to flow. The conductivity of flocculated suspensions was attributed to direct contact between carbon-black particles and to a continuous network of the floccules. Tapping and shaking destroyed the structure and greatly reduced the conductance. The

<sup>24</sup> Considerable work has been done on the engineering aspects of sedimentation. See, for example: H. H. Steinour, *Ind. Eng. Chem.*, **36**, 618-24; 840-47; 901-7 (1944). L. T. Work and A. S. Kohler, *ibid.*, **32**, 1329-34 (1940); K. Kammermeyer, *ibid.*, **33**, 1484-91 (1941). A useful review, with reference particularly to some of the early work, is that of M. B. Donald, *Chemistry & Industry*, **59**, 105-9 (1940).

<sup>25</sup> S. Werthan, R. H. Wien, and E. A. Fatzinger, *Ind. Eng. Chem.*, **25**, 1288-92 (1933); *ibid.*, **20**, 729-32 (1928).

<sup>26</sup> A. Hancock and T. F. Brown, *J. Oil & Colour Chemists' Assoc.*, **30**, 317-37 (1947).

<sup>27</sup> Toronto Club, *Nat. Paint, Varnish Lacquer Assoc., Sci. Sect., Circ.* 568, pp. 317-30 (1938).

<sup>28</sup> E. L. McMillen and D. W. Glaser, *J. Applied Phys.*, **9**, 502-7 (1938).

<sup>29</sup> C. M. McDowell and F. L. Usher, *Proc. Roy. Soc. (London)*, **A131**, 409-27; 564-76 (1931).

values for the measurement were not reproducible, a result attributed to the diversity in structure, which re-formed when the suspension was at rest.

Additional and more extensive data on the electrical properties of carbon black dispersed in rubber, mineral oil, and vegetable oil have been reported by Amon and Brown.<sup>30</sup> The electrical resistance of a fixed quantity of the dispersion was measured in a cell by determining the current flow at 100 volts. Resistance was found to decrease with blacks of large surface area. Wide differences were noted with different blacks, and, in general, the finer particle-size blacks exhibited the lowest resistance.

The resistance was found to follow the empirical relationship:

$$A = a \cdot b \log R$$

where  $A$  = surface area in sq. m. per gram,  $R$  = resistance in megohm-cm. at 100 volts, and  $a$  and  $b$  are constants. For a given type of carbon black, the resistance decreased greatly as the pigment content was raised (Table II). The inks with lowest yield value had the highest resistance when other factors were constant.

These findings lend support to the concept of structure as forming the network for passage of current.

TABLE II. ELECTRICAL RESISTANCE OF CARBON BLACK SUSPENSIONS IN MINERAL OIL<sup>30</sup>

Sample	Concentration (wt. %)	Specific Surface (sq.m./gram)	Specific Resistance (megohm-cm. at 100 v.)
A	10	95	640,000 × 10 <sup>2</sup>
	12		560,000
	15		510,000
B	10	110	450,000
	12		400,000
	15		330,000
C	10	160	55,000
	12		48,000
	15		17,000
D	10	285	260
	12		105
	15		25
E	10	360	9.9
	12		3.2
	15		0.72

<sup>30</sup> F. H. Amon and O. J. Brown, Jr., *Am. Ink Maker*, 19, No. 11, pp. 25-28 (November, 1941).

The electrical conductivity of rubber compounds is of considerable industrial importance, and several investigations have been made which provide additional evidence for internal structure of the carbon-black dispersions. Cohan and co-workers<sup>31</sup> studied the conductivity of rubber-tread stocks compounded with different types of carbon blacks. Rubber in the form of smoked sheet or pale crepe has a specific resistance of  $10^{12}$  to  $10^{16}$  ohm-cm. Addition of non-conducting pigments does not appreciably alter this value, but certain types of carbon blacks reduced the resistance to 30 to 500 ohm-cm., entirely comparable with the experiments of Amon and Brown, noted above, in which oils were used as dispersion media. The log of resistance was found to decrease linearly with increase in particle size. The volatile components present on the surface of the carbon black were connected with the electrical conductivity. When the blacks were "devolatilized" by heating in a non-oxidizing atmosphere, a gradual decrease in resistance occurred from an initial value of 5,000 ohm-cm. for an untreated channel black to 400 ohm-cm. for the treated carbon black. The non-carbon constituents on the surface are considered to act as an insulating layer, separating and preventing contact between the particles. Similar results were obtained with bulk, undispersed carbon black. The crystal structure of the carbon black influences conductivity markedly: particles showing a graphitic type of structure exhibit the highest conductivity. More recently, Wack, Anthony, and Guth<sup>32</sup> studied dispersions of conducting carbon blacks in both natural and synthetic rubber to elucidate the mechanism of conductivity. Dispersions containing from 15 to 40 volume percent of black were prepared according to standard compounding practice, and the resulting stocks were studied for the change in conductance with time, concentration, temperature, and extension of the blacks. It was found that the resistance of the stocks, which increased initially on extension, decayed exponentially at rest. Heating or annealing the samples hastened the attainment of a steady resistance.

These results were interpreted in terms of a picture of the state of flocculation of the carbon-black particles. The conductance of rubber itself is very low, and the carbon-black particles produce a conducting system only if they are sufficiently close to form a network or chain. In the relaxed state, the particles presumably are free to migrate and to associate with adjacent particles. The rubber molecules in the relaxed state would thus offer the minimum of resistance. If the stock is now stretched, the network is momentarily disrupted and the resistance in-

<sup>31</sup> L. H. Cohan and J. F. Mackay, *Ind. Eng. Chem.*, **35**, 806-8 (1943); L. H. Cohan and M. Steinberg, *ibid.*, **36**, 7-15 (1944).

<sup>32</sup> P. E. Wack, R. L. Anthony, and E. Guth, *J. Applied Phys.*, **18**, 456-69 (1947).

creases. At rest, particularly at an elevated temperature, the dispersed particles form again into a network and the resistance decreases.

### Flow properties

It would be expected that any internal structure in a suspension would affect the flow properties. An increase in apparent viscosity or a reduction of mobility is a consequence of flocculation of the dispersed material, and instrumental means are available for this measurement. This procedure is, indeed, one of the greatest utility in evaluating dispersions and will be discussed at length in a succeeding chapter. At this point, however, it will be sufficient to offer preliminary evidence for the connection between the flocculated state and the type of flow that results.

A true liquid flows when acted upon by any force however small; the rate of flow varies with a kind of internal liquid friction measurable as the fundamental physical property of viscosity. When solid particles are suspended in such a liquid, however, interaction between particles causes a change in the measured viscosity. If the concentration of the dispersed phase is greatly increased or if the particles are caused to flocculate and form an internal structure, the suspension acquires rigidity. Then an initial force is required to initiate flow. This yield stress has been given various terms, but it is now most commonly designated as yield value, and the flow characteristics, no longer viscous, are called plastic.

The connection between flocculation and plasticity seems to have been known for many years, intuitively perhaps, in industries such as ceramics manufacturing. A clear demonstration of the connection was given by Green in 1923.<sup>33</sup> By means of low-power photomicrographs of a suspension of zinc oxide in kerosene flowing in a capillary tube, Green showed how flocculation of the particles held the mass together at low rates of shear; at higher pressures, which produced corresponding increases in the rate of shear, the flocules were sheared apart. On a comparable system (zinc oxide in a mineral oil) the yield value was found to be 3.8 dynes per sq. cm.; on deflocculation this value dropped to a negligibly small figure. These experiments have been considerably extended in the intervening years by Green, as well as many others, and the role of flocculation in inducing plastic flow may be taken as well established.

### Dielectric constant

Some insight into the course of flocculation may be gained by measurement of the dielectric constant of dispersions. This procedure is based

<sup>33</sup> H. Green, *Ind Eng. Chem.*, **15**, 122-26 (1923).

on the fact that the dielectric constant of suspensions of spherical particles is appreciably less than that of non-spherical particles when the volume of the suspended phase is constant. Flocculation results in the formation of chains of particles and consequently should be associated with an increase in dielectric constant. Experimental and theoretical studies of this phenomenon have been made by several investigators. Guillien<sup>34</sup> investigated suspensions in air and organic liquids. Bruggeman<sup>35</sup> extended earlier mathematical studies. Wachholtz and Franceson<sup>36</sup> concluded that no generally valid mixture formula had been evolved. Parts<sup>37</sup> observed a change in dielectric constant of carbon black dispersions with time elapsed after stirring and noted a connection with the flow properties. These experiments were considerably extended by Voet,<sup>38</sup> who was able to demonstrate the validity of a relatively simple relationship.

Bruggeman<sup>35</sup> proposed the following equation for the dielectric constant of suspensions of spherical particles:

$$1 - V = \frac{\epsilon_p - \epsilon}{\epsilon_p - \epsilon_m} \left( \frac{\epsilon_m}{\epsilon} \right)^{1/3} \quad (2)$$

where  $V$  is the volume fraction of the dispersed phase,  $\epsilon$  is the dielectric constant of the dispersion,  $\epsilon_p$  the dielectric constant of the solid particles, and  $\epsilon_m$  the dielectric constant of the suspending medium. When the value of  $\epsilon_p$  becomes infinitely large,

$$\epsilon = \frac{\epsilon_m}{(1 - V)^3} \quad (3)$$

Voet modified this equation to an approximate formula,

$$\epsilon = \epsilon_m(1 + 3fV) \quad (4)$$

by neglecting higher terms of  $V$  and introducing a shape or form factor  $f$ . For spherical particles  $f = 1$ , and for non-spherical particles  $f > 1$ .

The experimental results obtained by Voet are of considerable interest. Measurements were made on the dispersions during shearing and at rest in a cylindrical cup fitted with a coaxial internal cylinder (bob) with a clearance of 6 mm. at the sides and bottom. By rotating the internal cylinder varying rates of shear could be obtained. A series-resistance capacity bridge was used for the capacity measurements which were made at 5,000 cycles per second.

<sup>34</sup> R. Guillien, *Ann. phys.*, **16**, 205-52 (1941).

<sup>35</sup> D. A. G. Bruggeman, *Ann. Physik*, **24**, 636-79 (1935).

<sup>36</sup> F. Wachholtz and A. Franceson, *Kolloid-Z.*, **92**, 158-69 (1940).

<sup>37</sup> A. Parts, *Nature*, **155**, 236-37 (1945).

<sup>38</sup> A. Voet, *J. Phys. & Colloid Chem.*, **51**, 1037-63 (1947); *ibid.*, **53**, 597-609 (1949).



When spherical iron particles 10 microns in diameter were suspended in liquids, the Bruggeman relation (Equation 3) was applicable to weight concentrations of 40 percent in mineral oil and 20 percent in linseed oil. The form factor was 1 for this case. At higher concentrations, however, the agreement was less satisfactory, a result attributed to flocculation. For particles that departed from spherical, the form factor increased, as shown by the following values for  $f$ : zinc powder, 1.4; titanium dioxide, 1.5; aluminum (leaflets), 8.2; carbon black, 3.9.

A measure of flocculation is provided by a change in the form factor. Thus the ratio between  $f$  at rest (for a given volume concentration of suspended material) and  $f$  during shear may be taken as an indication of flocculation. The equation modified to account for the flocculation of suspended particles is

$$\epsilon'_v = (1 - 3a_v fV) \quad (5)$$

where  $\epsilon'_v$  is the dielectric constant of the dispersion at rest and  $a_v$  is the "agglomeration factor." (In his paper Voet uses agglomeration with the meaning of flocculation as used throughout this monograph.) When the suspensions exhibited Newtonian flow,  $a_v$  was 1.0 or very close to unity; when plastic flow was evident, values of  $a_v$  to 10 were noted. At high shearing rates  $a_v$  decreased and, in the case of several carbon-black dispersions, became unity, indicating complete deflocculation. The index of deflocculation is defined by Voet as the maximum concentration at which individual particles are present. The interesting and important contribution from dielectric constant measurements on dispersions affords additional evidence for flocculation as a predominant factor in establishing certain physical properties of dispersions. In the next section we shall turn to probable mechanisms of particle flocculation.

### Forces between Particles

When two small particles are suspended in a liquid, the attraction between them, if any, can be attributed to a variety of causes. The nature of the attractive force, sometimes designated merely as the force of flocculation, and of the repulsive force depends on the following: particle size and surface area of the solid, the physical properties of the suspending medium, the chance presence of gases or a second liquid immiscible with the continuous phase, the proximity of the particles, and the presence of an electric charge. Because of the complexity of these relations it is not likely that a simple explanation could be adduced that would hold for all suspensions. We can, however, examine separately the probable causes for the related phenomena of flocculation and deflocculation

or, in analogous terms of the colloid chemist, of coagulation and peptization.

### Stability of suspensions

In a colloidal sense, a suspension is stable when aggregation of the dispersed particles is inappreciable, i.e., incapable of observation, over a relatively long period of time. Emulsions provide a fairly clear picture, for, if adherence of particles occurs, coalescence of the dispersed phase eventually follows and a gradual growth in particle size results. This change can be observed by size-distribution curves.<sup>39</sup> The coagulation of lyophobic colloids, particularly aqueous suspensions, has been extensively studied,<sup>40</sup> and some features of the theory will be noted in the next section. Colloidal sols are considered by some investigators to be thermodynamically unstable, exhibiting a coarsening with age, similar to that shown by emulsions. With suspensions, in which the particles are in the upper range usually classified as defining the limit of colloidal properties, other effects enter, such as fast sedimentation under gravity, and the evaluation of stability becomes partly a matter of definition.

One view of the process of flocculation has been stated by Steele.<sup>41</sup> If the free energy of the interface is so high that a decrease results when particles come into close approach, lowering the interfacial area of the suspension, then it would be expected from thermodynamic considerations that the flocculated suspension would be in a more stable state. This process evidently calls for actual contact of the surfaces of the solid particles, for which there is no clear evidence. Another view is based on the idea of a strongly bound liquid layer around each particle. This idea has been expressed by several investigators.<sup>42</sup> Each particle is considered to be surrounded by a shell of liquid much thicker than monomolecular, which is strongly adherent to the particle. This shell is considered to have properties different from the bulk of the liquid, being in a "compressed" condition, and the viscosity of the shell is correspondingly higher. Flocculation is attributed to forces operating through the liquid, with the particles in a flocculated state sharing the tightly bound

<sup>39</sup> W. D. Harkins and N. Beeman, *J. Am. Chem. Soc.*, **51**, 1674-94 (1929); E. K. Fischer and W. D. Harkins, *J. Phys. Chem.*, **36**, 98-110 (1932); S. Berkman, *ibid.*, **39**, 527-39 (1935).

<sup>40</sup> For a detailed discussion of this subject the reader is referred to treatises on colloid chemistry.

<sup>41</sup> F. A. Steele, *Physics*, **1**, 101-5 (1931).

<sup>42</sup> A. de Waele, *J. Am. Chem. Soc.*, **48**, 2760-76 (1926); A. de Waele and G. L. Lewis, *Kolloid-Z.*, **48**, 126-41 (1928); E. L. McMillen, *Ind. Eng. Chem.*, **22**, 890-93 (1930).

liquid layers. Steele<sup>41</sup> remarks that the existence of such a layer has never been demonstrated, and he appears skeptical of its theoretical justification. McDowell and Usher<sup>43</sup> compute that the liquid layer around uncharged lyophobic particles would have to be 0.005 mm. or 10,000 molecules thick to account for rigidity in this way. This may be considered extremely improbable. Nevertheless, the possibility cannot be entirely eliminated, for attractive forces at the surface of the solid can extend into the liquid a sensible distance and conceivably cause orientation of molecular species in the liquid at the interface, as will be noted later, giving rise to properties which suggest an immobile layer at the interface.

### Surface forces

The existence of attractive forces at the surfaces of solids appears now to be supported both theoretically and experimentally. Nineteenth century physicists (notably Plateau and Quincke) considered the range to be around 500 Å, perhaps as high as 1,000 Å. In more recent years, however, the range of such surface forces was considered extremely short—in the neighborhood of molecular dimensions—although many physical phenomena were then incapable of explanation. Nevertheless, Hardy,<sup>44</sup> as a result of extended experiments on boundary lubrication, came to the conclusion that the force fields at a surface extend through many molecular dimensions. Hardy postulated the following: the actual range of the surface forces extends through only a few molecules in contact with the surface but these molecules are oriented and “strained” and in turn affect adjacent molecules farther removed from the surface, until thermal action prevents further orientation. The spreading of polarization from one molecule to the next (a process termed “diachysis” by Hardy) would account for the surface force apparently extending through many molecular layers, perhaps as high as a thousand.

The properties of colloidal suspensions can be cited as evidence for forces of comparatively long range. Freundlich,<sup>45</sup> for example, states that the facts of coagulation and adhesion of particles require far-reaching forces of attraction for their explanation. Our purpose here, however, is to assay the evidence from other sources in order to find a credible hypothesis for the physical properties of pigment dispersions.

<sup>43</sup> C. M. McDowell and F. L. Usher, *Proc. Roy. Soc. (London)*, **A131**, p. 575 (1931).

<sup>44</sup> Sir W. B. Hardy, *Collected Scientific Papers of Sir William Bate Hardy*, Cambridge, 1936; pp. 799–801; 827–66; *Trans. Roy. Soc. (London)*, **A230**, 1–37 (1931).

<sup>45</sup> H. Freundlich, *Thixotropy*, Hermann & Cie, Paris, 1935.

Various kinds of experimental results may be cited to support the idea of forces of relatively long range at the solid surface. Much of the evidence, unfortunately, is circumstantial or at best indirect in character, so that the essential nature, magnitude, and range of surface forces can only be inferred.

Hardy, in the course of his extensive studies on lubricants, found that the nature of the solid had a large effect on boundary friction. The adhesion of dissimilar metals separated by films of organic liquids was intermediate between that of similar metals.<sup>46</sup> Adherence of the liquid to the solid was shown by allowing the liquid to flow into the space between two dry surfaces and comparing this with the condition where liquid was forced by squeezing from the space: equilibrium values for adhesion were obtained more quickly in the former case, and Hardy comments, “. . . fluid of low viscosity is drawn in, when it [cylinder on a plate] falls it presses out lubricant whose molecules are locked in place by the attraction fields of the solids. It is the difference between drawing in a light spirit and expressing a jelly.”

Experiments by McBain and co-workers over a period of many years also supply evidence that the adhesion of metals is affected by the metals themselves.<sup>47</sup>

Evidence for the attraction at a surface may be inferred also from experimental experience with measurement of viscosity. The theory of this measurement implies that no slippage occurs between the walls of the viscometer and the liquid, and, since these mathematical relations have been confirmed by experiment, it may be assumed that the layer of liquid immediately adjacent to the wall is immobile. Bikerman<sup>48</sup> shows how this layer may be considered to have properties ascribed to rigidity. Deryagin and co-workers<sup>49</sup> measured the viscosity of thin films of liquid by filling a slit 0.17 mm. in width and then blowing the liquid from the slit with an air jet. Thickness of the remaining film was measured by an optical method. Oils showed no anomalies at distances of the order of 1,600 Å from the wall, but oils that contained aluminum naphthenate exhibited an increase in the viscosity at the interface, extending to about

<sup>46</sup> *Collected Papers*, pp. 767-98; W. B. Hardy and M. Nottage, *Proc. Roy. Soc. (London)*, **A112**, 62-75 (1926); *ibid.*, **A118**, 209-29 (1928).

<sup>47</sup> J. W. McBain and W. B. Lee, *J. Phys. Chem.*, **31**, 1674-80 (1927); **32**, 1178-84 (1928); *Chem. Eng. News*, **27**, 473 (1948).

<sup>48</sup> J. J. Bikerman, *Surface Chemistry for Industrial Research*, Academic Press, New York, 1947; pp. 246-50.

<sup>49</sup> B. Deryagin, G. Strakhovskii, and D. Malysheva, *Acta Physicochim. U.R.S.S.*, **19**, 541-52 (1944); through *Chem. Abs.*, **39**, 2919-20 (1945). See also *Chem. Abs.*, **39**, 5145-46 (1945).

0.5 micron from the wall. When liquids flow through very fine capillary spaces, the usual viscometric principles fail to hold. This result has been explained as an increase in viscosity near a solid wall. The experiments are not conclusive, however, for asperities in the surface would effectively decrease the apparent capillary space, as shown by Bikerman.<sup>48</sup> Moreover, many of the cases investigated involve water as the fluid, and electrokinetic effects are likely.

Rothen<sup>50</sup> has described experiments on biological systems that seem to indicate action at a considerable distance. Films of an antigen were deposited on a slide and then covered by layers of barium stearate, the plastic, Formvar, and other substances for which the corresponding antibody has no affinity. It was found that the antigen, although covered by a biologically inert barrier, caused adsorption of the antibody when the slide was brought into contact with it. The thickness of the intervening layer through which the effect could be observed depended on the initial thickness of the antigen: in general, the maximum range was found to be about 200 Å. Similar experiments were performed with enzymes. Criticism of Rothen's results has been based largely on the possibility of diffusion through the intervening layer of barium stearate or resin. Because of the direct importance of these results for biological and medical science, it is likely that the subject will find extensive experimental elaboration.

Some conception of the depth of the mobile layer on solids is derived from Beilby's work on polishing.<sup>51</sup> By means of ingenious, although simple, experiments, Beilby was able to demonstrate the manner in which the surface rearranges during polishing. He concluded that polishing caused a freedom of movement of the surface aggregates of the material (termed "molecules" by Beilby) which simulated that of a liquid surface. When the polishing operation ceases, molecular attraction draws the surface into a continuous film, comparable to that of a liquid. The parallel between a liquid and a solid is thus considered very close, for, despite the fact that the mobility of the surface of a solid is far less than that of a liquid, it can nevertheless assemble the "molecules" of the surface into new forms of aggregation. The surface layer was found by etching procedures to extend as deeply as 10,000 Å. A further inference from Beilby's experiments is that, when fine, dry powders come into close contact, i.e., within the range of attractive (cohesive) force, the particles adhere and, as a consequence, the packing is open or loose.

<sup>48</sup> A. Rothen, *J. Biol. Chem.*, **163**, 345-46 (1946); **167**, 299-300 (1947); **168**, 75-97 (1947).

<sup>51</sup> Sir G. Beilby, *Aggregation and Flow of Solids*, Macmillan and Co., Ltd., London, 1921.

Von Buzagh<sup>52</sup> endeavored to measure such attractive forces between quartz powders of microscopic sizes and a quartz plate by determining the number and size of the particles that adhered.

From the evidence cited briefly above, attractive forces between dispersed particles appear at least theoretically admissible.<sup>53</sup> The important factors evidently are dimensional: what are the magnitude and range of such forces? Some indication has been given but unfortunately definite answers cannot be given to these questions, and the subject is considered by many investigators to hold several unsolved problems. It is known that the range of van der Waals' force of molecular attraction falls off inversely as a high power of the distance, possibly as great as the seventh power. A modification of the theory indicates that the attraction between a large area of surface and a particle falls off much less rapidly.<sup>54</sup> Edser<sup>55</sup> cites experimental data that suggest an attraction extending to a distance equivalent to 100 water molecules, or approximately 300 to 400 Å. These values are largely speculative, but precise experimental data have been obtained more recently from adsorption studies by Harkins and Jura.<sup>56</sup> From energy considerations the thickness of adsorbed polymolecular films on titanium dioxide (anatase crystal type) was found to be as follows: water, 15 Å; nitrogen, 36 Å; and butane, 64 Å. These data represent pressures of adsorption just below saturation. Other crystalline solids such as quartz exhibit comparable relations. The attraction of the solid falls off exponentially, and, as the film increases in thickness, orientation of the molecules decreases in degree until it approaches that of a film of the liquid under comparable conditions.

An extremely interesting experiment has been reported on the cohesive bonding of metal surfaces by Gwathmey and collaborators. Massive single crystals of copper were turned to spherical form and then electrolytically polished to produce strain-free surfaces. Oxide films present on the surface were reduced in hydrogen at 500° C. A technique was developed for identifying the crystal faces. When the 100 or 111 faces were brought into contact, bonding or seizure occurred, and the strength of the bond was found to be equal to that of bulk copper and independent of the crystallographic faces. Adsorbed gas films did not

<sup>52</sup> A. Von Buzagh, *Colloid Systems*, translated by O. B. Darbishire, The Technical Press, Ltd., London, 1937; pp. 153-57.

<sup>53</sup> Certain other evidence is given in the review by J. C. Henniker, *Revs. Modern Phys.*, **21**, 322-41 (1949).

<sup>54</sup> H. Kallmann and M. Willstaetter, *Naturwiss.*, **20**, 952-53 (1932).

<sup>55</sup> E. Edser, *Fourth Report on Colloid Chemistry*, British Association for the Advancement of Science, London, 1922; pp. 40-121.

<sup>56</sup> W. D. Harkins and G. Jura, *J. Am. Chem. Soc.*, **66**, 919-27 (1944).

inhibit bonding, but an oxide film, formed by contact of the crystal with air at room temperature, completely prevented bonding.<sup>57</sup>

It is conceivable that, if the particles dispersed in a liquid are extremely small and are brought very close together, the unbalance of forces on the surface of the solid would cause attraction between particles. If, then, particles were to approach within molecular distances, it could be expected that the attraction would be very great indeed. Presumably the attractive forces would operate in aqueous or ionizing media as well as in organic or non-ionizing media. Most of the particles with which we are concerned are irregular in shape and are in the upper range of colloidal dimensions; moreover, many of the dispersions requiring explanation are in media many times more viscous than water. In the absence of adequate experimental data, it may be reasonable to assume that the forces of attraction between these discrete particles are relatively small and may be neglected for many systems, since the actual number of possible contacting surfaces per unit volume of suspended material would be at the minimum. As the particle size decreases, however, and the viscosity of the dispersion medium approaches that of water, the influence of attraction becomes progressively greater. It is necessary, however, to consider also electrokinetic effects.

### Electric charge on particles

The electrostatic charge carried by dispersed particles is an important factor in the stability of aqueous suspensions. The charge originates by ionization of the surface or by adsorption of ions from the solution.<sup>58</sup> In its original conception by Helmholtz the ionic layer formed at the interface is analogous to that of the two plates of a condenser, with the double layer of ions of atomic dimensions. The idea of the double layer has been extended by other investigators, notably Gouy and Stern, and the present conception is that the layer is diffuse, with a thickness appreciably greater than atomic dimensions, and that the ions are distributed in the form of an ionic atmosphere.<sup>59</sup> The zeta potential, a

<sup>57</sup> G. P. Smith, H. Leidheiser, Jr., and A. T. Gwathmey, *Proc. Virginia Acad. Sci.*, 1946-47, p. 82.

<sup>58</sup> For a critical discussion of the mechanism of static electrification, see L. Loeb, *Science*, **102**, 573-76 (1945).

<sup>59</sup> For a detailed discussion of this subject the reader is referred to the treatise of Freundlich and the following: H. A. Abramson, *Electrokinetic Phenomena*, Reinhold Publishing Corp., New York, 1934; H. A. Abramson, L. S. Moyer, and M. H. Gorin, *Electrophoresis of Proteins and the Chemistry of Cell Surfaces*, Reinhold Publishing Corp., New York, 1942; "Electrophoresis," papers presented at a conference, *Ann. N. Y. Acad. Sci.*, **39**, 105-212 (November 6, 1939); "The Electrical Double Layer," papers presented at a symposium, *Trans. Faraday Soc.*, **36** (1940).

measure of the potential difference across this layer, is expressed as

$$\zeta = \frac{4\pi ed}{D} \quad (6)$$

where  $\zeta$  is the potential drop across the double layer,  $e$  is the electric charge of the double layer,  $d$  thickness, and  $D$  dielectric constant.

The magnitude of the zeta potential in millivolts may be seen from data quoted by Freundlich<sup>60</sup> for various substances in water: quartz, -44; iron blue (colloidal), -58; ferric oxide, +44; gold, -32; silver, -34. (Negative values indicate migration to the anode; positive values, to the cathode, in an electrophoresis cell.) The zeta potential is rarely greater than 100 millivolts. In contrast, the contact potentials of monolayers of fatty acids on water approach 400 millivolts.<sup>61</sup> Langmuir<sup>62</sup> points out that even higher potentials would seem probable for colloidal suspensions.

There is some uncertainty about the effects of particle size and shape on mobility of particles in an electrophoresis cell. Abramson<sup>59</sup> states that the mobility of particles coated with protein films is independent of size, shape, and orientation. Thickness of the double layer, defined as the distance from the solid surface to the shear boundary, is independent of particle size but varies with electrolyte concentration. The range is approximately 5 to 50 Å.

The coagulation of colloidal dispersed charged particles may take place according to the following hypothetical mechanism. Uncharged particles, when brought close together, adhere because of van der Waals' attractive forces. In a stable suspension, where the particles are similarly charged, electrostatic repulsive forces predominate and the particles are prevented from adhering since the electrostatic forces are of longer range than the van der Waals' forces. The magnitude of the repulsion is gauged roughly by the zeta potential. If the zeta potential is sufficiently high, the charges constitute a potential barrier and the colloidal system is stable. If the zeta potential is caused to decrease, as by the addition of an electrolyte, then the particles may have sufficient kinetic energy to cross the barrier and come within range of the van der Waals' attractive forces. The particles then adhere. The zeta potential corresponding to this limit is termed the critical potential. Two critical potentials are considered probable: one permitting slow, incomplete coagulation and the other rapid, complete coagulation. Lewis<sup>63</sup> in a study

<sup>60</sup> H. Freundlich, *Colloid and Capillary Chemistry*, H. S. Hatfield, translator, Methuen & Co., Ltd., London, 1926, p. 257.

<sup>61</sup> W. D. Harkins and E. K. Fischer, *J. Chem. Phys.*, **1**, 852-62 (1933).

<sup>62</sup> I. Langmuir, *J. Chem. Phys.*, **6**, 873-96 (1938).

<sup>63</sup> W. C. M. Lewis, *Trans. Faraday Soc.*, **30**, 958-67 (1934).



of the adherence and coalescence of particles in emulsions considers the second critical potential as the only one that can be characterized. The computations of Lewis suggest that the approach distance is of the order of 1 to 2 Å when coagulation occurs, and that the minimal area of adherence is roughly  $10^{-13}$  sq. cm., with a critical potential less than 30 millivolts.

An extensive analysis of the competing forces between colloidal particles has been made by Hamaker.<sup>64</sup> Using equations for electrostatic repulsion and van der Waals' attraction, potential energy distribution curves are obtained. These allow interpretation of the conditions for sol stability, coagulation, and thixotropy. This approach is of theoretical interest and has also been used by other investigators.<sup>65</sup> The reasoning depends on the idea that the repulsive force falls off more rapidly than the attractive force with distance between particles and that the energy-distance curves then exhibit a minimum corresponding to an equilibrium distance between particles. This distance is considered to be in the neighborhood of 1,000 Å. Suspended particles at equilibrium conform to this separation. Experimental data bearing on this theory are scanty, and the formulation of long-range forces is subject to controversy. All theories so far proposed may be considered general analysis; experimental verification is extremely difficult because of uncertainty in particle size and magnitude of the surface charge.

This mechanism of coagulation holds some credibility for aqueous systems despite a certain ambiguity in the definition and measurement of the zeta potential, as well as uncertainty in the magnitude and range of interparticle forces. For suspensions in non-aqueous media, particularly those with low dielectric constant (insulating liquids), the conception of charged particles is difficult to elaborate. Such colloidal systems are analogous to lyophilic colloids at the isoelectric point. Electrical effects in organic media are low in magnitude and badly defined but may, nevertheless, play some obscure part in establishing the conditions for stability.

<sup>64</sup> H. C. Hamaker, *Rec. Trav. Chim. (Pays-Bas)*, **55**, 1015-26 (1936); **56**, 3-25, 727-47 (1937); **57**, 61-72 (1938). See also, E. A. Hauser, *Colloidal Phenomena*, McGraw-Hill Book Co., New York, 1939; pp. 219-24.

<sup>65</sup> See R. Houwink, Chapter IV, pp. 185-240, in *Second Report on Viscosity and Plasticity*, Academy of Sciences at Amsterdam, Interscience Publishers, New York, 1938; S. Levine and G. P. Dube, *J. Phys. Chem.*, **46**, 239-80 (1942); S. Levine, *Trans. Faraday Soc.*, **42B**, 102-17 (1946); E. J. W. Vervey and J. T. G. Overbeek, *ibid.*, **42B**, 117-31 (1946); E. J. W. Vervey and J. T. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier Publishing Co., New York, 1948. See also, I. Langmuir, *J. Chem. Phys.*, **6**, 873-96 (1938).

This point has been examined by Reising<sup>66</sup> who placed dispersions of pigments in various vehicles in a 450-volt direct-current field. Observation was made by means of a microscope. In a non-polar medium (mineral oil and mineral spirits) the particles showed a "lines-of-force" arrangement between the electrodes, analogous to the alignment of iron filings between the poles of a magnet, but no migration occurred. In other vehicles (e.g., linseed oil, olive oil), migration occurred and the particles appeared to carry charges, some migrating to the anode, some to the cathode. Both positive and negative charges were stated to exist on a single particle. Similar results were obtained by Hedrick, Andrews, and Sutherland<sup>67</sup> on pulverized coal dispersed in oil. These investigators suggest that the charges on the coal particles are produced during grinding. Addition of stabilizers which promote gelation (e.g., rubber, paraffin, aluminum stearate) produced no change in the electrostatic response of the dispersed particles, but surface-active agents caused the particles to deposit on the electrodes. In concentrated suspensions the particles migrated to both poles. Soyenkoff<sup>68a</sup> examined many non-aqueous colloidal dispersions under electrostatic fields and concluded that potentials of less than 5 kv. per cm. have little or no effect on hydrocarbon sols. He states that fields of high intensity cause ponderomotive effects which are probably not electrophoretic in character. Winslow<sup>68b</sup> also examined suspensions under electrostatic fields and found that, in general, particles of semi-conductive solids of high dielectric constant were the most responsive. The conditions for marked flocculation or fibrillation of the suspended particles according to Winslow are (1) volume concentrations in excess of 38 percent (thus bringing the material into the region of dilatant flow), (2) presence of a small amount of moisture, (3) particle size of about 1 micron, and (4) field strengths of about 6 kv. per cm. A specific example cited is a suspension of silica gel powder dispersed in a kerosene fraction with the addition of surface-active agents (e.g., metallic soaps).

The theoretical significance of most of these observations is obscure, but the conclusion seems inescapable that electric charges are of minor importance as a factor contributing to the stability of particles suspended in non-ionizing media such as oils.

Induced flocculation of suspended particles has a practical application in the design of clutches and brakes. When a field is imposed on a

<sup>66</sup> J. A. Reising, *Ind. Eng. Chem.*, **29**, 565-71 (1937).

<sup>67</sup> J. E. Hedrick, A. C. Andrews, and J. B. Sutherland, *Ind. Eng. Chem.*, **33**, 1055-57 (1941).

<sup>68a</sup> B. C. Soyenkoff, *J. Phys. Chem.*, **35**, 2993-3010 (1931).

<sup>68b</sup> W. M. Winslow, *J. Applied Phys.*, **20**, 1137-40 (1949).

suspension of particles, the resulting flocculation permits the transmission of torque from one freely rotating surface to another. Winslow<sup>68b</sup> considered the conditions required primarily for electrostatic fields, and Rabinow<sup>68c</sup> designed a clutch operated by electromagnetic fields. For the magnetically responsive suspensions, carbonyl iron, stainless steel flakes, or magnetic iron oxide were dispersed in machine oil. The ratios ranged from 1/1 to 10/1 by weight of powder to suspending liquid. Another magnetically responsive suspension patented by Lucas<sup>68d</sup> has the following composition: steel dust, 12 parts, graphite, 3 parts, and mercury, 85 parts.

### Flocculation by immiscible liquids

A mechanism of flocculation that depends on the coherence of particles induced by a small quantity of a liquid immiscible with the continuous phase has been demonstrated experimentally. It will be recalled that water has been used for many years to prevent hard settling of the pigment in paint; frequent reference has been made to the effect of water on increasing the plasticity of paints.<sup>69</sup> Pigments that exhibit this property have been marketed with the designation "water sensitive." This is a practical example of controlled flocculation.

*Theory.* The manner in which flocculation is brought about can be visualized in the following way. The particles initially are distributed uniformly throughout a medium such as a mineral oil. It may be assumed that no material is adsorbed at the solid-liquid interface and that the oil has spread over the particle surface. If water, or certain other liquids (as will be shown later), is now added to the suspension, it concentrates at the interface and, if the surface of the solid is preferentially wetted by the water, the oil is displaced and a film of water forms on the solid, separating the solid from direct contact with the liquid. The interface is now completely changed and, if sufficient water is present it will act as a cementing medium between the dispersed particles, causing flocculation. It should be expected, therefore, that the yield value, taken as a measure of flocculation, would increase in proportion to the amount of water until some limiting quantity was reached. Further, the minimal amount of water causing an appreciable increase in yield

<sup>68c</sup> Experiments of J. Rabinow as described in *Tech. News Bull. Nat. Bur. Standards*, **32**, 54-60 (1948).

<sup>68d</sup> R. Lucas, U. S. Patent 2,149,782 (March 7, 1939).

<sup>69</sup> F. H. Rhodes and W. J. Jebens, *J. Phys. Chem.*, **35**, 382-404 (1931), attribute the function of water to emulsification and formation of a structure within the paint. See also, L. W. Ryan, *Official Digest Federation Paint & Varnish Production Clubs*, March, 1934.

value should be somewhat larger than that necessary to form a monomolecular film, because a liquid bridge between particles could be considered as the mechanism of attachment.

Experimental evidence has been given for this explanation by Kruyt and Van Selms<sup>70</sup> and the author.<sup>71</sup> The experiments of Kruyt and Van Selms were performed with rice starch, quartz powder, and glass spheres suspended in mineral oil diluted with various solvents. For the measurement of plasticity a type of rolling sphere viscometer was used. Although this instrument gave only relative values for yield value and was incapable of a reliable measure of thixotropy, the results are of great interest.

In quartz-powder suspensions, unit additions of water caused an increase of yield value until a fairly constant figure was reached at approximately 2 percent, computed on the weight of quartz. At higher water contents the yield value of the suspension dropped. The maximum yield value occurred at about the same point with quartz powders of different size fractions, but the yield value varied inversely with particle size. With glass beads in a similar suspension, maximum yield value was observed at 2.4 percent water. A computation of the average thickness of the water film on the particles was made: on quartz the film was about 70 molecules thick and on glass beads, 33 molecules thick.

Comparable experiments using pigment-grade powders and other flocculating liquids extend these data.<sup>71</sup> It was observed that immiscible polar compounds other than water, when added in small relative quantities, caused flocculation of the dispersed particles. Experiments showed marked differences in the extent of flocculation with different liquids. It was inferred that the immiscible reagent formed a bridge between adjacent particles and that the force necessary to separate the solid particles would be essentially that required to increase the liquid-liquid interface so formed. The tension at the interface between reagent and suspending liquid should, therefore, be related to the extent of flocculation that is measurable as the yield value of the bulk dispersion. In these experiments, titanium dioxide of a "water-dispersible" pigment grade was dried for ten days at 110° and ground on a three-roll mill in a mixture of equal parts by weight of a pharmaceutical mineral oil and isobutylene polymer to give a dispersed solid content of 30 percent by weight. The particle size ( $d_3$ ) of the pigment was 0.18 micron as calculated from adsorption measurements with nitrogen at -198° by the Brunauer-Emmett-Teller procedure. The viscosity of the oil mixture

<sup>70</sup> H. R. Kruyt and F. G. Van Selms, *Rec. trav. chim.*, **62**, 406-26 (1943).

<sup>71</sup> E. K. Fischer, E. N. Harvey, Jr., and A. S. Dyer, *J. Am. Chem. Soc.*, **68**, 522-23 (1946).

was 13.6 poises at 30°. Flocculating reagents (see caption to Figure 1) were mixed with portions of this dispersion, and the plastic viscosity and yield values were measured in absolute units on a rotational viscometer. Interfacial tension measurements of the various added reagents against the dispersion medium were made on a Cenco-du Nouy tensiometer at 30°.

The curve (Figure 1) shows the unmistakable upward trend of yield value with increasing interfacial tension as predicted, despite difficulties

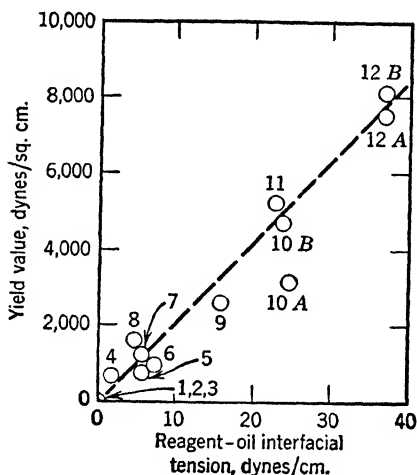


FIGURE 1. Variation of yield value of dispersions of titanium dioxide in non-polar oils on addition of polar liquids. (Legend: (1) control, no reagent; (2) octyl alcohol, 1.2%; (3) 2-ethyl-butyl alcohol, 1.0%; (4) propyl alcohol, 3%; (5) 2,3-butanediol, 3%; (6) furfuryl alcohol, 3%; (7) methanol, 3%; (8) ethanol, 3%; (9) ethylene glycol, 3%; (10) glycerol, A, 2.2%, B, 0.6%; (11) formamide, 2.0%; (12) water, A, 0.6%, B, 1.4%. Water content calculated to form a monomolecular film, 0.26%.

All percentages by weight on dispersed phase. Measurements at 30° C.)

in maintaining anhydrous conditions and in preventing evaporation of appreciably volatile reagents during experimental manipulation.

Other experiments with additional samples of titanium dioxide, ultramarine blue, barium sulfate, and zinc oxide gave similar results. It is not necessary to use a non-polar mineral oil for the dispersion medium, since various grades of bodied linseed oil lead to comparable results, although the absolute magnitude of the yield value differs.

It could be expected that a powder with hydrophobic surface properties dispersed in water would be flocculated on the addition of an oil. Kruyt<sup>70</sup> observed that the addition of xylene to suspensions of coal and graphite in water caused a very large increase in yield value, and the

suspensions were converted to plastic solids. Freundlich<sup>72</sup> noted flocculation of quartz in aqueous suspension on the addition of lecithin. Further, the addition of oil-soluble surface-active agents to pigments dispersed in glycerine resulted in a very large increase in the consistency of the suspension.<sup>73</sup>

The explanation for this behavior is quite simple. When water is added to a suspension of a hydrophilic solid dispersed in an organic medium, each particle takes up some of the water and, if two or more particles approach each other, by the circumstance of stirring or Brownian movement, the water films are brought together and the particles then cohere. When this happens to a large number of the dispersed particles, a flocculated structure is formed, and, on shearing, work is performed in separating the particles from each other. It is evident that the work necessary to separate any pair of particles then is proportional to that required to enlarge the liquid-liquid interface formed between the continuous phase and the immiscible liquid which has been added in small quantity, as is shown by rough proportionality between yield value and interfacial tension (Figure 1).

This mechanism for flocculation is not, of course, universal in application, for other factors, some only vaguely inferred from present knowledge, must certainly be involved also. However, it is possible to understand the role of surface-active agents in promoting deflocculation by this means. Any reagent that lowers the liquid-liquid interfacial tension would thus reduce the work necessary to separate particles in a flocculate. Under certain conditions, the surface-active agent can be either water- or oil-soluble and still function, a result which has been observed. (See Chapter 6 on surface-active agents.) Electrical phenomena are probably absent; indeed, Kruyt, in describing his experiments, points out that boundary tension data only are needed for explanation.

Of considerable historical interest in this connection are the early attempts to devise a practical flotation process by means of oil added to aqueous slurries of finely divided ores. Rickard<sup>74</sup> has given a detailed description of the development of flotation processes. The first and simplest, although impracticable, method was to add oil in rather large quantity, and, since the metallic or mineral portions of the ore were wetted by the oil while the gangue remained wetted by the water, flotation occurred merely by the difference in specific gravity of the two phases. This process is identical in principle with that of the so-called

<sup>72</sup> H. Freundlich, *J. Soc. Chem. Ind.*, **53**, 223T (1934).

<sup>73</sup> E. K. Fischer and C. W. Jerome, *Ind. Eng. Chem.*, **35**, 336-43 (1943).

<sup>74</sup> T. A. Rickard, *Concentration by Flotation*, John Wiley & Sons, Inc., New York, 1921; pp. 1-31.

flushing process for pigment slurries described in Chapter 12. By accident in some of the early processes, air was entrained in the phase consisting of oil and minerals, and added buoyancy was contributed by this agency, although investigators up to 1900 failed to see the importance of air as an essential factor in promoting separation. In some flotations, gases were also liberated by the reaction of acids, added during the process, with carbonate or sulfide minerals, and the bubbles occluded by the viscous oil phase aided separation.

The action of flotation may be summarized in simplified form as follows: oil is added to a suspension of the finely divided ore; the metallic or mineral components are wetted by the oil which induces flocculation, while the gangue, consisting of particles preferentially wetted by water (e.g., silicates), remains deflocculated; air introduced into the system is trapped by the oil-mineral floccules and, by making the mass buoyant, effects separation. The amount of oil is dependent on a number of conditions including the concentration of the slurry, the relative proportion of the mineral and gangue components, and the degree of aeration. In general, however, it is about one percent.

*Applications.* The patent literature contains examples of the control of flocculation by means of additives which presumably affect the coherence of particles by an immiscible liquid. Eide and Depew<sup>75</sup> reduce the "reactivity" of zinc oxide in various vehicles by adding phosphorous pentoxide or other dehydrating oxides to the vehicle before dispersing the pigment. When this is done, the plastic viscosity of the finished dispersion is considerably reduced, or, as expressed in the patent, the paint is prevented from thickening. Presumably the reaction between zinc oxide and fatty acids of the vehicle is considerably inhibited by dehydration of the pigment dispersion with phosphorous pentoxide.

The addition of hygroscopic organic liquids to pigments used in formulating lacquers has been patented as a means of preventing flocculation of the pigment.<sup>76</sup> For this purpose anhydrous ethyl alcohol is mixed with the pigment powder before incorporation into the nitrocellulose solution. Superior gloss on the finished lacquer is claimed. For the same purpose dispersion of pigments at high temperatures has been advocated as an aid in promoting wetting of the pigment, especially for titanium dioxide. The procedure is to mix the pigment and oil at a temperature of about 500° F., allow the mixture to "sweat," and then grind it cold.<sup>77</sup>

<sup>75</sup> A. C. Eide and H. A. Depew, U. S. Patent 2,333,367 (Nov. 2, 1943).

<sup>76</sup> A. M. Taylor and A. R. Chapman, U. S. Patent 1,824,177 (September 22, 1931).

<sup>77</sup> H. A. Gardner, *Am. Paint. J.*, **23**, No. 21, 19 (1939); C. R. Draper, *Paint Manuf.*, **14**, No. 2, 37-40 (1944).

The promotion of flocculation prevents hard settling of pigments in paint and similar formulations. Water is usually added for this purpose, often in the form of a soap solution, which is sometimes euphemistically termed a colloidal solution in the formula on the label. Although water in paint is considered an adulterant if used in excessive quantities, it nevertheless serves an extremely useful purpose in moderate proportions. Frequently the pigment contains sufficient water to provide a measure of flocculation, or it can be specially treated. Thus Clapson<sup>78</sup> treats basic lead sulfate with steam. In this disclosure, the lead pigment is placed in an autoclave and subjected to steam under pressures to 100 psi for approximately two hours. In the examples given an increase of weight of 0.5 to 1.0 percent was noted. This gain, attributed to moisture, and other changes in the surface of the pigment particle during the treatment resulted in dispersions in raw linseed oil of appreciably higher plastic viscosity. Diatomaceous earth in combination with water is mentioned by Burwell<sup>79</sup> to prevent hard settling and to provide a "salve-like" consistency.

Substances other than water have been patented for the prevention of hard settling of pigments and flattening compounds. Among these reagents are the following: alcohols such as ethylene glycol, glycerol, butanol, and octanol,<sup>80</sup> triethanolamine, pentaerythritol,<sup>81</sup> water-soluble amine soaps formed from triethanolamine, ethylene diamine, and other amines with fatty acids.<sup>82</sup> If the reagents are soaps, as in the last group, water assists in forming a flocculated structure.

Flocculation of the dispersed pigment has been observed to result in decreased gloss in a paint or enamel film. This property has been turned to advantage by Lent<sup>83</sup> who formulates oil-cloth coatings with a dead matte finish by the addition of water in the form of a glue solution. When flat or matte finishes are formulated with an excess of pigment or

The idea of high-temperature mixing is far from new. Moxon in his *Mechanick Exercises*, published in 1683, states that Dutch printing ink manufacturers proceeded as follows: "they . . . to save the *Pressman* the labour of *Rubbing the Blacking* into the *Varnish* on the *Inck-Block*, *Boyl* the *Blacking* in the *Varnish* or at least put the *Blacking* in whilst the *Varnish* is yet *Boyling-hot*, which so *Burns* and *Rubifies* the *Blacking* that it loses much of its brisk and vivid black complexion." Moxon's original treatise is very rare, but it is available in a literal reprint, edited by Theo. L. De Vinne, and published by the Typothetae of the City of New York in 1890.

<sup>78</sup> W. J. Clapson, U. S. Patent 2,315,188 (March 30, 1943).

<sup>79</sup> E. C. Burwell, U. S. Patent 2,151,184 (March 21, 1939).

<sup>80</sup> E. K. Fischer, U. S. Patent 2,370,648 (March 6, 1945).

<sup>81</sup> W. W. Plechner and J. M. Jarmus, U. S. Patent 2,130,560 (September 20, 1938).

<sup>82</sup> P. Kümmel, U. S. Patent 2,267,240 (December 23, 1941).

<sup>83</sup> C. M. Lent, U. S. Patent 2,381,915 (August 14, 1945).



by the incorporation of oversize extenders, they are apt to exhibit impaired flexibility and wear-resistance. On the other hand, by causing the pigment to flocculate, the oil binder can be retained at approximately the same percentage as that used for gloss coatings. When dried, the film has a rough texture.

Various other expedients have been disclosed for the control of flocculation. Gamble and Grady<sup>84</sup> treat pigments to impart controllable thixotropic properties to paints by means of hydrophilic coating substances. For this purpose water-soluble gums are used, including gum arabic, agar, gum tragacanth, alginates, and dextrin. The quantity recommended is less than one percent, but some control in the thixotropic properties of the paint may be achieved by varying the quantity. Pigments readily wetted by water, such as titanium dioxide, zinc oxide, clays, and silica, require very small quantities. The quantity of water required to produce suitable thixotropic properties in a paint is stated as usually less than one percent. A similar objective is sought by Marcot<sup>85</sup> who describes a treatment combining sodium silicate (0.05 to 0.5 percent on the pigment) with a water-repellent material (e.g., oleic acid).

Flocculation of pigments used in offset or lithographic printing inks is a source of difficulty. In the operation of this printing process, the ink is in contact with an aqueous fountain solution and some water is emulsified in the ink. The emulsion itself is unobjectionable, but flocculation of the dispersed pigment causes the ink to assume a high yield value and serious printing defects ensue. The remedy does not lie in the addition of surface-active agents; instead, the formulation of the ink requires skill to avoid water-sensitive pigment and vehicle combinations.

One of the most interesting examples of flocculation induced by immiscible liquid pairs is utilized in the process of Wiegand and Venuto<sup>86</sup> for the manufacture of carbon-black beads or pellets. Carbon black in powder form is first dispersed in water. Gasoline or another volatile liquid that is immiscible with water (benzene, chloroform, carbon tetrachloride, turpentine, etc.) is then added. The carbon black flocculates, since the organic liquid wets it preferentially, and the mass "thickens," until, with continued stirring, pellets of the pigment are formed. Approximate ratios mentioned are as follows: carbon black, 5; water, 40 to 80 parts; gasoline, 7 to 9 parts. The compacting thus effected is retained on drying, and the product then is unchanged carbon black with

<sup>84</sup> D. L. Gamble and L. D. Grady, U. S. Patent 2,135,936 (November 8, 1938).

<sup>85</sup> G. C. Marcot, U. S. Patent 2,255,263 (October 9, 1941).

<sup>86</sup> W. B. Wiegand and L. J. Venuto, U. S. Patent 1,889,429 (November 29, 1932); Reissue 22,454 (March 7, 1944).

greatly reduced bulking volume. Various other methods are also employed for the manufacture of carbon black in the form of pellets, and the process has been applied to other pigments that cause difficulty in handling because of dusting.

An entirely comparable process is solvent flushing of pigments present in aqueous slurry form (see Chapter 12). In this process, a solvent is added until the pigment flocculates into the form of curds; these are readily separable from the water by straining through a sieve. Since it is difficult to remove the water completely from the resulting pigment-solvent paste, this technique is useful mainly for the manufacture of pigmented emulsions.

A variation on this idea is the preparation of "soft-process" pigments which require a minimum of grinding to effect satisfactory dispersion. Manufacture of soft-grinding phthalocyanine pigments by means of organic liquids used in the acid-pasting process is described by Lacey and Lecher.<sup>87</sup> The pigment is first dissolved in concentrated sulfuric acid and then precipitated by dilution with water in which an organic liquid is emulsified or suspended by rapid stirring. The liquids mentioned include hydrocarbons, esters, ethers, etc., but toluene and xylene are considered generally most satisfactory. Quantities of the liquid specified range up to 20 percent computed on the pigment.

Flocculation of dispersed pigments as an aid in the quantitative separation from oil and varnish vehicles has been described by Robinson.<sup>88</sup> For this purpose, solutions of nitrocellulose, ethyl cellulose, and other cellulose derivatives are added to the pigment dispersion; the mixture is precipitated by a hydrocarbon solvent, and the pigments are separated finally by centrifuging.

## Solubilization

Most soaps and surface-active materials are capable of causing a remarkable increase in the solubility of substances normally insoluble, or very slightly soluble, in a liquid. This property has been termed solubilization and is connected with the formation of colloidal micelles of the solubilizing agent.<sup>89</sup> Enhanced solution occurs because of the pas-

<sup>87</sup> H. T. Lacey and H. Z. Lecher, U. S. Patent 2,359,737 (October 10, 1944).

<sup>88</sup> F. B. Robinson, *Ind. Eng. Chem., Anal. Ed.*, **16**, 364-65 (1944).

<sup>89</sup> There are two meanings for the term *micelle*: (1) a particle with an electrical double layer, applicable to lyophobic systems in which solvation is negligible; (2) an internal colloidal structure, highly solvated, formed usually from materials that are capable of electrolytic dissociation. It is the latter meaning with which we are concerned in this section. A good review of the evidence for micelle structures is by G. S. Hartley, *Aqueous Solutions of Paraffin-Chain Salts: A Study in Micelle Formation*, Hermann & Cie, Paris, 1936.

sage of molecules of the substance into the ordered structure of the micelle, or by some kind of association at the exterior of the micelle.

Solubilization is a property of colloidal electrolytes that has been known for many years. It has long been the empirical basis for pharmaceutical preparations, dye baths, and detergent and scouring processes in textile finishing, but only recently have the remarkable properties of these systems been fully recognized. In some respects, solubilization is comparable to the action of protective colloids, but it is to be distinguished from the action of hydrotropic solutions,<sup>90</sup> which, in one form, are aqueous salt solutions of high concentration exhibiting greater solubilizing action than water at the same temperature. Such hydrotropic solutions may be said to cause "salting in" of difficultly soluble substances, but colloidal material may be absent.

McBain and collaborators<sup>91</sup> have extensively investigated the solubilizing action of colloidal electrolytes on dyes and organic liquids. As an example, the dye orange OT (1-*ortho*-tolylazo- $\beta$  naphthol) is considered insoluble in water, but on shaking in a 1 percent solution of cetyl pyridinium bromide for 24 hours, an appreciable quantity was taken into solution. A wide variety of materials of the class of soaps and surface-active agents are effective in promoting solubilization, but, because of the complexity of the system, a certain specific action is evident. Thus, polar organic compounds were found more readily solubilized than hydrocarbons.

This subject is of considerable interest and importance, since it is related to several manufacturing processes, the most active being the synthesis of elastomers such as GR-S. Harkins<sup>92</sup> has presented a general theory for emulsion polymerization with data on micelle formation and structure.<sup>93</sup>

The nature of the micelle has been the subject of numerous experimental studies. Colloidal electrolytes (McBain) or paraffin-chain salts (Hartley) form aggregates of individual molecules in solution. These micelles are composed of a variable number of molecular units, depend-

<sup>90</sup> The term hydrotropy was introduced by Professor Carl Neuberg in 1916. See R. H. McKee, *Ind. Eng. Chem.*, **38**, 382-84 (1946).

<sup>91</sup> J. W. McBain and M. E. L. McBain, *J. Am. Chem. Soc.*, **58**, 2610-2 (1936); J. W. McBain and R. C. Merrill, Jr., *Ind. Eng. Chem.*, **34**, 915-19 (1942); J. W. McBain and P. H. Richards, *ibid.*, **38**, 642-46 (1946); J. W. McBain, Chapter 4, pp. 99-142 in *Advances in Colloid Science*, Vol. 1, E. O. Kraemer, Editor, Interscience Publishers, Inc., New York, 1942.

<sup>92</sup> W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 1428-44 (1947).

<sup>93</sup> Cf. also M. L. Corrin and W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 679-83; 683-88 (1947); W. D. Harkins, R. W. Mattoon, and M. L. Corrin, *J. Colloid Sci.*, **1**, 105-26 (1946); W. D. Harkins, *J. Chem. Phys.*, **16**, 156-57 (1948).

ing on the concentration, the presence of ionizing salts, and the structure of the compound. Three types are believed to exist: (1) a lamellar or plate-like micelle, (2) a small, spherical micelle which is highly ionized, and (3) a cylindrical micelle. These types are, of course, models and the structures are inferred from x-ray diffraction data.

For an ordinary soap, sodium myristate, for example, the paraffin chains ( $C_{13}H_{27}$ ) are pictured as oriented against each other with the polar  $COO^-$  groups toward the water, thus forming a double layer of soap molecules. When hydrocarbons are introduced into the colloidal system, solution occurs in the spacing between the hydrocarbon radicals of the soap molecules. The separation of the layers is increased by the presence of the hydrocarbon.

Since solubilization is considered the result of the interaction of micellar structures and the "solute," the question of wetting is largely hypothetical. That many surface-active materials used as wetting agents form micelles is incidental; good solubilizing action is also obtained with substances that do not lower the surface tension of water appreciably (e.g., sodium lignin sulfonate).

The role of solubilization in pigment dispersion has received comparatively little attention, and it is possible merely to speculate on the possible relations. Because of dimensional factors, it is not likely that pigment particles will be carried into the micellar structure, although some organic pigments and carbon blacks are near the limit where this effect would be theoretically admissible. The high concentration of suspended material usually encountered in pigment dispersions is a more difficult problem to reconcile with current concepts of micellar structure. However, the picture of micelles as developed is highly idealized and could not be expected to account for all observed experimental facts. Harkins and co-workers<sup>94</sup> point out that there are four types of solubilization: (1) non-micellar or molecular solubility; (2) adsorption on outer surface of micelle; (3) penetration into the middle of the micelle; and (4) penetration into the micellar soap layers. Evidently the mechanism for solubilization can be quite complex, and, if we concede that the micelle could also serve as the locus for the attachment of particles of colloidal size, then many practical instances of stabilization could be explained. This idea departs, however, from the accepted view.

Solubilization effects are not limited to aqueous systems. McBain and collaborators<sup>95</sup> present qualitative data on solubilization in non-

<sup>94</sup> W. D. Harkins, R. W. Mattoon, and R. Mittelman, *J. Chem. Phys.*, **15**, 763-64 (1947).

<sup>95</sup> J. W. McBain, R. C. Merrill, Jr., and J. R. Vinograd, *J. Am. Chem. Soc.*, **62**, 2880-1 (1940).

aqueous solvents and infer that solubilizing effects are possible for all solvents, but they stipulate that a good solubilizer should be effective at concentrations of 1 percent or less. Resin solutions can act as solubilizers as shown by Palit.<sup>96</sup> Thus, ester gum, abietic acid, shellac, and an alkyd resin provide a strong solubilizing action for various water-soluble dyes in toluene solutions of the resins. Palit attributes the effect to an association of the resin molecules to dimers and polymers with the dye molecules. There is some evidence for micelle formation in non-aqueous media.<sup>97</sup>

### Differential Separation of Pigments in Mixtures

The most common example of pigment separation is observed in paints. Tints and colors formulated with two or more pigments frequently dry to a color different from that in bulk. This property, termed *flooding*, is the differential separation of pigments in a dispersed pigment mixture. In a paint film it usually results in a concentration of one of the pigments in the surface, thus altering the hue of the completely blended mixture of pigments. The term floating is sometimes used with the same meaning, but it may be more appropriately applied to separation of pigments in the bulk dispersion or to mottling in a surface film.

Although flooding is most likely to be encountered in paint films, it is by no means limited to this combination. On a two-roll mill, for example, striations in the sheet may be observed which persist throughout prolonged milling. Dispersions made on the three-roll mill frequently show streaks on the apron as the milled paste flows into a container. Mixing tints of colors with white ink on a slab by means of a spatula often shows striations, despite thorough mixing. Drawdowns used for estimates of tinting strength may give misleading results, for this reason, since the tinting colors flood to varying degrees. Comparable effects are observed in textile dyeing processes where dye mixtures level unevenly. The causes of flooding are to be ascribed to differences in the physical properties and the state of flocculation of the pigments comprising the mixture. Before proceeding to a more detailed examination of the mechanism of flooding, it will be helpful to describe pigment separation in a paint film.<sup>98</sup>

<sup>96</sup> S. R. Palit, *Nature*, **153**, 317 (1944).

<sup>97</sup> A. S. C. Lawrence, *Trans. Faraday Soc.*, **34**, 660 (1938).

<sup>98</sup> E. N. Harvey, Jr. and E. K. Fischer, *The Rheology of Surface Coatings*, Chapter IV, pp. 50-3, S. Hoagland, Editor, R-B-H Dispersions, Inc., Bound Brook, N. J., 1946.

During application of a layer of paint by brushing, the suspended pigments, vehicle, and solvents are thoroughly mixed. Immediately after application, however, solvent evaporation begins, and as the solvent finds its way from the body of the film toward the surface, preferred release or escape channels are set up. These channels sometimes form geometrical patterns in the surface. The streaming solvent and vehicle carry the suspended pigments: the fine pigment particles have the greatest surface and are transported most readily; coarser particles with smaller relative surface area move less readily. Consequently, the convection currents of the solvent and vehicle redistribute the pigment particles, carrying one in greater concentration to the surface.

The streaming effect may be likened to the transport of solids by a river. Boulders in the river bed are little affected by the stream of water, but, as the size diminishes from pebbles to sand, the particles are carried with greater ease until finally the finest particles, represented by clays, remain suspended in the flowing water.

Flooding is not limited to any specific pigment combination. It may occur with any group of pigments of different colors. Some pigments that are considered a single chemical entity, especially those prepared by blending different lots of dry colors, will exhibit flooding when dispersed, although here the magnitude of the effect is relatively small.

The control of flooding is important in maintaining product quality. Several studies of this subject have been reported, and a few patents have been issued on means for minimizing flooding. It is generally recognized that many variables need to be considered. Chief among these are particle size, specific gravity, viscosity of the suspending vehicle, and the extent of flocculation of the particles. More obscure are the specific effects of the vehicle, additives such as surface-active agents, and electrokinetic relationships. On the whole, however, the subject is confused, and frequent reference is made to "poor wetting" and imperfect dispersion as the primary causes. Ellis<sup>99</sup> recommends thorough grinding and the selection of compatible pigments with comparable dispersion qualities. Others have inferred that equalization of particle-size differences by protracted grinding would result in reduced flooding, but it may be seen that this is an uneconomical if not impossible procedure. The importance of the fine particles in flooding has been noted by Sloan,<sup>100</sup> who points out that flooding was observed with iron blue in the absence of other pigments. Evidently this pigment sample was inhomogeneous, and the finer particles differed in color from the larger.

<sup>99</sup> C. Ellis, *Printing Inks*, Reinhold Publishing Corp., New York, 1940, p. 420.

<sup>100</sup> C. K. Sloan, *Am. Ink Maker*, 15, No. 2, pp. 16-19 (February, 1937).

The electric charges carried by pigment particles cannot be directly connected with flooding. Reising<sup>101</sup> states that dispersions that contain particles with both positive and negative charges flocculate on dilution and do not flood. Mixed pigments with either charge do not flocculate, but the smaller particles flood. Other investigators have considered the possibility of attributing flooding to electric charges, but their experiments are not conclusive.

The viscosity of the dispersion medium, on the other hand, is an important factor in flooding. It is common practice in the printing ink industry to mix chrome yellow and iron blue for the pigmentation of green inks. Rarely is there any difficulty with flooding in this system. The reason is that the viscosities of the bodied oils used as vehicles are so high and the film thickness so small that differential migration of the particles is prevented. Newkirk and Horning<sup>102</sup> connected flooding with viscosity quantitatively. These investigators made a series of panels coated with an alkyd resin-chrome green finish reduced with differing quantities of thinner. The viscosities of the compositions represented a fairly wide range. Most of the changes in formulation which were found to affect the severity of flooding could be ascribed to consistency.

The effect of viscosity may be easily visualized. During evaporation of solvents from a film, at least initially, the vehicle brought to the surface has a relatively low viscosity. Separation of the particles of different sizes and specific gravities is accelerated, and flooding is aggravated. This action is comparable to the more rapid settling of particles in a liquid of low viscosity. Low viscosity also increases the opportunity for collisions between particles, and more rapid flocculation may result. If all these floccules are of one color, flooding will be severe. The effects of high viscosity are, as might be expected, the reverse of those just described, and, accordingly, a viscous medium inhibits pigment separation. In addition, the increased plastic viscosity resulting from a concentrated dispersion would result in lowered tendency toward flooding, since there are fewer open spaces between particles through which other finer particles could migrate.

When flocculation of the pigments is appreciable and the yield value is high in comparison with the plastic viscosity, the resulting film is apt to show marked flooding. In some specimens the pattern is large and can be more fittingly described as mottling. When one pigment is flocculated and the second pigment deflocculated, movement of the latter through the interstices of the structure is possible. If high yield value

<sup>101</sup> J. A. Reising, *Ind. Eng. Chem.*, **29**, 565 (1937).

<sup>102</sup> A. E. Newkirk and S. C. Horning, *Ind. Eng. Chem.*, **33**, 1402-7 (1941).

is accompanied by high plastic viscosity, flooding is less severe, for the high viscosity will prevent movement of the particles through the gel structure.

The relative movement of particles in a liquid is of importance in several industries, and theoretical as well as practical studies have been made. For convenience in discussion, the particles can be considered spheres and they can be grouped according to size in three categories. The first group may be designated as that of coarse particles, above 1 mm. In this class the Newton-Rittinger equation applies.<sup>103</sup> Since pigment particles are invariably smaller than 1 mm., this equation is of limited interest, and the well-known Stokes' law applies to particles in the second category, below 0.1 mm. or 100 microns. When particles are moving in a liquid under laminar flow conditions, the velocity is determined by the difference in the specific gravity of the particle and the suspending liquid and by the square of the radius.

The movement of suspended particles is not exactly described by Stokes' law, however. One discrepancy arises from the fact that pigment particles are not true spheres, for which the law was derived. This factor is of importance chiefly for needle-shaped particles. A second factor is hindered settling. The particles in a suspension affect each other by preventing free settling, and in a concentrated suspension the effect is very serious. Martin<sup>104</sup> found, for example, that free settling occurred only in concentrations of less than 3 percent in aqueous titanium dioxide suspensions. At this concentration the separation between any two particles in a uniform dispersion is approximately equal to three particle diameters. The effect of hindered settling is to cause an apparent increase in the calculated surface area (decrease in particle size). With increasing concentrations the effect increases until, at 15 percent titanium dioxide, the apparent surface increases by 20 percent.

With particles in the third or smallest category, settling may be completely obscured by Brownian motion. This motion, attributed to bombardment of the particle by molecules in the suspending liquid, results in a displacement of the particle which is dependent on the time of observation. In general, the average velocity  $v_t$  for a spherical particle from zero time to time  $t$  is dependent on  $(1/r)^{1/2}$ .

The effect of specific gravity may be compared for particles in the two categories. When Stokes' settling operates, only the difference in

<sup>103</sup> For a detailed analysis of the properties of particles in this size range, the reader is referred to A. M. Gaudin, *Principles of Mineral Dressing*, pp. 165-201, McGraw-Hill Book Co., New York, 1939.

<sup>104</sup> S. W. Martin, American Society for Testing Materials, "Symposium on New Methods for Particle-Size Determination in the Subsieve Range," pp. 66-89, Philadelphia, 1941.



specific gravity is important; when Brownian movement predominates there is no dependence on specific gravity.

Although attempts have been made to delimit separate regions of Stokes' settling and Brownian movement, such a distinction is arbitrary.<sup>105</sup> It is more reasonable to consider that, for large particles, the former applies, and, as the size range decreases, Brownian movement assumes more importance; with very small particles Stokes' settling does not occur.

Flooding effects of a film on a surface or floating and settling of the components of a dispersion are both manifestations of differences in the mobility of the separate pigment components. The relative importance of particle size and specific gravity may be made clearer by an example. In a pigment dispersion such as a gray paint, a white pigment (e.g., titanium dioxide) is tinted with a very fine black pigment (carbon black). Initial settling by gravity causes the white pigment to move downward in the container, leaving the upper part with an increased concentration of the black pigment. Black particles also migrate toward the top from the sediment of pigment which is formed. The black particles ordinarily are in the range in which Brownian motion is a primary factor in keeping them in suspension, but Brownian motion is only a minor factor in impeding the settling of the white pigment. This is a simple picture. Actual computation of the rate of settling is difficult because the practical conditions of settling do not accord with the basic assumptions of Stokes' law. In this example it was assumed, further, that both pigment components were in a completely deflocculated state.

If one or both of the pigments is flocculated, then settling occurs rapidly and a soft sediment forms. Floccule formation greatly increases settling rates at the same time that Brownian motion is reduced. In general it may be concluded that flocculated pigments will settle so rapidly that the effect of Brownian motion may be disregarded.

Flooding of the pigment mixture in a thin film on a surface can be explained in a similar way. Some of the possible cases are given in Table III. Suppose that the pigment particles were uniform and both components were of the same size and specific gravity: no flooding would result. This is an ideal condition, represented by Case I, and can never be realized in practice. A marked difference in specific gravity would lead to slight flooding (Case II). If both components are highly flocculated, differential movement of the pigment particles is inhibited by the structure within the system and flooding is also at the minimum.

<sup>105</sup> E. F. Burton in *Colloid Chemistry*, Vol. I, J. Alexander, Editor, The Chemical Catalog Co. (Reinhold Publishing Corp.), New York, 1926, pp. 165-67; E. E. Ayres, Jr., *ibid.*, pp. 855-60.

TABLE III. FLOODING OF PIGMENT MIXTURES

(Theoretical cases of two pigments in vehicle of low viscosity.)

Particle Size	Degree of Flocculation	Specific Gravity	Extent of Flooding
I Equal	Both deflocculated	Equal	None
II Equal	Both deflocculated	Different	Slight
III Immaterial	Both components highly flocculated	Immaterial	None
IV Equal	One flocculated	Equal	Mottling
V Equal	One flocculated	Different	Mottling
VI Different	Both deflocculated	Equal	High
VII Different	Both deflocculated	Different	High
VIII Different	One flocculated	Different	High: mottling

Where one of the components is flocculated and the other deflocculated, defects such as mottling can be observed (Cases IV, V). The severity of the defect depends on the ratio of the tinting to the base pigment. If, for example, the tinting pigment is present in small relative concentration, the effect of flooding or mottling will be more pronounced than if the pigment present in largest concentration is highly flocculated. All these cases are based on pigments of equivalent particle size. When a difference in particle size of the components is appreciable, flooding is inevitable (Cases VI-VIII). Many of the pigment mixtures commonly used have large differences in particle size and specific gravity; accordingly, flooding is to be expected, especially in low viscosity compositions such as enamels. Examples of these cases are abundant: perhaps the most common are tints composed of a white pigment and one or more colors and chrome greens made from chrome yellow and iron blue.

The practical control of flooding in commercial products continues to be the concern of manufacturers. Formulations should be made on the basis of pigments with minimum particle-size differences whenever possible. Attempts to grind a mixture to obtain equalization of particle sizes is uneconomical, and selection of suitable pigments is preferred. Venuto<sup>106</sup> states that carbon blacks, because of their small particle sizes, as a class contribute to flooding and floating and recommends instead the use of bone black, lampblack, or furnace black for gray tints. Venuto observes, further, that no general rule can be given and that each problem must be considered individually. Several attempts at empirical formulations designed to reduce flooding have been reported.<sup>107</sup> One

<sup>106</sup> L. J. Venuto, Chapter 21, pp. 504-37 (especially, p. 535) in *Protective and Decorative Coatings*, Vol. II, J. Mattiello, Editor, John Wiley & Sons, Inc., New York, 1942.

<sup>107</sup> Toronto Club, *Nat. Paint, Varnish Lacquer Assoc., Sci. Sect., Circ.* 546, pp. 239-45 (1937); Cleveland Club, *ibid.*, *Circ.* 523, pp. 379-82 (1936).

procedure is to test vehicles with respect to the flooding properties of a given pigment mixture: differences in wetting properties, as shown by the extent of flocculation, can be detected directly. Borger<sup>108</sup> claims the use of tricalcium phosphate and bismuth phosphate in amounts of 5 to 7 percent on the pigment. In addition there are claims made for special-purpose reagents by various manufacturers, but none of these has proved of general utility.

A method that practically eliminates flooding is the use of matrix pigments. The pigment mixture is treated with a bonding agent which cements the components into a mass. Gelatin, methyl cellulose, nitrocellulose, rubber, casein, gums arabic and tragacanth, cellulose, and cellulose xanthate were used in tests by the Cleveland Club.<sup>107</sup> The bonding material must be insoluble in the vehicle in order to prevent separation of the pigments. A convenient procedure is to treat a slurry of the mixed pigments with the bonding material, filter, dry, and pulverize. The process described by Widmer<sup>109</sup> utilizes insoluble urea-formaldehyde resins. Variations on this idea are apparent. The resulting matrix pigment, however, has a coarse texture, but it is suitable for products such as flat or semi-gloss finishes.

Other expedients may be used for the control of flooding. Increasing the viscosity of the vehicle is of real assistance. Reagents added to the dispersion are sometimes useful. Surface-active materials, for example, may be used to deflocculate the pigments in the dispersion: this is especially effective if one of the components is flocculated. On the other hand, certain oils or resins, water, or other reagents may cause flocculation of all the pigments in the mixture and thus prevent flooding by the formation of an internal structure.

### Distribution of Pigment in a Dried Paint Film

The distribution of pigment in a dried paint film has been examined by means of microtome sections by Conolly.<sup>110</sup> In most specimens the pigment was densely concentrated near the base, with a concentration gradient extending toward the surface. The region nearest the surface contained the finest particles, with larger particles and aggregates accumulated near the base. A rather remarkable observation was made that the pigment-concentration gradient is found whether the paint film dries on the upper or the lower surface of a panel, thus leading to the in-

<sup>108</sup> C. J. Borger, U. S. Patent 2,147,083 (May 4, 1936).

<sup>109</sup> G. Widmer, U. S. Patents 2,119,189 (May 31, 1938); 2,197,442 (April 16, 1940); G. Widmer and E. Pierce, U. S. Patent 2,093,651 (September 21, 1937).

<sup>110</sup> S. Conolly, *Paint Technol.*, **12**, 49-53 (1947).

ference that settling under gravity is not alone a sufficient explanation and that the flow set up within the film during evaporation of volatile components of the vehicle is an important factor in establishing the pigment-concentration gradient. Conolly questions the idea, generally held, that a clear layer of vehicle is essential for high surface gloss, for film sections of gloss paint were examined in which no clear surface layer was found. In mixtures of pigments (particularly extenders and toners), considerable separation of the components was noted.

The pigment-concentration gradient is of some consequence in accounting for the properties of paint films on metal surfaces during bending and thermal expansion. Presumably the portion of the film nearest the base, being highest in pigment content, would be less extensible than the surface. Thus, when the base is bent with the paint on the outside of the curve, the strain is distributed in a way conforming more nearly to the extensibility of the film. On thermal expansion of the base metal, the variation in extensibility through the film would probably result in greater strain than in a film with a uniform pigment distribution.

### Particle Flocculation and Opacity

The effect of flocculation on the opacity of pigment dispersions has received relatively little attention. It can be deduced that, if the pigment particles are separate and unassociated, the number of interfaces for light reflection and refraction within the film is greater than if the particles are flocculated. This result was observed experimentally by transmission measurements on films of controlled thickness.<sup>111</sup> A water-dispersible grade of titanium dioxide (anatase) was dispersed in a mineral oil in a ratio of 40 parts pigment to 60 oil. To a portion of this dispersion zinc naphthenate was added as a deflocculating agent; to a second portion, glycerine was added as a flocculating agent; to the third portion, retained as a control, an equivalent portion of the original vehicle was added in order to have all samples equal in pigment content. These compositions were then applied to glass plates in a series of known, graded film thicknesses. Light transmission measurements were made on a photoelectric photometer. The data shown in Table IV are for films of equal thickness. It will be noted that the addition of zinc naphthenate caused a marked deflocculation of the dispersion, as shown by a reduced yield value, and there was a corresponding increase in opacity. Glycerine, by flocculating the particles, caused a decrease in

<sup>111</sup> E. K. Fischer, pp. 54-7 in *The Rheology of Surface Coatings*, S. Hoagland, Editor, R-B-H Dispersions, Inc., Bound Brook, N. J., 1946. (Experiments with C. W. Jerome.)

TABLE IV. CHANGE IN LIGHT TRANSMISSION OF A FILM OF TITANIUM DIOXIDE DISPERSED IN MINERAL OIL AS RELATED TO YIELD VALUE

Yield Value (dynes/sq.cm.)	Relative Light Transmission	Reagent Added *
120	0.38	Zinc naphthenate
7,500	0.42	None—control
20,000	0.47	Glycerine

\* 3 percent by weight calculated on pigment content.

opacity. Lightbody and Dawson<sup>112</sup> found differences of 20 percent in hiding power of enamels formulated with different vehicles, a result attributable to the flocculating effects.

### Summary

A generalized summary of the properties discussed in this chapter is given in Table V.

TABLE V. GENERALIZED SUMMARY OF PHYSICAL PROPERTIES OF SOLID-LIQUID DISPERSIONS

Property	Deflocculated	Flocculated
Appearance, visual	Fluid	Paste
Rheological properties	Low or zero yield value	High yield value
Sedimentation volume	Low; equilibrium volume attained slowly	High; equilibrium volume attained rapidly
Heat of immersion	High	Low
Work of adhesion	High	Low

<sup>112</sup> A. Lightbody and D. H. Dawson, *Ind. Eng. Chem.*, **34**, 1452-5 (1942).

## 5. Rheological Properties of Dispersions

A knowledge of the flow properties of pigment dispersions supplies an insight into manufacturing and usage variables of unique value. The flow of substances is a matter of everyday observation, and our language contains many phrases and similes associated with the motion of fluids: "slow as molasses," "thin as water," "thick as cream" are examples. Such qualitative ratings are apt to obscure the true nature of flow, for as the analysis becomes more complete and quantitative we find several factors which need consideration.

Before proceeding to the details of the subject, it will be helpful to note the way in which data on flow properties can be utilized. The initial preparation of a pigment dispersion by grinding depends on shear transmitted through a viscous vehicle. The operation of some mills is efficient only when the flow properties of the mixture are adjusted to fall within a limited range. The utility of a product such as paint depends on the correct balance of ingredients to achieve acceptable brushing and leveling qualities. Apart from the practical aspects of product control, data on flow properties offer information on the colloidal structure of the pigment dispersion.

The study of flow is the province of rheology.<sup>1</sup> Numerous instruments and procedures have been devised to measure rheological properties, but many of these methods provide data that are grossly empirical and difficult to interpret. To a large extent investigators in different industries have designed measuring methods specifically adapted to the

<sup>1</sup> *Rheology* is defined as the science of the deformation and flow of matter. The term was originally proposed with this meaning in 1929 by E. C. Bingham and J. R. Crawford and has since been widely adopted. A prior use (1901) of *rheology* in the biological sciences apparently was unknown to Bingham and Crawford. Cf. E. K. Fischer, *J. Colloid Sci.*, **3**, 73-74 (1948).

task and product at hand. Fortunately, the increasing use of the rotational viscometer is bringing order to the subject and is supplementing the information gleaned from necessary special-purpose instruments.

This chapter is an examination of the basic concepts of rheology as applied to the technology of colloidal dispersions. An effort has been made to define terms without ambiguity, to present a system of measurement that has a certain physical validity, and to review available information on a variety of materials.

The literature on rheological measurements is extensive.<sup>2</sup>

### Concept and Measurement of Viscous Flow

The basic law of viscosity was deduced by Newton,<sup>3</sup> for it was he who considered the flow of a liquid over a solid bounding surface as characterized by a gradient of velocity: the fluid at the boundary was stationary, while adjacent "layers" or regions of the liquid increased in velocity as the distance from the stationary bounding surface became greater. Newton anticipated the cylindrical rotational viscometer, as the following quotation will attest:

*Corollary V:* . . . if the fluid and outward cylinder are at rest, and the inward cylinder revolve uniformly, there will be communicated a circular

<sup>2</sup> One book is now a classic in the field: E. C. Bingham, *Fluidity and Plasticity*, McGraw-Hill Book Co., New York, 1922. A standard reference is by G. Barr, *A Monograph of Viscometry*, Oxford University Press, London, 1931. Other volumes of value include E. Hatschek, *Viscosity of Liquids*, G. Bell & Sons, Ltd., London, 1928; W. Philippoff, *Viskosität der Kolloide*, Steinkopf, Dresden and Leipzig, 1942 (Reprinted by Edwards Bros., Inc., Ann Arbor, Mich., 1944); G. W. Scott Blair, *An Introduction to Industrial Rheology*, P. Blakiston's Sons & Co., Inc., Philadelphia, 1938; G. W. Scott Blair, *A Survey of General and Applied Rheology*, Pitman Publishing Corp., New York, 1944; and R. Houwink, *Elasticity, Plasticity, and Structure of Matter*, Cambridge University Press, 1940. The most recent monograph is by H. Green, *Industrial Rheology and Rheological Structures*, John Wiley & Sons, Inc., New York, 1949.

For general reviews and details of special-purpose instruments the reader is referred to the monographs cited above and to the following: H. A. Gardner and G. G. Sward, *Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors*, Eleventh edition, Henry A. Gardner Laboratory, Bethesda, Md., 1950; Chapter 17, pp. 299-331F.

<sup>3</sup> Those interested in pursuing the historical aspects of fluid flow will find the theorem in a readily available and authoritative translation of the classic *Principia* of Newton: F. Cajori, *Sir Isaac Newton's Mathematical Principles of Natural Philosophy and His System of the World*, University of California Press, Berkeley, 1947. The citation is to Book II, Section IX, Proposition 51, Theorem 39, pp. 385-87. The first edition of the *Principia* was published in 1687, and an extensive revision, including Book II on the resistance of fluids, appeared in 1713.

motion to the fluid, which will be propagated by degrees through the whole fluid. . . .

*Corollary VI:* And because the fluid endeavors to propagate its motion still farther, its impulse will carry the outmost cylinder also about with it, unless the cylinder be forcibly held back; and accelerate its motion till the periodic times of both cylinders become equal with each other. But if the outward cylinder be forcibly held fast, it will make an effort to retard the motion of the fluid; and unless the inward cylinder preserve that motion by means of some external force imposed thereon, it will make it cease by degrees.

Although the *Principia* was first published in the seventeenth century, it was not until the nineteenth century that physicists turned to the experimental measurement and definition of viscosity. Poiseuille, beginning about 1830, made a thorough study of the flow of liquids in capillaries. His interest was aroused by the faulty theories of the flow of blood which were then current.<sup>4</sup> Poiseuille related the rate of liquid flow to the dimensions of the tube, and the experimental data led directly to the laws of viscous flow. Other investigators, notably Hagen, confirmed the experimental results of Poiseuille, and later students supplied various correction factors, a theoretical analysis of flow, and the definition of the coefficient of viscosity.

Viscosity or internal friction in a liquid can be visualized by the model employed by Maxwell.<sup>5</sup> Suppose a liquid is confined between two planes, one fixed and the other movable, of area  $A$ , and separated by the distance  $x$ . A constant force  $F$  is then applied to the movable plane, and after acceleration it assumes a constant velocity  $v$ . The liquid between the planes is subjected to shearing. A measurement of viscosity can be made from the force applied, the velocity of the moving plane, and the area and separation of the two planes,

$$F = \eta A \frac{dv}{dx} \tag{1}$$

where  $\eta$  is the coefficient of viscosity, often simply termed viscosity.

<sup>4</sup> Poiseuille's original investigation was published in 1846 in the *Mémoires présentés par divers savants à l'Institut de France*, Vol. 9. This paper has been translated by W. H. Herschel and published under the title, "Experimental Investigations upon the Flow of Liquids in Tubes of Very Small Diameter by J. L. M. Poiseuille," *Rheol. Mem.* (Society of Rheology), 1940. Citations to other papers by Poiseuille are given in the notes in this volume and by Bingham in *Fluidity and Plasticity*, p. 406.

<sup>5</sup> J. C. Maxwell, article "Heat," *Encyclopaedia Britannica*, Ninth edition, Vol. XI, p. 578. Reprint editions of this reference vary considerably; the citation is to that of the R. S. Peale reprint, Chicago, 1890.



The equation may also be written for planes of unit area as

$$\tau = \eta \frac{dv}{dx} \quad (2)$$

where  $\tau$  is the shearing stress. The unit of viscosity, the *poise*, derives from this model and is defined as the shearing force in dynes per sq. cm. that will induce a unit rate of shear. An alternative definition is as follows: a substance has a viscosity of one poise when a shearing stress of one dyne per sq. cm. produces a velocity gradient of one cm. per sec. per cm.

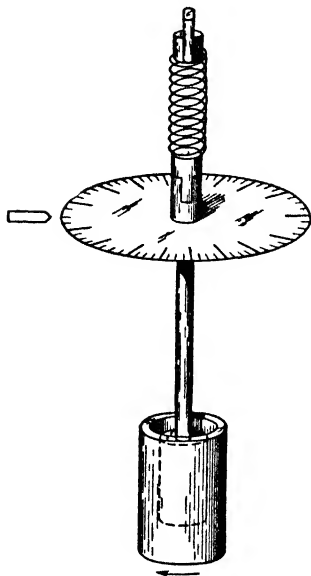


FIGURE 1. Diagram showing elements of rotating cup viscometer.

This picture of the property of viscous flow is capable of demonstration by the placing of one cylinder inside another cylinder with a small clearance of, let us say, 2 mm. When a liquid is placed in the annular space between the two cylinders and one of the cylinders is rotated, the force transmitted through the liquid exerts a traction on the other cylinder. The coaxial cylinder viscometer is, in effect, a practical adaptation of the model of the two planes mentioned above. It is possible to measure the viscosity of the liquid by either one of the following methods: (1) to rotate the outer cylinder and measure the traction on the inner cylinder by means of

a torsion wire or spring; (2) to rotate the inner cylinder by means of weights acting through a pulley system and determine the rate of rotation as a function of the weight. Both methods are utilized in commercial instruments. (Figures 1 and 2.)

### Types of flow

The classical model of a substance under shear between two planes or its experimental counterpart, the shearing of the material in the annular space between two coaxial cylinders, is of great assistance in visualizing the physical relationships involved. If the relative movement of the two surfaces can be varied, it is possible to obtain a curve showing rate of shear to shearing stress. This is a distinct advantage of the rotational viscometer, for it makes possible identification of different kinds of flow properties. The conventional method of plotting data so obtained is

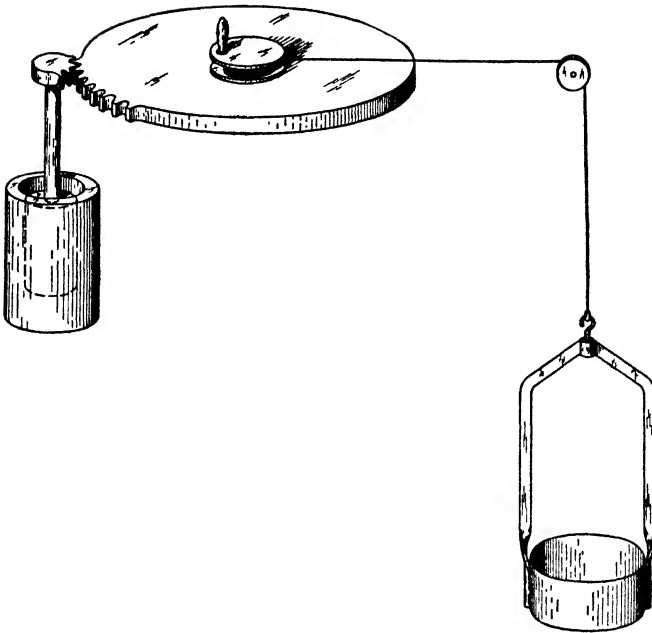


FIGURE 2. Diagram showing elements of the rotating bob viscometer.

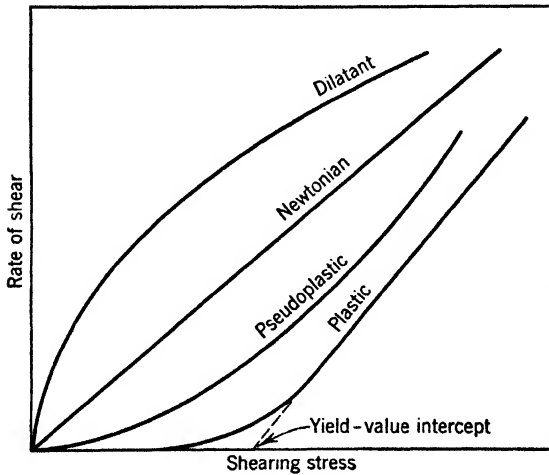


FIGURE 3. Generalized curves showing four different types of flow measured on rotational viscometers.

illustrated in Figure 3. Shearing stress is plotted on the abscissa, and rate of shear on the ordinate.

Characteristic differences in flow properties are readily detected by this method, and the several types of flow may be classified.<sup>6</sup> A *Newtonian liquid* flows when acted on by any force, however small. The rate of shear is directly proportional to the shearing stress as shown by the straight line extending to the origin in Figure 3. In everyday experience, gravity usually supplies the moving force. Most pure substances (water, glycerine, etc.), oils (except highly viscous oils at high rate of shear), and solutions of low-molecular-weight compounds exhibit Newtonian flow properties. Materials showing Newtonian flow are sometimes referred to as true liquids.

Many of the materials used in industry do not behave like true or Newtonian liquids. They exhibit more complicated flow properties which are often designated, by way of contrast to Newtonian flow, as anomalous. One very common type is *plastic flow*. Materials exhibiting this property do not flow until the applied shearing stress exceeds a certain minimum value. They act as if a barrier had to be surmounted before flow can occur. This minimum shearing stress is designated as the *yield value*<sup>7</sup> and is indicated by an intercept on the stress axis. In terms of a general equation,

$$F - f = UA \frac{dv}{dx} \quad (3)$$

where  $f$  is the yield value and  $U$  is the coefficient of plastic viscosity.

When the yield value has been exceeded, laminar or streamline flow takes place throughout the mass of the substance. At lower values, the material is not being sheared uniformly: this is the region of plug flow.

Plastic flow is frequently associated with an internal structure that is temporarily destroyed by stirring or shaking but reforms again on standing. This property is designated *thixotropy*. Originally this term was applied to a reversible isothermal, gel-sol-gel transformation: a thixotropic material was defined as a gel that seemingly liquefied on stirring but returned to the gel state at rest. When studied on a rotational viscometer (preferably of the rotating-cup type) this change in flow properties is termed thixotropic breakdown and is characterized by a

<sup>6</sup> The viewpoint of the author may be described as that of the "Bingham School" as developed by E. C. Bingham, H. Green, M. Reiner, and numerous other investigators.

<sup>7</sup> *Yield value* as a designation for the intercept has been adopted by many authorities, although some prefer alternative terms (which are not entirely equivalent in meaning) including the following: yield point, yield stress, yield torque, shear force, rigidity, static rigidity, and shearing resistance.

loop in the flow curve as shown in Figure 4. At any given rate of shear the shearing stress decreases until a steady state is reached in which further breakdown is balanced by re-formation of structural units. At higher rates of shear the balance is shifted in the direction of further breakdown. By taking a series of readings starting at low rates of shear and increasing to an arbitrarily fixed limit, and then continuing the measurement with a second series of readings at decreasing rates of

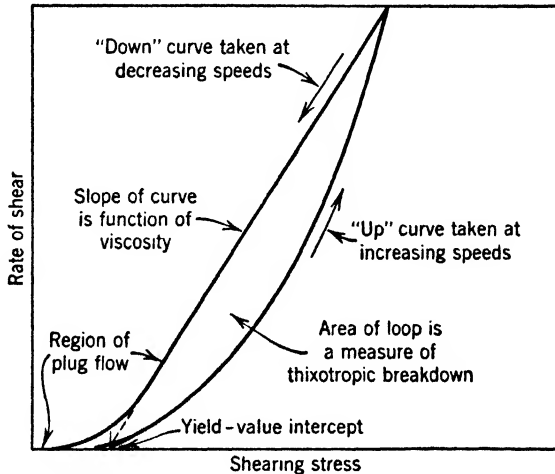


FIGURE 4. Generalized curve showing thixotropic flow measured on a rotational viscometer.

shear, a loop in the flow curve is obtained. One measure of thixotropic breakdown is the area of the loop between the two curves. The difficulty in defining thixotropy lies in the fact that the behavior is dependent not only on the properties of the material under study but also on the method and rate of measurement. Thus, if shearing is not continued until a balance has been established, the viscometer reading obtained will represent some intermediate state. If the re-formation of structural units is very rapid, thixotropic breakdown may be completely overlooked.

Another type of flow is designated *pseudoplastic*. A substance that exhibits this property flows more readily as it is stirred or sheared, but there is no reversible structural breakdown as found in thixotropic flow. The curve for this type of flow is convex to the shearing stress axis.

A fourth type is *dilatant flow*. A dilatant material shows increased resistance to flow as it is agitated or sheared, but when allowed to stand without disturbance it reverts to its original condition. In some re-

spects dilatancy is the reverse of pseudoplasticity; the curve illustrating this property is concave to the shearing stress axis.

Examples of the different types of flow that can be studied on a rotational viscometer follow.

#### *Newtonian Liquids*

Pure substances (e.g., glycerine, water, etc.)

Oils (except highly viscous oils at high rates of shear)

Many solutions, especially of low-molecular-weight compounds

#### *Plastic Materials*

Pigment dispersions, including paints, printing inks, textile printing pastes

#### *Pseudoplastic Materials*

Many high-polymer "solutions"

Cooked starch pastes

Emulsions

#### *Dilatant Materials*

Deflocculated pigment dispersions with high proportion of suspended solid

Starch slurries (uncooked) at 40–50 percent by weight of starch

### Definitions and units of measurement

It is in attempting to compute viscosities or related physical properties from experimental data that attention should be given to the type of flow observed. Units of measurement are collected in Table I, and

TABLE I. VISCOMETRIC UNITS

Property	Symbol	Unit	Dimensions
Viscosity (Newtonian)	$\eta$ or $\mu$ *	Poise	dyne-sec/cm <sup>2</sup> [ML <sup>-1</sup> T <sup>-1</sup> ]
Fluidity	$\phi$	Rhe	cm <sup>2</sup> /sec/dyne [M <sup>-1</sup> LT]
Plastic viscosity	$U$	Poise	dyne-sec/cm <sup>2</sup> [ML <sup>-1</sup> T <sup>-1</sup> ]
Mobility	$\mu$	Rhe	cm <sup>2</sup> /sec/dyne [M <sup>-1</sup> LT]
Yield value	$f$	.....	dynes/cm <sup>2</sup> [ML <sup>-1</sup> T <sup>-2</sup> ]
Thixotropic breakdown	$M$	.....	dyne-sec/cm <sup>2</sup> [ML <sup>-1</sup> T <sup>-1</sup> ]
Rate of shear	$S$	.....	reciprocal seconds [T <sup>-1</sup> ]
Shearing stress	$\tau$	.....	dynes/cm <sup>2</sup> [ML <sup>-1</sup> T <sup>-2</sup> ]

\* International Critical Tables and many authorities prefer  $\eta$ .

the connotations of some of the rheological terms that have been applied by different investigators are noted below.

The problems of precise definition are nowhere more perplexing than in rheological studies. Difficulties arise out of the necessity for a parlance for everyday usage, and, however unprecise such terminology may be, it nevertheless forces connotations into objective physical definition. Physicists have been reluctant to engage in psychophysical disputation,

and the result has been a confusion of subjective terminology with objective measurement. Perceptual, usually tactile, impressions acquire a kind of authority by universal use, and an attempt to analyze these subjective ratings in terms of objective physical measurements is a formidable task. In an effort to chart the physical properties of various products derived from pigment dispersions, the writer collected the ratings shown in Table II.<sup>8</sup>

Inspection of a solid-liquid dispersion leads to the characterizing phrases noted. It may appear, for example, "stringy" or "long" as molasses; or it may be fluid, perhaps as limpid as water. The composition, on the other hand, may be a stiff paste such as painter's putty, or a soft paste such as mayonnaise or whipped cream. These properties are apparent on stirring the dispersion; for some applications an impression of "tackiness" is obtained by tapping a film of the composition between the forefinger and a smooth surface. These visual and tactile impressions describe flow properties that are too complex to permit description by a single unit mathematical expression. There are other inferences often attached: it is fairly common practice to note that the solid dispersed in a freely flowing composition is "well wetted," whereas that in a non-fluid paste is "poorly wetted."

The author prefers to let the subject rest at this point. Scott Blair<sup>9</sup> has given the problem considerable thought. An attempt has been made by Smith<sup>10</sup> to define mathematically the following terms for textile fiber studies: strength, stiffness, toughness, resilience. The reader will find the problems of psychophysics interesting for speculation and experimentation.

Apart from the psychophysical aspect of rheological nomenclature, fairly standard usage has evolved for many of the terms we shall use repeatedly.<sup>11</sup>

<sup>8</sup> E. K. Fischer and D. M. Gans, Chapter 14, p. 309, in *Colloid Chemistry*, Vol. VI, J. Alexander, Editor, Reinhold Publishing Corp., New York, 1946.

<sup>9</sup> G. W. Scott Blair, *A Survey of General and Applied Rheology*, Part II, pp. 125 ff. A tribute is paid by Scott Blair to the workman who has acquired skill in rating a product entirely by perceptual means and whose perspicacious judgment establishes successful factory control. Cf. also *J. Colloid Sci.*, **2**, 21-32 (1947).

<sup>10</sup> H. DeW. Smith, *Textile Fibers: An Engineering Approach to Their Properties and Utilization*, Marburg lecture, 1944, American Society for Testing Materials, Philadelphia.

<sup>11</sup> Discussions of rheological terms and symbols will be found in the following references: British Rheologists' Club *Essays in Rheology*, Chapter IV, pp. 61-75, Pitman Publishing Corp., New York, 1947; *Rheol. Bull.*, **18**, 8-13 (1947); L. H. Cragg, *J. Colloid Sci.*, **1**, 261-69 (1946); J. M. Burgers and G. W. Scott Blair, "Report on the Principles of Rheological Nomenclature," *Proceedings of the International Congress on Rheology, Holland 1948*, North Holland Publishing Co., Amsterdam and Interscience Publishers, Inc., New York, 1949, Section V, pp. 1-72.

TABLE II. TERMS COMMONLY USED TO DESCRIBE FLOW PROPERTIES OR CONSISTENCY OF PIGMENT DISPERSIONS WITH APPROXIMATE RANGES IN ABSOLUTE UNITS

Descriptive Terms Frequently Used	Plastic Viscosity		Yield Value		Example
	Magnitude	Range (poises)	Magnitude	Range (dynes/sq.cm.)	
Watery; thin; soupy; highly fluid; non-tacky	Low	0.1-1.0	Low	0-10	Spraying lacquer; gravure ink
Creamy	Low	1-5	Medium	50-500	Paints; ketchup
Pasty; stiff; buttery; high-consistency; non-fluid; non-tacky; short	Low	0.1-5	High	500-5,000	Textile color pastes; stippable paints; shaving cream; mayonnaise
Fluid; low-tack	Medium	5-50	Low	0-1,000	Black news ink
Buttery; stiff; pasty; salve-like; short	Medium	5-50	High	1,000-10,000	Ointments
Long; molasses-like; tacky; highly viscous	High	100-1,000	Medium	100-10,000	Rotary press ink
Long; heavy-bodied; high consistency; tacky	High	100-1,000	Med. high	1,000-30,000	Job press; offset inks
Leathery; tough; rubbery; sticky	Very high	1,000-10,000,000	Very high	.....	Resin melts; rubber; asphalt

*Viscosity* is defined as the property of a material in flow that gives rise to retarding forces. The *coefficient of viscosity*  $\eta$  is the factor of proportionality between rate of shear and stress in Equation 1. Very frequently  $\eta$  is called the viscosity of the material measured. This dual use of the term sometimes leads to confusion, since *viscosity* as a property belongs to all materials capable of flowing, whereas *viscosity* with the meaning *coefficient of viscosity* should be applied only to Newtonian substances. This distinction should be kept in mind.

Because *viscosity*, as a measure, has a limited meaning, it should be qualified when used to designate other types of flow. When applied to plastic flow, it is now frequently called plastic viscosity with the intended meaning of *coefficient of plastic viscosity*,  $U$ . This quantity may be defined, by analogy with  $\eta$ , as the force in dynes per sq. cm., in excess of the yield value, tangentially applied, that will induce a unit viscosity gradient. Since  $U$  is parallel in physical significance to  $\eta$ , any unit of plastic viscosity would have the same dimensions; consequently, the poise is also used in designating plastic viscosity. Both Newtonian and plastic viscosity are computed from the reciprocal of the slope of the line in the flow curve.

For pseudoplastic and dilatant materials, however, this simple concept is not applicable. With these systems the ratio of stress to rate of shear changes continuously: in pseudoplastic materials the ratio decreases, and in dilatant materials the ratio increases with rate of shear. Consequently, the rate of shear must be specified if a value analogous to viscosity is to be computed from the data. Despite some ambiguity, the term *apparent viscosity* has long been used, and, by analogy with Newtonian viscosity, we may define the apparent viscosity  $\eta_a$ , at rate of shear  $S$ , as the reciprocal of the slope of the tangent to the curve rate of shear vs. shearing stress at  $S$ .

It is recognized that the term *apparent viscosity* has a variable meaning. Thus, in some industrial laboratories, a single value of rate of flow at a given shearing stress is determined, and it is then tacitly assumed that the flow curve is a straight line extending to the origin, giving in effect a hypothetical (but erroneous) curve for a Newtonian material. Such a curve, of course, does not coincide with an experimental curve obtained with a sequence of readings. This method of computation has, unfortunately, had wide use and leads to the definition that apparent viscosity is the quantity obtained by dividing the shearing stress by the rate of shear.<sup>12</sup> Although the dimensions are those of viscosity (dyne-

<sup>12</sup> E. K. Fischer, H. Green, and R. N. Weltmann, *Interchem. Rev.*, **2**, 9-15 (1943); H. Green and R. N. Weltmann, *Ind. Eng. Chem., Anal. Ed.*, **15**, 201-6 (1943); C. C. Winding, G. P. Bauman, and W. L. Kranich, *Chem. Eng. Progress*, **43**, 527-36 (1947).



sec. per sq. cm.), it is evident that values so computed may be far from a correct representation of the physical properties of the material. Apparent viscosity is defined in a different way by Williamson,<sup>13</sup> who assumes that the curve for a pseudoplastic material becomes a straight line at high rates of shear. The slope of this linear portion of the curve is taken as the apparent fluidity, and its reciprocal as the apparent viscosity. The qualification "apparent" is intended to indicate that the measured viscosity varies with rate of shear. Further, measurements made with different instruments which yield data incapable of analysis in rational units are given as apparent viscosities. When so used the term is considered permissible, provided, however, that it is not associated with the coefficient  $\eta$  in the Newton equation.

Throughout this discussion the term *apparent viscosity* is applied to the differential rate of change of stress with change in rate of shear,  $d\tau/ds$ , at any specified rate of shear. It is thus unambiguously defined.

It will be appropriate at this time to express a practical point of view regarding industrial instruments and measurements. Rheological measurements of all types are finding increasing utility in a variety of industries. Frequently it is necessary to devise an instrument for a specific purpose, but too often little attention is given to the principles upon which the measurement is made or the units in which the data are expressed. Completely empirical results obtained on special-purpose instruments are extremely valuable for control of processes and charting of day-to-day variation and, as such, are a great advance over individual judgment. When interpretation of the results in terms of physical properties is attempted, however, difficulties arise. Adoption of a standard empirical test by a standardizing authority offers the advantage that a uniform procedure is followed by all persons making the measurement, but such standardization is not a substitute for measurement of a physical property capable of exact definition. Moreover, in rheological measurements on pastes and suspensions, concealed systematic errors are inherent in the use of some well-established instruments.

A few examples of such difficulties will serve for illustration. One form of efflux viscometer is a cup with an orifice of standard size. The time of outflow, the basic datum, depends on the make and the size of the instrument, which must be specified if the measurements are to have permanent reference value. More serious objections can be raised: (1) the flow from the orifice is not laminar, and it is not possible to derive a valid mathematical relationship between time of flow and viscosity, although the instrument can be calibrated with liquids of known viscosity; (2) the driving force (stress), and hence the rate of shear, diminishes as

<sup>13</sup> R. V. Williamson, *Ind. Eng. Chem.*, **21**, 1108-11 (1929).

the material flows from the cup, a serious limitation for materials that exhibit anomalous flow properties; (3) the quantity of a thixotropic material remaining in the cup may be determined by the amount of agitation it received prior to testing. Despite these limitations the efflux viscometer in various forms is widely used in many industries.

The capillary viscometer is a basic reference instrument and is highly satisfactory for measuring viscosities of simple liquids and solutions. It is less reliable for suspensions or turbid liquids, for any obstruction in the capillary introduces unsuspected errors in the time of flow. Furthermore, it yields only a single figure for time, unless an arrangement is made to apply variable pressure and thus obtain a series of readings at different rates of flow. Even with this arrangement, new material is continually entering the capillary and the effects of extended shearing on the same volume of material cannot be observed. Similar limitations may be noted with the falling-sphere viscometer. Shearing is not uniform and cannot be estimated or controlled, and the effect of continuous shear on a given volume of material cannot be studied.

The advantages of the cylindrical rotational viscometer are so numerous that it deserves wider use for industrial measurements. It may be used on suspensions as well as on clear liquids, and it is suitable for determination of viscosities over a wide range at variable rates of shear. Different types of flow properties may be identified, and the data may be expressed in dimensionally consistent units. As it is commonly used, however, the data cannot be expressed in rational units, and, as a consequence, the literature is cluttered with meaningless measurements. The unsatisfactory state of instrumentation in this field is in part responsible, since commercially available instruments of moderate cost need modification before they can be used to best advantage.

### Rotational Viscometers

The practical cylindrical rotational viscometer is derived from the design of Couette,<sup>14</sup> in which the outer cylinder is rotated and the torque on the inner measured. The simple theory for the instrument was given some years earlier.<sup>15</sup> In general, it is immaterial whether the internal or external cylinder rotates, and both designs are in current use. The requirements for a practical viscometer of the rotating-cup type have been described by Weltmann.<sup>16</sup> This design is desirable because it al-

<sup>14</sup> M. Couette, *Ann. Chim.*, **21**, 433-510 (1890).

<sup>15</sup> See Barr, *A Monograph of Viscometry*, p. 223.

<sup>16</sup> R. N. Weltmann, *Interchem. Rev.*, **2**, 43-52 (1943); cf. also H. Green, U. S. Patent 2,365,339 (December 19, 1944).

lows rapid changes in the speed of the cup, but the constant-temperature bath complicates the construction. The rotating-bob instrument permits simple and precise means for controlling temperature, but operation is more cumbersome since speed changes are made by altering the weights on a pulley-gear system.<sup>17</sup> Viscometer instrumentation has been in an unsatisfactory state, but several manufacturers are bringing precision instruments to the market. The low-cost commercial instruments, Stormer (rotating bob) and MacMichael (rotating cup), need modification before they are satisfactory.<sup>18</sup>

### Modification of the Stormer viscometer

Relatively simple and inexpensive modification of the Stormer viscometer can be readily made.<sup>19</sup> The instrument is then suitable for Newtonian viscosities in the range of 0.4 to 150 poises. It is particularly useful for materials such as varnishes, paints, textile printing colors, and starch pastes. With very viscous materials, a rotating-cup instrument is preferable. The following changes were made. A constant-temperature water bath was constructed, the aluminum cup supplied with the instrument being used. The cup was wound with a layer of asbestos paper attached by means of a thin layer of sodium silicate solution. Twenty turns of No. 22 (B & S gauge) Nichrome resistance wire were then wound over the asbestos, and the winding was covered with several layers of the asbestos paper. This heater was connected to a fixed-point thermoregulator and relay through a voltage control. For stirring, a small motor with an impeller agitator was attached to the support for the cup. Although the water bath held a relatively small volume of water, the temperature control was satisfactory when the voltage control was set to give a uniform cycle of heating and cooling. With this arrangement temperature control was maintained within  $\pm 0.1^\circ \text{C}$ . at  $30^\circ \text{C}$ . Higher temperatures, to  $90^\circ \text{C}$ ., were obtained by changing to the appropriate thermoregulator and a higher setting on the voltage control. It was also found helpful to extend the pulley arm by 12 cm. Laboratory weights were used to vary the load, and a fine nylon thread was used to support the weights. An angle-iron support was constructed to raise the viscometer from the table and to provide a mount for the relay (Figure 5).

<sup>17</sup> Several designs of the rotating-bob instrument have been described. See G. F. C. Searle, *Proc. Cambridge Phil. Soc.*, **16**, 600-6 (1912); L. E. Gurney, *Phys. Rev.* (First Series), **26**, 98-120 (1908).

<sup>18</sup> These instruments are available from laboratory supply houses in the United States.

<sup>19</sup> E. K. Fischer and C. H. Lindsley, *Textile Research J.*, **18**, 325-37 (1948).

The cup and bob or paddle supplied by the manufacturer are unsuited to measurement of viscosity in rational units. Accordingly, they were replaced by several cylindrical cups and bobs, of various diameters, ac-

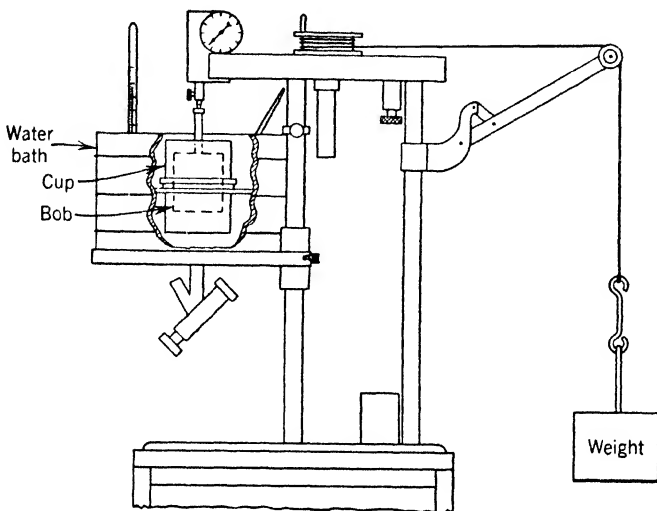


FIGURE 5. View of viscometer showing water bath, cup and bob in operating position, stand, and accessory equipment.

curately machined from brass (Figure 6). One bob was made of a laminated plastic for use at high temperatures in order to reduce heat conduction. With different combinations, different clearances and hence a

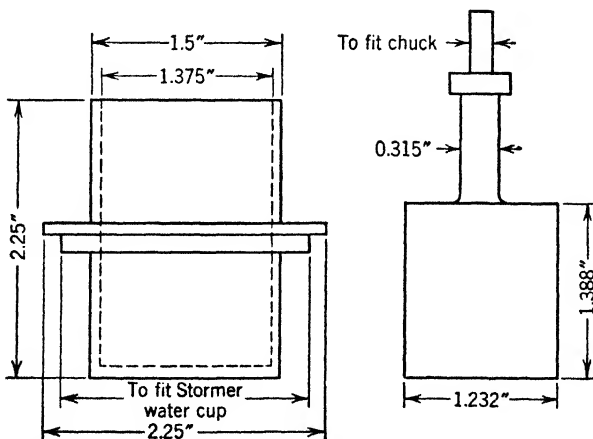


FIGURE 6. Machine drawing of modified cup and bob for Stormer viscometer. (Cup 1, bob 1, Table III.)

variety of rates of shear at a given r.p.m. were possible. Table III gives the dimensions; for the cups, inside dimensions are given.

TABLE III. DIMENSIONS OF CUPS AND BOBS

	Radius (cm.)	Height (cm.)
Cup 1	1.746	5.2
2	2.342	4.9
Bob 1	1.565	3.53
13 (plastic)	1.565	3.53
4	2.104	3.49

*Procedure for using viscometer.* The cup and bob selected for a particular test are carefully aligned in the viscometer, the cup being raised to about 1.3 cm. from the bottom of the bob. The cup is filled nearly to the top with the sample, and the bob is then rotated slowly for a few minutes to help bring the contents to the temperature of the bath. At least ten measurements of the time of rotation with different loads are taken, and the results are plotted as illustrated in the curves reproduced in succeeding sections of this chapter.

### Basic factors in operation

In any measurement of viscosity by means of a concentric-cylinder viscometer, the following factors must be considered: (1) the retarding torque produced by the liquid being sheared in the annular space between the two cylinders; (2) the contribution of end traction on the inner cylinder to the total traction (the end-effect); (3) the variation in rate of shear between cup and bob. These will be considered in turn.

*The retarding torque.* In rotational viscometers, equilibrium is established when the driving force is balanced by the retarding force arising in the material being sheared. At equilibrium, the rate of rotation is constant and the following relation holds:<sup>20</sup>

$$T = 4\pi r^2 \eta h \omega \quad (4)$$

where  $T$  is the applied torque,  $\eta$  the viscosity, and  $\omega$  the rate of rotation. The factors  $r^2$  and  $h$  are found from the dimensions of the cup and bob used:  $r^2 = (R_c^2 \times R_b^2)/(R_c^2 - R_b^2)$ , where  $R_c$  and  $R_b$  are the radii of the cup and bob;  $h$  is the height of the bob. The radii and height of the bob being known,  $T$  and  $\omega$  are found experimentally, and hence  $\eta$  may be calculated.

<sup>20</sup> H. Lamb, "Hydrodynamics," Sixth edition, Cambridge University Press, London, 1932, p. 587.

For materials that exhibit plastic-flow properties the equation given by Reiner and Riwlin<sup>21</sup> is now considered to account fairly well for the results obtained. This equation may be written in the following form:

$$U = \frac{T}{4\pi r^2 h \omega} - \frac{f}{\omega} \ln \frac{R_c}{R_b} \quad (5)$$

where  $U$  is the plastic viscosity (poises) and  $f$  is the yield value (dynes per sq. cm.); the other symbols have the same significance as above. When  $f$  is 0, Equation 5 reduces to Equation 4. The yield value may be expressed in terms of the intercept  $T_f$  on the torque axis of the linear portion of the flow curve, thus:

$$f = \frac{T_f}{4\pi r^2 h \ln R_c/R_b} \quad (6)$$

For Equation 4 it is immaterial whether the bob is driven and the cup remains stationary (as in the Stormer viscometer) or whether the cup is rotated (as in the MacMichael instruments). When the Stormer is used, it is convenient to replace  $T$  by  $Wgl$ , where  $W$  is the load (in grams),  $g$  the acceleration of gravity (980 cm./sec./sec.), and  $l$  the effective length of the lever arm on which the load acts (dependent on the gear ratio and diameter of the drum on which the cord is wound). Angular velocity  $\omega$  in radians per second is converted to r.p.m. by inclusion of the factor  $2\pi/60$ . After these substitutions, Equation 4 may be solved for  $\eta$ :

$$\eta = \frac{60gl}{8\pi^2} \times \frac{1}{r^2h} \times \frac{W}{\text{r.p.m.}} = K \times \frac{1}{r^2h} \times \frac{W}{\text{r.p.m.}} \quad (7)$$

For the rotating-cup viscometer, the torque is measured by the deflection  $\delta$  (in degrees) and the torsional constant  $c$  of the wire or spring attached to the bob ( $T = c \cdot \delta$ ), and Equation 4 becomes:

$$\eta = \frac{60c}{8\pi^2} \times \frac{1}{r^2h} \times \frac{\delta}{\text{r.p.m.}} = K' \times \frac{1}{r^2h} \times \frac{\delta}{\text{r.p.m.}} \quad (7a)$$

*The end-effect.* In the derivation of the preceding equations, it has been assumed that the cylinders were without ends, or rather, that the traction of the viscous liquid on the ends of the inner cylinder was negligible in comparison with the traction on the cylindrical surface. A detailed study of this end-effect showed that it is by no means negligible.<sup>22</sup>

<sup>21</sup> M. Reiner and R. Riwlin, *Kolloid-Z.*, **43**, 1-5 (1927); M. Reiner, *J. Rheology*, **1**, 5-10 (1929); H. Green, *Ind. Eng. Chem., Anal. Ed.*, **14**, 576-85 (1942), has examined this equation critically and found experimental evidence to support it.

<sup>22</sup> C. H. Lindsley and E. K. Fischer, *J. Applied Phys.*, **18**, 988-96 (1947).

Several ways of taking account of the effect have been tried, among which may be mentioned: (1) calibration of the instrument with standard liquids of known viscosity to obtain an empirical instrument constant to use instead of  $K/r^2h$  or  $K'/r^2h$  in Equation 7 or Equation 7a; (2) reduction in relative motion of the liquid above and below the bob by means of "guard rings" or other mechanical features; (3) use of a bob with a cylindrical surface much greater than the area of the ends; (4) experimental measurement of the end-effect so that it may be included in calculations of viscosity and yield value. In the paper cited, a brief review of the first three ways was given with references to their application. The fourth method was carefully investigated. The end-effect can be expressed in terms of increased length of bob. In Equation 7 or Equation 7a the actual length  $h$  is replaced by an effective length  $h^*$ , where  $h^* = h + h_0$ , and  $h_0$  is nearly the same for bobs of different diameters (from 2.5 to 4.2 cm.) for a given clearance between cup and bob; as the clearance increases,  $h_0$  also increases. For a given cup and bob, the end-effect was found to change only slightly in the range of 1 to 150 poises. The separation between the bottom of the bob and the cup is without effect as long as it is greater than about 1.3 cm.; the end-effect becomes larger as the bottom of the bob and the cup are brought closer together.

By use of one bob partially immersed to varying depths (single-bob method) or by use of two bobs of the same radius but of different length (multiple-bob method), it is possible to determine the viscosity of a liquid without actual evaluation of the end-effect. Let  $h_1$  and  $h_2$  be the length of the immersed portion of the single bob or the total length of each of the two bobs used in the second method; and let  $P_1$  and  $P_2$  be the corresponding values for the ratio  $W/\text{r.p.m.}$  or  $\delta/\text{r.p.m.}$  in Equation 7 or Equation 7a. Then it can be shown that:

$$\eta = \frac{K}{r^2} \times \frac{P_1 - P_2}{h_1 - h_2} \quad (8)$$

where  $K$  and  $r$  have the meaning previously given and can be calculated from known constants and dimensions of the instrument. When Newtonian liquids are being studied,  $P$  is constant at values of r.p.m. below turbulence, so that average values may be substituted in Equation 8.

In practice it has been found more convenient to determine a value for  $h_0$  for a given cup and bob combination and then to use  $h + h_0$  instead of  $h$  in Equation 7 or Equation 7a. Then  $\eta$  can be found from a single value of  $P$ . To find  $h_0$  one uses the same data as in Equation 8 to

determine  $\eta$ , along with that value of  $\eta$ , for it is clear that

$$h^* = h + h_0 = \frac{K}{r^2} \times \frac{P}{\eta}$$

Hence

$$h_0 = \frac{K}{r^2} \times \frac{P_1}{\eta} - h_1 = \frac{K}{r^2} \times \frac{P_2}{\eta} - h_2 \quad (9)$$

There is some loss in accuracy in using a single value for  $h_0$  over the whole viscosity range above 1 poise, but the greater convenience in measurement usually compensates for the loss, unless maximum accuracy is demanded. Below 1 poise, a separate value for  $h_0$  must be found for each 0.1-poise interval because of the marked variation in end-effect with viscosity in this range. This can be done by either of the methods already described or by calibration with samples of known viscosity.

*Rate of shear.* The rate of shear  $S$  (or the velocity gradient) in a rotational viscometer is determined by the rate of rotation, radius of the bob, and clearance between cup and bob. For any angular velocity  $\omega$ ,  $S$  is not uniform throughout the annular space but depends on the distance  $x$  from the axis of rotation:<sup>23</sup>

$$S = \frac{2R_c^2 \times R_b^2}{R_c^2 - R_b^2} \times \frac{\omega}{x^2} \quad (10)$$

The mean value  $\bar{S}$  of  $S$  throughout the annular space may be found as follows:

$$\bar{S} = \frac{\int_{R_b}^{R_c} S dx}{\int_{R_b}^{R_c} dx} = \frac{2R_c R_b}{R_c^2 - R_b^2} \times \omega = \frac{4\pi}{60} \cdot \frac{r^2}{R_c \times R_b} \times \text{r.p.m.} \quad (11)$$

For small clearances  $S$  may be taken as equal to  $\bar{S}$ , within the usual experimental error. Even for relatively large clearances when there is considerable variation in  $S$  throughout the liquid, it was found that the average value was close to  $\bar{S}$ . For non-Newtonian liquids, where different values for apparent viscosity are found at different rates of shear, the mean value of  $\eta_a$  is found experimentally to be approximately the same for large and small clearances, so that the effect of variable rate of shear apparently balances out. The portions of liquid under high shear with corresponding low apparent viscosity are counterbalanced

<sup>23</sup> E. K. Fischer and C. H. Lindsley, *J. Colloid Sci.*, **3**, 111-28 (1948); E. Hatschek, *Viscosity of Liquids*, G. Bell & Sons, London, 1928.



by other portions where the effects are reversed, and the over-all measurement gives a value in agreement with that found when the variation in  $S$  is negligible.

*Calculations.* For convenience in computation, working equations are set up in which the several dimensional constants are included.

Newtonian viscosity (poises):

$$\eta = \frac{K}{r^2 h^*} \times \frac{W}{\text{r.p.m.}} \quad (12)$$

$$= K_v \times P \quad (13)$$

Plastic viscosity (poises):

$$U = \frac{K}{r^2 h^*} \times \frac{W - W_f}{\text{r.p.m.}} \quad (14)$$

$$= K_v \times \frac{W - W_f}{\text{r.p.m.}} \quad (15)$$

Yield value (dynes per sq. cm.)

$$f = \frac{2\pi}{60} \times \frac{K}{r^2 h^*} \times \frac{1}{2.303 \log R_c/R_b} \times W_f \quad (16)$$

$$= K_f \times W_f \quad (17)$$

Rate of shear (reciprocal seconds):

$$\bar{S} = \frac{0.209r^2}{R_c \times R_b} \times \text{r.p.m.} \quad (18)$$

$$= K_s \times \text{r.p.m.} \quad (19)$$

In these equations  $K$  ( $= 60 gl/8\pi^2$ ) is a constant depending only on the effective lever arm of the viscometer (i.e., the radius of the drum plus that of the cord carrying the driving weight divided by the ratio of the large gear to the small gear). For most locations  $g$  may be taken as 980 cm./sec./sec. (For the other factors see pages 162-64).  $K$  is an instrument constant not involving the dimensions of the cup and bob, whereas  $K_v$ ,  $K_f$ , and  $K_s$  depend on the combination used. Values for these constants are given in Table IV. It is clear that  $K_v$  may be determined by calibration with standards of known viscosity. Such liquids may be obtained from the National Bureau of Standards to cover a wide range of viscosity. The ratio  $W/\text{r.p.m.}$  is found experimentally for one or more of these standards. Substitution of that value and

TABLE IV. WORKING CONSTANTS FOR DIFFERENT CUP AND BOB COMBINATIONS

	(K = 99.0)				
	$r^2$	$h_0$	$K_v$	$K_s$	$K_f$
Cup 1—Bob 1 or 13	12.46	0.58	1.93	0.95	1.85
Cup 2—Bob 1 or 13	4.43	1.00	4.94	0.25	1.28
Cup 2—Bob 4	22.95	0.82	1.00	0.97	0.98

the certified viscosity in Equation 13 permits immediate evaluation of  $K_v$ .

Similar working equations can be established for the rotating-cup instrument. (See Equations 7 and 7a.)

The experimentally determined values for r.p.m. at different loads ( $W$ ) are plotted. For Newtonian liquids a straight line may be drawn through these points and the origin (see Figure 7). The reciprocal of the slope of this line is determined, and this value  $P$  multiplied by  $K_v$  for the cup and bob used gives the viscosity  $\eta$  in poises (Equation 13). For plastic materials a similar plot is made. A straight line may be drawn through the points above the yield value of the material, intersecting the load axis at the point  $W_f$ . The reciprocal of the slope of this line is  $(W - W_f)/\text{r.p.m.}$  and is used in Equation 15 to calculate the plastic viscosity  $U$  in poises. The same intercept, multiplied by  $K_f$ , gives the yield value  $f$  in dynes per sq. cm. (Equation 17).

For pseudoplastic and dilatant compositions, a somewhat more complicated computation results.<sup>24</sup>

It is generally desirable to state the apparent viscosity for some particular rate of shear, say  $100 \text{ sec}^{-1}$ . Since only by coincidence will one of the experimental rates of shear correspond to this particular value, some method of interpolation is desired. The "tangent method" is the simplest. The r.p.m. corresponding to the given rate of shear is found from Equation 19. Then on the graph of r.p.m. vs. load, the tangent is drawn to the curve at that value for r.p.m. and its slope is found by direct measurement. The reciprocal of this slope multiplied by the appropriate  $K_v$  gives the value for  $\eta_a$  at the specified rate of shear.

In many instances an exponential equation is useful. Thus, for the rotating-bob instrument,

$$W = A(\text{r.p.m.})^n \quad (20)$$

<sup>24</sup> H. Green prefers a qualitative rating of consistency as judged from a comparison of flow curves. As an alternative, he suggests calculation of a Newtonian viscosity as near to the origin of the curve as possible. Neither of these methods is satisfactory. Cf. *Industrial Rheology and Rheological Structures*, pp. 208-12, and references in footnote 25.

and for the rotating-cup viscometer,

$$\delta = A(\text{r.p.m.})^n \quad (21)$$

Then

$$\eta_a = K_v \cdot n A (\text{r.p.m.})^{n-1} \quad (22)$$

$$= K_v \cdot n W / \text{r.p.m.} \quad (22a)$$

or

$$\eta_a = K'_v \cdot \eta \delta / \text{r.p.m.} \quad (23)$$

It is of interest that different types of flow are readily classified by the value of  $n$ . When  $n = 1$ , the material shows Newtonian flow properties,  $\eta$  being independent of rate of shear, as is seen from Equation 22. For  $n$  between 0 and 1, the material is pseudoplastic, and for  $n$  greater than 1 it is dilatant. An equation of the form of Equation 20 cannot be used to represent plastic materials, because the yield-value intercept prevents the curve r.p.m. vs.  $W$  from passing through the origin.

To determine  $n$ , it is convenient to plot the experimental data on log-log paper (see Figure 11); such a plot is equivalent to the equation:

$$\log W = \log A + n \log \text{r.p.m.} \quad (24)$$

Hence, if this type of equation is applicable, a straight line results; its slope can be found by direct measurement, and the reciprocal is equal to  $n$ . From the same plot, one reads off the value of  $W$  for the particular value of r.p.m. Substitution of these values of  $n$ ,  $W$ , and r.p.m. in Equation 22a gives  $\eta_a$ .<sup>25</sup>

### Application of the viscometer

The utility of the rotational viscometer is shown in a series of measurements on different substances. Experimental data on the standard oils which exhibited Newtonian flow are given in Figure 7. It will be noted that excellent alignment of the points is obtained and all the lines pass through the origin. Plastic flow is shown in a composition prepared by dispersing titanium dioxide in a bodied linseed oil (Figure 8). The pigment concentration was 15 percent. It will be noted that the data when plotted form a loop, indicating thixotropic structure, and that the

<sup>25</sup> The validity and utility of power equations, so-called, have been extensively debated: see the remarks of M. Reiner and Scott Blair in *The Principles of Rheological Measurement*, Thomas Nelson and Sons, Ltd., Edinburgh and New York, 1949, pp. 129-30, 206-8. Examples of different methods of computation for non-Newtonian materials will be found in the following references: C. M. Conrad, *Ind. Eng. Chem.*, **13**, 526-33 (1941); J. D. Ferry, *J. Am. Chem. Soc.*, **64**, 1330-36 (1942); W. J. Lyons, *J. Chem. Phys.*, **13**, 43-52 (1945); E. K. Fischer and C. H. Lindsley, *J. Colloid Sci.*, **3**, 111-28 (1948); J. G. Kriebel and J. C. Whitwell, *Textile Research J.*, **19**, 253-58 (1949).

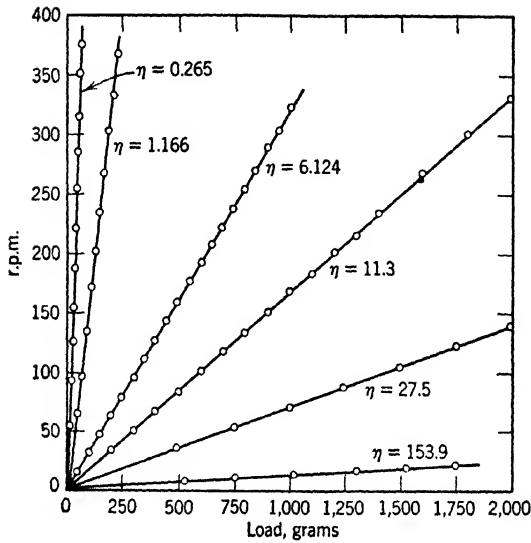


FIGURE 7. Experimental values for load and r.p.m. for oils showing Newtonian flow.

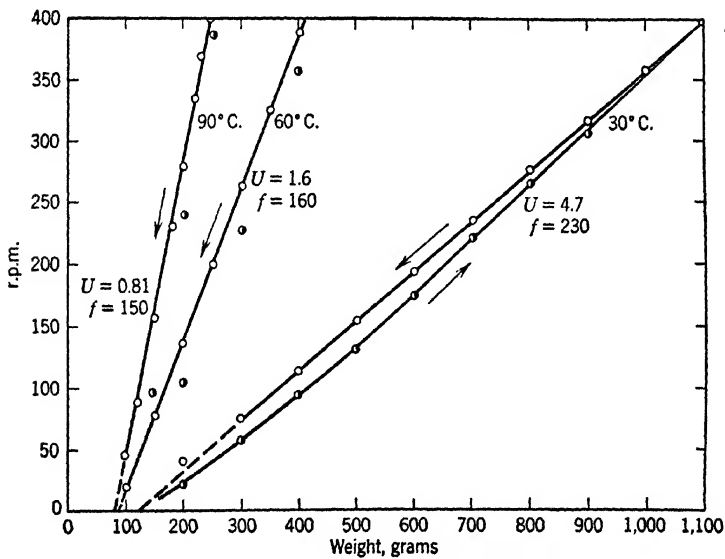


FIGURE 8. Plastic and thixotropic flow properties of a 15 percent by weight dispersion of titanium dioxide in linseed oil.

points taken at decreasing rates of shear fall on straight lines with a positive intercept on the weight (stress) axis. The computed plastic viscosities and yield values are shown on the graph for three temperatures.

Colloidal solutions of starch, methyl cellulose, alginates, gelatin, water-soluble gums, etc., exhibit pseudoplastic flow, as shown in Figure 9.

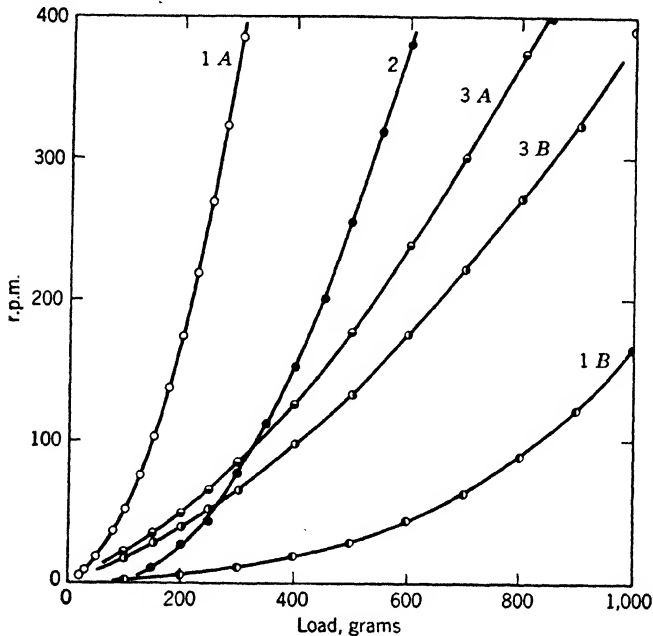


FIGURE 9. Experimental curves for materials showing pseudoplastic flow. (1A) Sodium alginate, 1% in water; (1B) at 2% concentration; (2) acid-modified corn-starch paste, 10% (dry basis); (3A) methyl cellulose solution, 4,000 cps. grade 1.95% (dry basis); (3B) 1,500 cps. grade 2.29% (dry basis). All solutions in water. Measurements at 30° C. except for starch pastes, which were at 90° C. Cup 1, bob 1.

For most of these colloidal materials the curves measured at both increasing and decreasing rates of shear are, within experimental error, identical. At the gel point, however, a structure is formed that, once broken down by shearing, does not re-form with the same initial physical properties. Since the criterion of thixotropy is a reversible, isothermal sol-gel transition, these materials should not be considered thixotropic. Examples of dilatant flow are shown in Figure 10. Dilatancy becomes evident at about 42 volume percent of starch and is extreme at 50 volume percent. Entirely similar properties are observed in aqueous suspensions of ungelatinized starch granules. The measurements on di-

latancy are difficult if the clearance between cup and bob is small, for the composition on shearing becomes granular (i.e., appears to form lumps) and pulls away from the surfaces. For this reason the measurements were made with cup 2, bob 1, with a clearance of 0.78 cm. It will be observed that the curves are regularly concave to the weight axis.

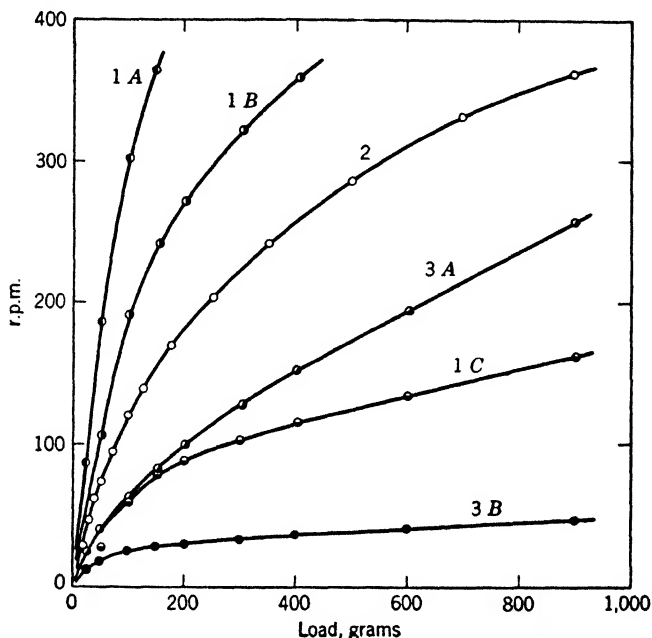


FIGURE 10. Experimental curves for materials showing dilatant flow. (1A) Iron oxide suspension, 11.3 vol.% in aqueous solution of sodium lignin sulfonate 10%; (1B) same, iron oxide, 11.7 vol.%; (1C) same, iron oxide, 12.4 vol.%; (2) barium sulfate, 39.2 vol.%, suspension in aqueous solution of sodium lignin sulfonate; (3A) starch suspension in ethylene glycol, 46.9 vol.%; (3B) same, 50.8 vol.%.  $T = 30^{\circ}\text{C}$ . Cup 2, bob 1.

Log-log plots of data obtained from Newtonian, pseudoplastic, and dilatant flow are shown in Figure 11.

The Stormer viscometer modified as described above has been shown to be capable of measurement of viscosity of Newtonian materials to an accuracy better than  $\pm 5$  percent, without dependence on viscosity standards, over a range from 1 to 150 poises. The use of two or more bobs of the same radius but different lengths yields the most accurate results. In practice, however, it is much easier to use a single bob and to apply the correction for the end-effect. Below 1 poise the correction for end-effect becomes increasingly large, as has been shown, and should be found

by calibration with a standard the viscosity of which is near that of the material to be measured. Alternatively the method of multiple bobs, without calibration, may be employed for low viscosities. A series of  $K_v$  values may be calculated for each 0.1 poise difference.

The computation of yield value from Equations 3 and 6 is subject to greater uncertainty than the calculation of viscosity. There are, more-

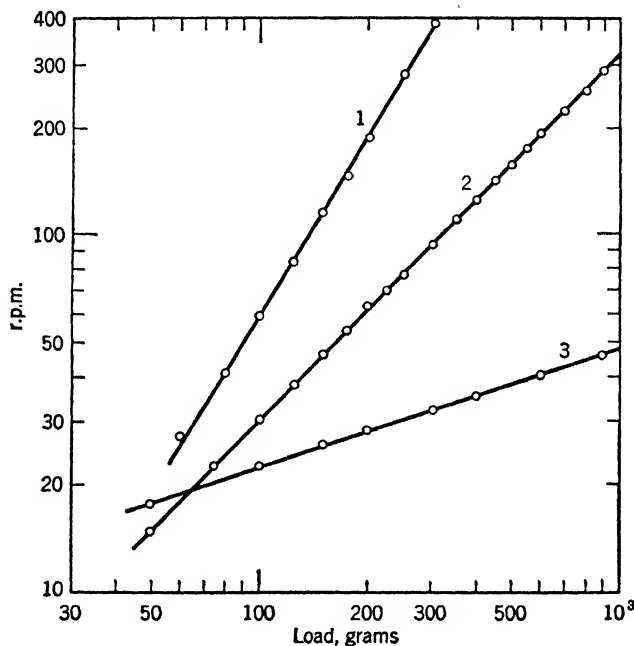


FIGURE 11. Log-log plots of data obtained with a pseudoplastic (curve 1), Newtonian (curve 2), and dilatant (curve 3) materials. (1) Sodium alginate sol, 1% concentration; (2) NBS standard oil; (3) starch suspension in ethylene glycol, 50.8 vol.%.  $T = 30^{\circ}\text{C}$ .

over, no materials established as reference standards. An accuracy of  $\pm 10$  percent may be expected in yield-value measurements on a rotational viscometer. This may seem an inordinately large error. When it is realized, however, that many instruments are quite incapable of distinguishing different types of flow properties, yielding information of only the crudest sort, then even this accuracy will be considered a distinct contribution.

The precision of the measurements will, of course, be within narrower limits if careful technique is followed and the necessary precautions are observed. It is estimated that viscosities of Newtonian liquids can be

easily duplicated within  $\pm 2$  percent and plastic viscosities, by means of a standardized technique, to  $\pm 5$  percent. Differences in magnitude in yield value of the order of 20 dynes per sq. cm. can be distinguished. These are conservative estimates for accuracy and precision.

In making measurements on Newtonian liquids, such as oils, it is sufficient to obtain 5 to 10 readings at different loads since these will be enough to establish and confirm the linearity of the curve. With plastic compositions (which are usually thixotropic as well) it is necessary to obtain more points for both increasing loads and decreasing loads. Either of two procedures may be followed: (1) taking a series of readings from the lowest to the largest weight and then following the same sequence of loads in reverse, back to the lowest weight; or (2) running the viscometer with the weight that gives the maximum rate of shear desired until a constant value of the time for 100 revolutions is observed; then decreasing the weight in convenient steps, as in procedure (1), and taking a reading at each load. In either case the maximum load or rate of shear must be selected; the basis for such selection lies in the purpose for which the measurements are being made. It is usually preferable to follow the former procedure and add the weights in a sequence to approach a selected maximum r.p.m. as closely as possible. The sequence of readings with smaller and smaller weights should be completed without interruption, whichever procedure is followed. If this precaution is not observed, thixotropic build-up (the reverse of structural break-down) will result and the points will not fall on a straight line.

With the rotating-cup instrument the selected r.p.m. can be obtained directly from the drive.

In the sections that follow, additional properties of plastic, thixotropic, pseudoplastic, and dilatant materials will be described. Practical aspects of commercial products will then be examined.

## Analysis of the Basic Types of Flow

### Plastic flow

The property of plastic flow has long been associated with the ceramic arts. The potter required a clay paste that could be shaped readily but one that would retain a given shape after the deforming stresses were removed. Like many other concepts, truly conceived in subjective terms, plasticity has been difficult for many to comprehend. It bridges the borderline between fluids and solids. The idea of a critical shearing stress before flow can occur in certain materials was noted by Maxwell,<sup>26</sup> who states: "If the form of the body is found to be permanently altered

<sup>26</sup> Quotation from E. C. Bingham, *Fluidity and Plasticity*, pp. 215-16.



when the stress exceeds a *certain* value, the body is said to be soft or plastic. . . .”

The idea of a limiting shearing stress below which flow does not occur in a plastic substance is one that has been greatly extended chiefly through the experimental investigations of Bingham, and it has proved of great utility in many industrial applications. Plasticity has been variously defined, but the following definition is generally acceptable: *plasticity* is that property of a material that allows it to be deformed continuously and without rupture during the action of a shearing stress which exceeds the minimum necessary to initiate flow and which allows the material to hold its shape for extended periods of time when the shearing stress is below that necessary to start flow.

The yield value (or yield stress) is the minimum stress that must be applied to a plastic material to start laminar flow.

At this point it will be necessary to consider another term, *consistency*, which continues to have wide use. Consistency (or consistence) in a very old definition means rigidity sufficient to retain its form; in a more modern definition, “consistency is that property of a material by which it resists permanent change of shape and is defined by the complete force-flow relation.”<sup>27</sup>

Neither *plasticity* nor *consistency* is capable of mathematical definition with appropriate physical units. It seems far better to consider them as terms essential for qualitative description and to depend on other phrases to characterize objective measurements.

In the preceding sections the method for computation of yield value was described; in this section certain other aspects of the measurement will be noted.

Houwink<sup>28</sup> considers the possibility for three yield values:  $f_B$ , the Bingham type, which is an extension of the straight-line portion of the stress vs. rate of shear curve;  $f_L$ , a lower value, which is fixed at the beginning of shear (although not necessarily laminar flow); and  $f_M$ , the maximum yield value which is established presumably by the beginning of laminar flow. (See Figure 12.) All three yield values are in use:  $f_L$  is sometimes considered a “practical yield value” and is usually derived from measurements that depend on a weight-actuated viscometer, such as the Stormer;  $f_M$  is infrequently used, unless it is incidental to some established measuring procedure. Extrapolation of the line to provide the Bingham yield value,  $f_B$ , can be justified mathematically.

There have been objections to the Bingham yield-value idea, and Hatschek<sup>29</sup> has been one of the more insistent in denying physical sig-

<sup>27</sup> E. C. Bingham, *J. Rheology*, **1**, 510 (1930).

<sup>28</sup> R. Houwink, *Elasticity, Plasticity, and the Structure of Matter*, pp. 9–15.

<sup>29</sup> E. Hatschek, *The Viscosity of Liquids*, pp. 209–10.

nificance to the extrapolated value. His criticisms, however, are not acceptable in the light of work in which numerous experimentally derived flow curves can be cited to justify, at least empirically, the calculation of  $f_B$ . Scott Blair<sup>30</sup> has noted measurements in which the concept of a yield value is difficult to reconcile with observation, but these are, for the most part, special instances concerned with very slow yield at stresses considerably below any computed yield value. An emended definition of yield value has been suggested by Scott Blair<sup>30</sup> as follows: the yield value is a critical shearing stress below which no flow can be observed under the conditions of experimentation.<sup>31</sup>

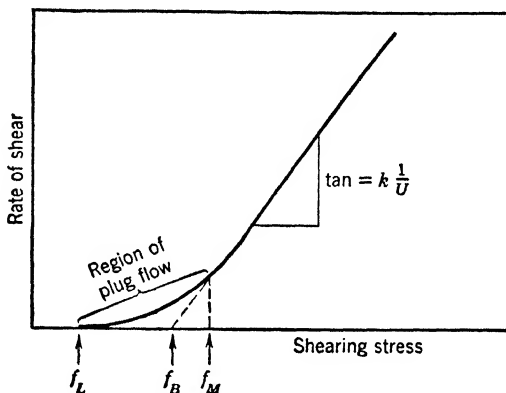


FIGURE 12. Different yield values according to Houwink.

The cause of plastic flow of suspensions was stated by Bingham<sup>32</sup> in clear terms, although numerous earlier workers had provided clues. A suspension showing plastic flow contains particles that touch each other, and the flow of the system requires, then, breaking of the contacts and movement of the particles with respect to each other. Bingham speaks of "arches" of the particles, distributing the stresses applied and contributing to the internal friction of the system. In the terminology adopted in this monograph, the particles form a reticulum or network of floccules which is broken during shearing. Re-formation and breaking of the structure occurs during shearing, and, if the rate of shear is held constant, the flocculates no longer change in effective average grouping and achieve a steady state. At another rate of shear, a different equi-

<sup>30</sup> G. W. Scott Blair, *J. Applied Phys.*, **4**, 113-18 (1933).

<sup>31</sup> For a further discussion of the evolution of the concept of yield value the reader is referred to the monographs cited earlier in this chapter and to the following: H. Green, *J. Colloid Sci.*, **2**, 93-98 (1947); *ibid.*, **3**, 129-33 (1948); *Ind. Eng. Chem.*, **14**, 576-85 (1942).

<sup>32</sup> E. C. Bingham, *Fluidity and Plasticity*, pp. 228-31.

librium between breakdown and re-formation of structure is attained, and the internal resistance of the system reaches a steady value. When measured on a rotational viscometer the curve obtained at increasing rates of shear is similar to that of a pseudoplastic material, but, after a steady state of breakdown is reached at some maximum rate of shear, the curve obtained at decreasing rates of shear is usually a straight line. This picture of the nature of plastic flow is entirely credible, especially since direct microscopic evidence for flocculation and correlation with measured flow characteristics has been presented. Plasticity is frequently associated with thixotropy, and in the next section the subject is examined at greater length.

The effect of a solid on the flow characteristics of a suspension is extremely complex. The following factors need consideration: (1) volume of the solid in relation to total volume of the suspension; (2) particle size of the solid; (3) shape of the solid particles; and (4) extent-of flocculation (as reflecting wetting relationships). In addition, the method of measuring the flow properties determines the kind of data and theoretical analysis that result. There is an extensive literature on the subject, competently summarized by Bredée and de Booy<sup>33</sup> to 1937, but numerous aspects of the flow of suspensions remain to be elucidated.

Equations established empirically to express the viscosity of liquid mixtures or the viscosity of colloidal sols have been adapted for suspensions. Among these are

$$\eta = \eta_0 e^{kc} \quad (25)$$

and

$$\eta = \eta_0(1 + AC)^k \quad (26)$$

where  $\eta$  is the viscosity of the suspension,  $\eta_0$  that of the suspending liquid,  $c$  or  $C$  the concentration of the suspended material, and  $k$  is a constant.<sup>34</sup> The Einstein equation represents the first attempt to obtain a theoretical expression. Originally presented in 1906, it is widely known, being discussed at length in most treatises on colloid chemistry; this equation, moreover, has been the starting point for most work on viscosity of suspensions. The equation is

$$\eta = \eta_0(1 + kV) \quad (27)$$

where  $V$  is the volume of particles in unit volume of the suspension, and the other symbols have the same meaning as in the previous equations.

<sup>33</sup> H. L. Bredée and J. de Booy, *Kolloid-Z.*, **79**, 31-49 (1937).

<sup>34</sup> Equation 25 has been attributed to S. Arrhenius, *Z. physik. Chem.*, **1**, 285-98 (1887). See also, M. J. DuClaux and E. Wollman, *Bull. Soc. chim. France* (Series 4), **27**, 414-20 (1920), for Equation 25 and F. Baker, *J. Chem. Soc.*, **103**, 1653-75 (1913), who applied Equation 26 to nitrocellulose sols.

Equation 27 represents, of course, limiting or simplified conditions; it holds only for low concentrations of the solid and assumes uniform, rigid, spherical particles in a deflocculated state. The constant  $k$  is usually given the numerical value 2.5, but it varies considerably even under conditions approximating those for which the equation was de-

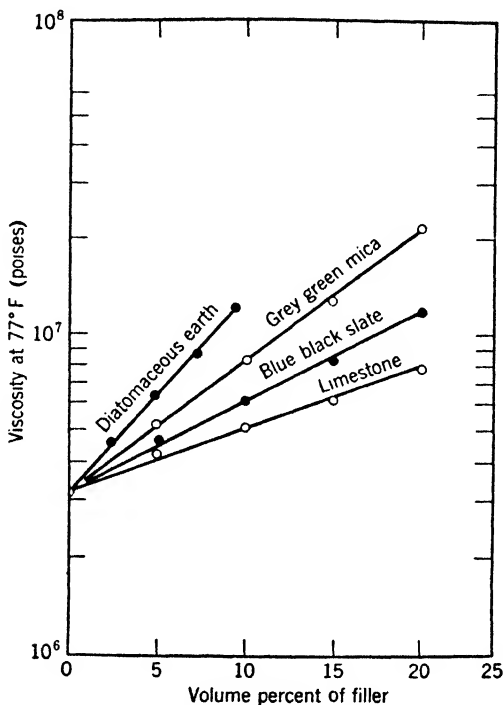


FIGURE 13. Viscosity-concentration curves for asphalt-mineral powder mixtures. (After Traxler, with permission.)

vised.<sup>35</sup> Equations that hold to higher concentrations have been derived.<sup>36</sup> Because of the complexities of shearing suspensions of non-spherical particles at high concentrations no equation that is applicable has been deduced. Some success has attended empirical evaluations, however. Traxler and co-workers,<sup>37</sup> after an extensive study of asphalt

<sup>35</sup> For experimental verification of Equation 27, see G. Broughton and C. S. Windbank, *Ind. Eng. Chem.*, **30**, 407-9 (1938); F. Eirich, M. Bunzl, and H. Margaretha, *Kolloid-Z.*, **74**, 276-85 (1936); and H. Freundlich, *Colloid and Capillary Chemistry*, H. S. Hatfield, translator, Methuen & Co., London, 1926, pp. 367-69.

<sup>36</sup> V. Vand, *J. Phys. & Colloid Chem.*, **52**, 277-321 (1948); J. V. Robinson, *ibid.*, **53**, 1042-56 (1949); R. Simha, *J. Research Nat. Bur. Standards*, **42**, 409-18 (1949).

<sup>37</sup> R. N. Traxler, H. E. Schwyer, and L. R. Moffatt, *Ind. Eng. Chem.*, **29**, 489-92 (1937).

dispersions of mineral powders, concluded that the viscosity  $U_m$  is related to the voids in the mixture, and they give the following equation:

$$U_m = \frac{K}{v} \quad (28)$$

where  $K$  is a constant characterizing a particular solid-liquid combination and  $v$  is the average void diameter of the powder present in the mixture. Data illustrating the application of this equation are given in Table V. The average void diameter  $v$  is established by particle size,

TABLE V. CALCULATION OF VISCOSITIES OF ASPHALT DISPERSIONS

Mineral Powder	Solid (vol. %)	Viscosity (poises $\times 10^{-6}$ )	Pore Diameter, Av. ( $\mu$ )	$K$ ( $\times 10^{-6}$ )
<i>California asphalt</i>				
Red slate	0	3.22	.....	....
	10	5.14	4.31	22.1
	20	7.85	2.78	21.8
	30	12.0	1.80	21.6
Trap rock	0	3.22	.....	....
	10	4.95	12.8	63.3
	20	7.69	8.27	63.6
	30	12.0	5.34	64.1
<i>Venezuelan asphalt</i>				
Limestone	0	3.18	.....	....
	5	4.05	16.5	66.8
	10	5.05	13.2	66.7
	20	7.88	8.55	67.4
Silica	0	3.18	.....	....
	10	5.25	9.91	52.0
	15	6.80	7.96	54.1
	19	8.36	6.40	53.5
	23.8	10.7	5.42	58.0

R. N. Traxler, H. E. Schweyer, and L. R. Moffatt, *Ind. Eng. Chem.*, **29**, 489-92 (1937).

shape, and uniformity of shape.<sup>38</sup> See also Figure 13. The viscosity of a mixture, from the analysis by Traxler, is established by the size and mass of the liquid films separating the solid particles. At high concentrations of solid, interaction of the dispersed particles alters the flow of liquid associated with the particles and Equation 28 is not valid.

<sup>38</sup> R. N. Traxler and L. A. Baum, *Physics*, **7**, 9 (1936); *Ind. Eng. Chem., Anal. Ed.*, **5**, 165-68 (1933); *Chem. & Met. Eng.*, **44**, 200-3 (April, 1937).

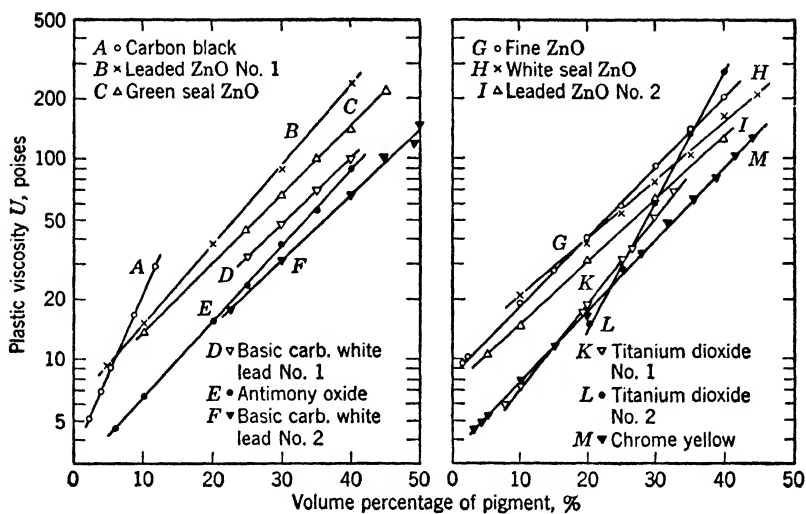


FIGURE 14. Effect of volume concentration of pigments on plastic viscosity as shown by plot of  $\log U$  vs. vol.%. (After Weltmann and Green, with permission.)

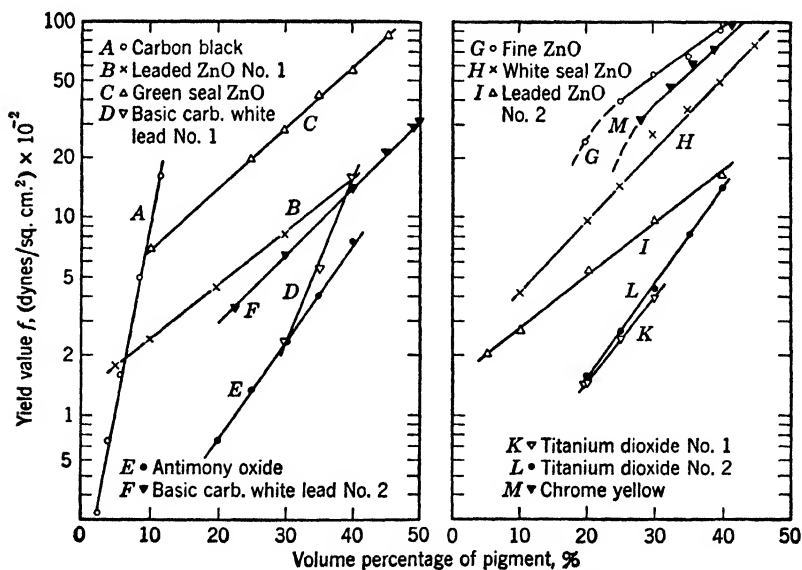


FIGURE 15. Effect of volume concentration of pigments on yield value as shown by plot of  $\log f$  vs. vol.%. (After Weltmann and Green, with permission.)

A more involved analysis utilizing four constants and accounting for plastic flow has been given by Weltmann and Green.<sup>39</sup> Their equation for plastic viscosity  $U$  is:

$$U = (\eta_0 + A)e^{Bc} \quad (29)$$

where  $c$  is the volume concentration of the dispersed solid (in percent) and  $A$  and  $B$  are constants characteristic of the material. The relation for yield value  $f$  is:

$$f = Mc^{Nc} \quad (30)$$

where  $M$  and  $N$  are constants. The constants  $A$ ,  $B$ ,  $M$ , and  $N$  are related to particle size, shape, and shape uniformity as well as to the method of measuring the flow properties. The constants are evaluated from plots of volume concentration vs. log of viscosity and log of yield value (see Figures 14 and 15). Data presented by Weltmann and Green for a variety of pigments are given in Table VI.

TABLE VI. THE MATERIAL CONSTANTS  $A$ ,  $B$ ,  $M$ ,  $N$ , OF EQUATIONS 29 AND 30 FOR THE VARIOUS PIGMENT SUSPENSIONS

Constant top rate of shear = 150 sec.<sup>-1</sup>

Constant temperature = 30° C.

Oil viscosity  $\eta_0$  = 3.9 poises

Pigment Suspended in a Linsced Oil	$A$	$B$	$M$	$N$
Carbon black	-0.6	0.186	12.5	0.434
Leaded zinc oxide, no. 1	+2.1	0.091	132	0.060
Green seal zinc oxide	+2.1	0.080	330	0.072
Basic carbonate white lead, no. 1	+0.9	0.077	0.86	0.188
Antimony oxide	-1.2	0.087	7.6	0.114
Basic carbonate white lead, no. 2	-0.7	0.075	60	0.080
Fine zinc oxide	+4.5	0.080	96	0.150
White seal zinc oxide	+6.6	0.066	180	0.083
Leaded zinc oxide, no. 2	+3.4	0.071	150	0.062
Titanium dioxide, no. 1	-1.2	0.103	20	0.101
Titanium dioxide, no. 2	-3.15	0.147	17.5	0.111
Chrome yellow	-0.5	0.082	400	0.074

R. N. Weltmann and H. Green, *J. Applied Phys.*, **14**, 569-76 (1943).

The correlation of particle size with the flow properties was studied by Weltmann and Green with a series of zinc oxide pigments in which a growth in particle size was accomplished by controlled heating (Figures 16, 17 and Table VII). It was found that the constant  $A$  was independent of particle size, whereas  $B$  and  $N$  were related to  $d_3$ , logarithmically.

<sup>39</sup> R. N. Weltmann and H. Green, *J. Applied Phys.*, **14**, 569-76 (1943).

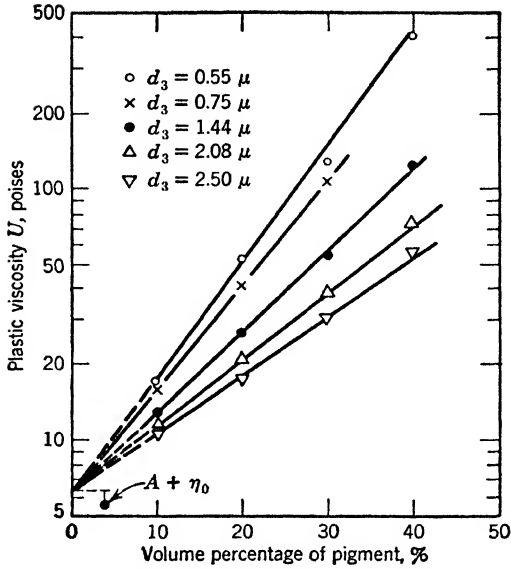


FIGURE 16. Effect of particle size of leaded zinc oxides on plastic viscosity of dispersions as shown by plot of  $\log U$  vs. vol.%. (After Weltmann and Green, with permission.)

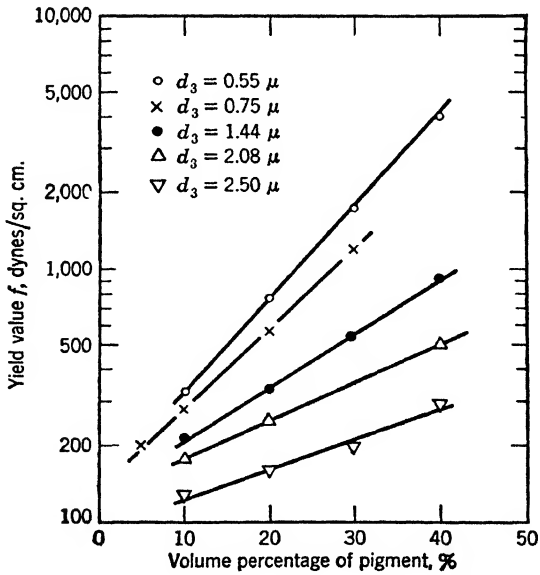


FIGURE 17. Effect of particle size of leaded zinc oxides on yield value as shown by plot of  $\log f$  vs. vol.%. (After Weltmann and Green, with permission.)



TABLE VII. RELATION OF PARTICLE SIZE ( $d_3$ ) OF ZINC OXIDE TO CONSTANTS IN THE EQUATIONS FOR PLASTIC VISCOSITY AND YIELD VALUE

Particle Diameter $d_3$ ( $\mu$ )	Constant			
	<i>A</i>	<i>B</i>	<i>M</i>	<i>N</i>
0.55	2.3	0.107	140	0.085
0.75	2.3	0.097	137	0.072
1.44	2.3	0.074	129	0.048
2.08	2.3	0.062	126	0.034
2.50	2.3	0.055	95	0.026

R. N. Weltmann and H. Green, *op. cit.*, Table VI.

Although an analysis of this type is empirical, it has several applications, particularly where the system under investigation is restricted in the variety of components.

In rubber technology, the measurement of modulus (stress at a given elongation) is analogous in some respects to the calculation of plastic viscosity of a pigment suspension. Cohan<sup>40</sup> has reviewed the status of this subject.

### Thixotropic flow

The property of certain suspensions of becoming fluid on agitation and of setting to a gel when undisturbed has been noted briefly in previous sections. Evidently this behavior had been observed at times by various investigators of colloidal structure, but in 1927, when Paterfi coined the term thixotropy, attention was focused on the phenomenon and many examples were described shortly thereafter. One of the first to be extensively examined was an aqueous suspension of basic iron hydroxides and chlorides. This material readily became fluid on agitation, reverting again to a gel at rest. Numerous other colloidal systems show thixotropic flow; among these are clay pastes and, especially, bentonite suspensions in water, many pigments in aqueous or oily vehicles, and possibly protoplasm itself.

In its general colloidal meaning, thixotropy refers to an isothermal, reversible gel-sol-gel transformation.<sup>41</sup> Freundlich<sup>42</sup> points out that the

<sup>40</sup> L. H. Cohan, *India Rubber World*, **117**, No. 3, 343-48, 354 (December, 1947); Institution of Rubber Industry, paper presented at Rubber Technology Conference, London, June 23-25, 1948.

<sup>41</sup> The thixotropic transition is accompanied by heat effects, but the magnitude is so small that it can be considered an isothermal process. Cf. H. G. F. Winkler, *Kolloid-Z.*, **105**, 29-38 (1943).

<sup>42</sup> H. Freundlich, *Thixotropy*, Hermann & Cie, Paris, 1935. This brochure contains a brief discussion of early work on thixotropy.

transformation from a true gel to a true liquid is a limiting case, and that thixotropic behavior of varying degree may be observed with suspensions that cover an extreme range in consistency. This observation is of importance, for it means that the broadened connotation of the term remains valid. The difficulty in defining thixotropy lies in the fact that the behavior of a suspension is dependent not only on the properties inherent in the material under observation but also on the method and rate of measurement. A more general definition of thixotropy in rheological terms is as follows: the property of a body by virtue of which the ratio of shearing stress to rate of deformation is temporarily reduced by previous deformation.

Since 1930 a large amount of experimental work has been published and a few hypotheses have been advanced to explain the phenomenon. There is considerable disagreement among investigators on suitable methods of measurement, and the classification of thixotropic systems suffers from lack of adequate definition. If we adopt the general criterion of an isothermal reversible gel-sol-gel transition, then various methods of observation can be brought into accord. Any suspension that exhibits a "thinning" when stirred and "thickening" when allowed to stand meets the definition. Indeed, one of the early tests for thixotropy was to shake a test tube of the suspension vigorously and to note the time required for it to set to a point at which it no longer would flow from the inverted test tube.

These simple test procedures (and the rheological properties associated with this general terminology) have suggested various instrumental means for measurement. In all, however, the change in rate of flow or resistance to flow is related to time.

A classification of the methods for measuring thixotropy has been given by Green and Weltmann<sup>43</sup> as follows: (1) single-point measurements; (2) deflection-time curves; (3) single consistency curves; and (4) double consistency curves. These categories need brief amplification.

The first method depends on a measurement of the time required for a suspension to form a gel after agitation which converts it to a fluid consistency. As noted above, this is the kind of observation that originally led to the concept of thixotropy and served as the basis for many early studies.<sup>44</sup>

<sup>43</sup> H. Green and R. N. Weltmann, Chapter 15, pp. 328-47, "Thixotropy" in *Colloid Chemistry*, Vol. 6, J. Alexander, Editor, Reinhold Publishing Corp., New York, 1946.

<sup>44</sup> H. Freundlich and L. L. Bircumshaw, *Kolloid-Z.*, **40**, 19-22 (1926); H. Freundlich and W. Rawitzer, *ibid.*, **41**, 102-3 (1927); H. Freundlich, *ibid.*, **45**, 348-55 (1928), **46**, 289-99 (1929); H. Freundlich and W. Kross, *ibid.*, **52**, 37-46 (1930).

The second group of methods represents a refinement in technique: a cylinder, fork, or paddle is attached to a torque-measuring system, and the time required for an initial deflection to decrease is recorded. Variations on this procedure are numerous.<sup>45</sup>

Another group of instruments depends on a measure of the change in force or torque (depending on the design) required to stir or agitate a thixotropic material at different speeds. It is thus possible to obtain a curve corresponding to a rate of shear-shearing stress diagram. One design, for example, is arranged to pull a ball through a trough of the suspension at different speeds.<sup>46</sup>

Rotational viscometers have been used by several investigators, notably Goodeve and Whitfield,<sup>47</sup> to obtain essentially single consistency curves. Whether or not the methods used by Goodeve *et al.* represent a valid measure of thixotropic flow is controversial.<sup>48</sup> A somewhat different procedure is used by Mooney<sup>49</sup> in which a rotational viscometer is equipped with a ring by means of which the suspension may be agitated and the change in flow properties can be measured. Measurements of thixotropic flow characteristics have been made also on capillary<sup>50</sup> and falling ball viscometers,<sup>51</sup> but these instruments have nothing to commend them for this purpose.

When thixotropic materials are studied in a viscometer, preferably of the rotating-cup type, the change in flow properties is most conveniently described as thixotropic breakdown. At a given rate of shear the shearing stress decreases until a steady state is reached in which further breakdown is balanced by re-formation of structural units within the suspension. At higher rates of shear, the balance is shifted in the direc-

<sup>45</sup> See for example: J. Pryce-Jones, *J. Oil & Colour Chemists' Assoc.*, **17**, 305-75 (1934); D. L. Gamble, *Ind. Eng. Chem.*, **28**, 1204-10; R. N. J. Saal and J. W. A. Labout, *J. Phys. Chem.*, **44**, 149-65 (1940); T. Alfrey and C. W. Rodewald, *J. Colloid Sci.*, **4**, 283-98 (1949).

<sup>46</sup> H. L. Röder, *Rheology of Suspensions*, H. C. Paris, Amsterdam, 1939; H. Freundlich and H. L. Röder, *Trans. Faraday Soc.*, **34**, 308-16 (1938); R. W. Kewish, and D. F. Wilcock, *Ind. Eng. Chem.*, **31**, 76-83 (1939); R. W. Kewish, *Ind. Eng. Chem., Anal. Ed.*, **13**, 195 (1941); R. K. Schofield and G. W. Scott Blair, *Trans. Faraday Soc.*, **27**, 629-32 (and insert facing p. 632) (1931).

<sup>47</sup> C. F. Goodeve and G. W. Whitfield, *Trans. Faraday Soc.*, **34**, 511-20 (1938); C. F. Goodeve, *J. Sci. Instruments*, **16**, 19 (1939); J. E. Arnold and C. F. Goodeve, *J. Phys. Chem.*, **44**, 652-70 (1940); G. W. Whitfield, *Am. Ink Maker*, **17** (No. 5), pp. 27, 29, 45 (May, 1939).

<sup>48</sup> Note the comments of Green and Weltmann<sup>43</sup> and G. W. Scott Blair in *A Survey of General and Applied Rheology*, pp. 57-58.

<sup>49</sup> M. Mooney, *J. Colloid Sci.*, **1**, 195-208 (1946).

<sup>50</sup> A. DeWaele, *J. Rheology*, **2**, 141-62 (1931).

<sup>51</sup> G. W. Scott Blair, *J. Phys. Chem.*, **39**, 213-19 (1935).

tion of further breakdown. By taking a series of readings, starting at low rates of shear and increasing to an arbitrarily fixed limit, and then continuing the measurement with a second series of readings at decreasing rates of shear, a loop in the flow curve is obtained (Figure 4). This is the method of the double consistency loop. Pryce-Jones<sup>52</sup> was the first to recognize the meaning of the curve.

Several implications of this method for measurement of thixotropic breakdown need consideration. It is apparent that a substance that requires a very long time to recover a gel state after shearing will give a curve which is indisputably of this form, and, if the area of the loop is large, the substance may be described as highly thixotropic. At the other extreme there may be a substance that has an extremely short period for recovery; such a material would exhibit no separation between the two curves, and, if the instrument used for the measurement is the arbiter of thixotropy, the suspension could be considered as non-thixotropic. Suppose, however, that the entire measurement were to be performed in an extremely short time interval, then the suspension (previously designated as non-thixotropic) may not have sufficient time to recover, and the curve obtained would exhibit a loop. Accordingly it would be described as thixotropic. The point of these comments is to show the relative nature of the terminology, and the dependence on methods of observation and measurement. With regard to classification of thixotropic materials, some confusion results from variable criteria used by different investigators. We find, for example, that colloidal preparations such as starch pastes, gelatin sols, high-polymer solutions, and emulsions are sometimes described as thixotropic. Many of these conform, however, to the flow characteristics of pseudoplastic materials.

The empirical measurement of thixotropic flow is, at present, most effectively accomplished by the Pryce-Jones method which has been extensively studied by Green and Weltmann.<sup>53</sup> Their system of measurement has been elaborated with great thoroughness. Green and Weltmann define thixotropic properties entirely in terms of the loop in the flow curve obtained with a rotational viscometer. Coincidence of the upcurve and downcurve is taken to indicate purely plastic flow without thixotropic effects. For their system of measurement this view may avoid confusion in meaning, although, as noted above, it has certain elements of arbitrariness that remove it from the concept entertained

<sup>52</sup> J. Pryce-Jones, *J. Oil & Colour Chemists' Assoc.*, **19**, 295-337 (1936); *J. Sci. Instruments*, **18**, 39-48 (1941).

<sup>53</sup> H. Green and R. N. Weltmann, *Ind. Eng. Chem., Anal. Ed.*, **15**, 201-6 (1943); *ibid.*, **18**, 167-72 (1946); R. N. Weltmann, *J. Applied Phys.*, **14**, 343-50 (1943); H. Green and R. N. Weltmann, *ibid.*, **15**, 414-20 (1944).

more generally by colloid chemists. The important principle of the method is that thixotropic flow cannot be measured from a single curve taken at either increasing or decreasing rates of shear, but a double curve, which provides information on the rheological change to the material during shearing, can define the thixotropic breakdown characteristic of the suspension.

It is evident that the measurement of thixotropy requires an instrument capable of controlled variation of rates of shear. In the rotational

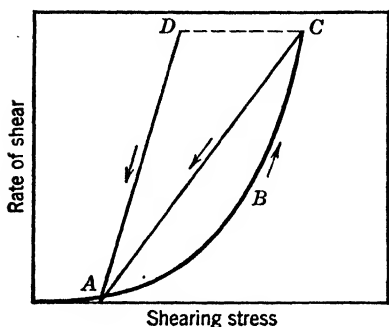


FIGURE 18. Generalized curves of the type obtained on a rotational viscometer with thixotropic suspensions. The curve represented by *ABCA* is representative of the "hysteresis loop," and the curve *ABCD* the "equilibrium" method.

viscometer, altering the r.p.m. of the cup or bob in a systematic manner, starting with low speeds and continuing to the maximum (or top) r.p.m., produces the curve *ABC* of Figure 18. If the measurement is continued by taking readings at decreasing speeds, the curve *CA* is usually obtained. This is one procedure. If the material is sheared at a constant rate of shear, the shearing stress observed with most materials will decrease along the line *CD* to an equilibrium value at *D*. Continued shearing at a constant r.p.m. will then produce no further breakdown of the thixotropic structure, and, if the readings are then taken at decreasing

rates of shear, the line *DA* is obtained. Figure 19 shows an actual measurement of pigment dispersions with a rotating-cup viscometer, using the "equilibrium method" just described. If different top speeds are taken for the measurement, separate curves, as shown in Figure 20, are obtained. These experimentally determined curves indicate some of the difficulties in making measurements of thixotropic breakdown. The area of the loop is influenced by the time taken in recording the upcurve. The slope of the downcurve is determined by the top rate of shear selected for the measurement. The calculation of plastic viscosity from the slope of the downcurve is thus dependent on the conditions for the experiment, with the exception of the equilibrium method (Curve *ABCD*A, Figure 18), where the influence of the time factor in this measurement is reduced.

For many purposes in industrial work a qualitative comparison of flow curves of different materials is sufficient. Visual comparison of measurements made under comparable conditions is possible merely by super-

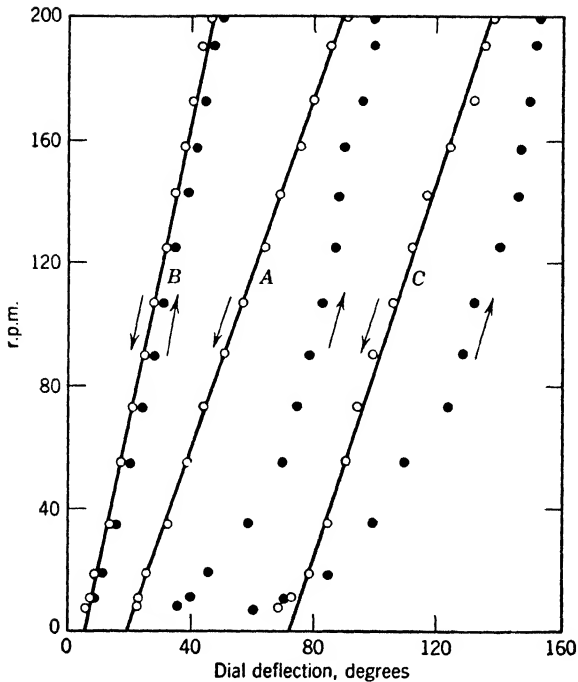


FIGURE 19. Viscometer curves for thixotropic suspensions of ultramarine blue dispersed in mineral oil as measured on a rotating-cup instrument. (A) No reagent, control; (B) plus Aerosol OT added as deflocculating agent; (C) Aresket as deflocculating agent. Open circles, readings at decreasing rates of shear; closed circles, readings at increasing rates of shear. Torque conversion,  $1^\circ = 96.2$  dyne-cm.  $T = 30^\circ \text{C}$ .

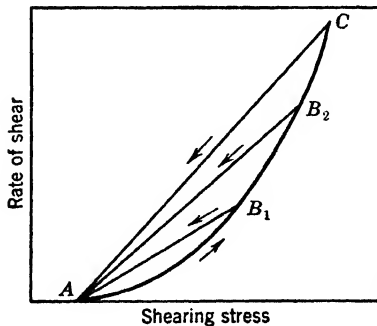


FIGURE 20. Generalized curves obtained on a rotational viscometer with thixotropic suspensions measured to differing maximum rates of shear (points  $B_1$ ,  $B_2$ , etc.).

imposing flow curves as drawn on coordinate paper. The actual computation of the coefficient of thixotropic breakdown,  $M$ , however, can be made by the methods described by Green and Weltmann,<sup>53</sup> in which the area of the loop is measured. It has been shown, however, that  $M$  may be calculated more simply from the relationship between the plastic viscosity and corresponding rate of shear obtained from two separate measurements made at different top speeds on the same material. The coefficient of thixotropic breakdown,  $M$ , then is given by the equation

$$M = \frac{2(U_1 - U_2)}{\ln (\omega_2/\omega_1)^2} \quad (31)$$

The coefficient  $M$  is the loss in shearing force per unit area per unit increase in rate of shear for the time selected in determining the curve. It is expressed in dyne-seconds per sq. cm. Other quantities have the following significance:  $U_1$  and  $U_2$  are the plastic viscosities measured at the lower and higher r.p.m., respectively (e.g., at  $B_1$  and  $C$ , Figure 20), and  $\omega_2$  and  $\omega_1$  are the corresponding angular velocities.

Certain complicating factors in the measurement have been considered by Green and Weltmann, and the reader is referred to the original papers of these authors for further details. The time interval for the measurement is of primary importance, but it cannot be controlled with precision unless an automatic recording mechanism is employed.<sup>54</sup>

Relatively few data have been published on the magnitude of the thixotropic breakdown for pigment dispersions, and quantitative correlation with application in various processes awaits additional research. Some indication of the practical role of thixotropy will be given later in this chapter, but at this point it is of interest to note a few experimental observations that reveal additional properties associated with thixotropy. Many investigators consider loose packing of the dispersed particles a primary requirement for thixotropy. This is the view expressed by Freundlich. It appears to be an essential condition only for simple observing means; thus there is evidence of the equivalent of a thixotropic structure in closely packed suspensions that exhibit dilatancy.

Particles of various shapes produce thixotropic suspensions, but generally particles of anisometric shapes lead to more pronounced thixotropy, provided that a minimum size (which varies with the solid and the suspending medium) is exceeded.<sup>55</sup> Needle and disc-shaped particles produce more noticeable thixotropic effects than spherical particles.<sup>56</sup> Mixtures of powdered solids are sometimes thixotropic, whereas the

<sup>54</sup> R. N. Weltmann, *J. Applied Phys.*, **16**, 184-91 (1945).

<sup>55</sup> H. G. F. Winkler, *Kolloid Beihefte*, **48**, 341-76 (1938).

<sup>56</sup> W. vonEngelhardt, *Kolloid-Z.*, **102**, 217-32 (1943).

suspension of a single solid component is not. Introduction of finely divided alumina into a suspension of quartz particles produced thixotropic gelation.<sup>57</sup> The effect of water in altering the flow properties of certain pigment suspensions in oily vehicles has been noted in Chapter 4. The reverse of this case is also of interest: the addition of lecithin to a non-thixotropic quartz-water suspension changed it to a plastic and thixotropic material.<sup>58</sup> Suspensions that have been found to give no loop in the flow curve are quartz in mineral oil and carbon black and certain varieties of organic colors (especially toluidine toner) in glycerine.

Any theory of thixotropic flow must account for the diversity of materials that in suspension exhibit this property. Although much of the experimentation has been with aqueous systems, thixotropy is observed just as frequently in a variety of solvents and oils.

At this point it should be noted that thixotropic buildup or gelation in some suspensions is accelerated by gentle stirring or agitation. This property has been termed *rheoperxy* by Freundlich and Juliusburger.<sup>59</sup>

The mechanism responsible for thixotropy has been the subject of considerable theorizing. One explanation is based on the idea of a lyosphere or shell of bound solvent with a thickness of perhaps 100 molecular diameters. During shear, this lyosphere is supposed to be deformed or detached from the colloidal particle, and the resulting effect is "liquefaction." As an explanation for thixotropy, this idea has been criticized by a number of investigators.

A more credible explanation for which some evidence is available depends on a structure within the colloidal system. The particles associate, through the action of long-range forces or the presence of some agent, to form a flocculated structure. This has been called a "scaffolding" process, resulting in a "house-of-cards" structure. Evidence has already been presented for the existence of such structures. During shear the links connecting separate particles are broken, and the time required for the re-formation of the structure is the essential feature of thixotropy. Goodeve,<sup>60</sup> in an important article, considers the rupture of these links and the transmission of a series of impulses from one moving layer to an adjacent layer in the suspension the only mechanism by which thixotropic flow can be adequately explained.

In an effort to explain certain features of the curve obtained with a thixotropic suspension, Green postulates two flocculating structures in a

<sup>57</sup> J. L. Russell and E. K. Rideal, *Proc. Roy. Soc. (London)*, **A154**, 540-60 (1936).

<sup>58</sup> H. Freundlich, *J. Soc. Chem. Ind.*, **53**, 223T (1934).

<sup>59</sup> H. Freundlich and F. Juliusburger, *Trans. Faraday Soc.*, **31**, 920-1 (1935). Cf. also E. A. Hauser and C. E. Reed, *J. Phys. Chem.*, **41**, 911-34 (1937).

<sup>60</sup> C. F. Goodeve, *Trans. Faraday Soc.*, **35**, 342-58 (1939).



pigment suspension: one is composed of primary particles that adhere immediately on contact; the other, a purely hypothetical structure, is formed from a micellar component (pictured as thin, needle-shaped particles) that requires a relatively longer time to associate. If a suspension exhibits purely plastic flow, without any evidence of thixotropy, it could be explained on the basis of the flocculated pigment particles breaking contact during shear and re-forming new contacts at the same rate. Time effects would then be of no consequence. On the other hand, the elongated colloidal particles would adhere only if certain parts came together, resulting in a time-consuming orientation to achieve the formation of a structure.

That plasticity and thixotropy are different aspects of the same phenomenon and that both arise from internal structure is certainly a credible view. If the time for flocculation of the particles of a dispersed substance is appreciable, then the flow curve exhibits a large loop; but if the time is progressively shorter, then the area of the loop decreases in proportion. It hardly seems necessary to postulate two separate mechanisms. Apparently McMillen<sup>61</sup> was the first to present this interpretation of rheological data on pigment dispersions.

### Pseudoplastic flow

Many colloidal sols exhibit a characteristic type of flow in which the rate of flow increases at a greater rate than the shearing stress. The viscosity thus appears to decrease as the rate of shearing becomes greater. This property is connected with the presence of swollen granules, solvation, and aggregation. Many industrial products exhibit this kind of flow, and suitable measuring procedures are consequently of importance.

Ostwald<sup>62</sup> described numerous colloidal systems in which the dispersed material is solvated to an extent that leads to marked swelling. Particles thus increased in size were considered to interact with each other and to form some kind of internal structure; the term *structural viscosity* was adopted as descriptive of these materials. The curves published by Ostwald and his co-workers show continuous curvature up to a region where a straight line results; at higher rates of shear, turbulence sets in and the curve falls off. It is doubtful, however, that the curve shape given by Ostwald and co-workers is entirely general for this class of materials. The data are frequently plotted on log-log coordinates: thus log rate-of-shear vs. log stress results in a straight line for the region below turbulent flow. (See Figures 9, 21, and 22.)

According to the precedent set by Ostwald and many others, colloidal sols are described as showing structural viscosity, and the use of this

<sup>61</sup> E. L. McMillen, *J. Rheology*, **3**, 179-95 (1932).

<sup>62</sup> Wo. Ostwald, *Kolloid-Z.*, **36**, 99-117; 157-67; 248-59 (1925).

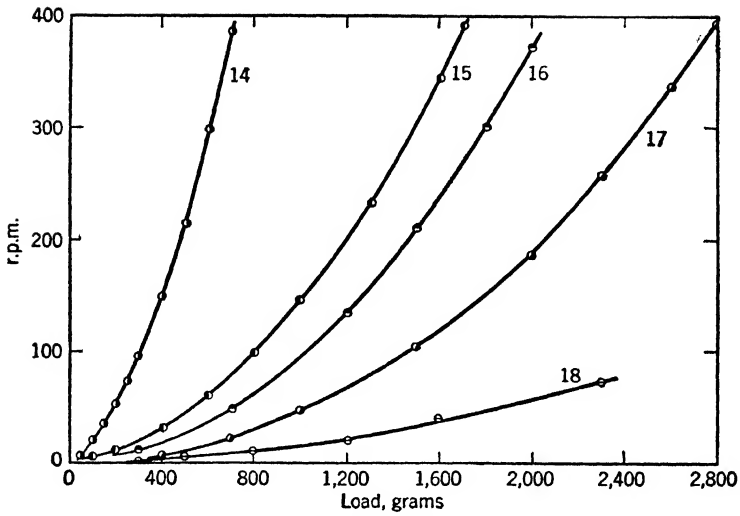


FIGURE 21. Pseudoplastic flow of a series of methyl cellulose sols. ( $T = 30^{\circ}\text{C}.$ )

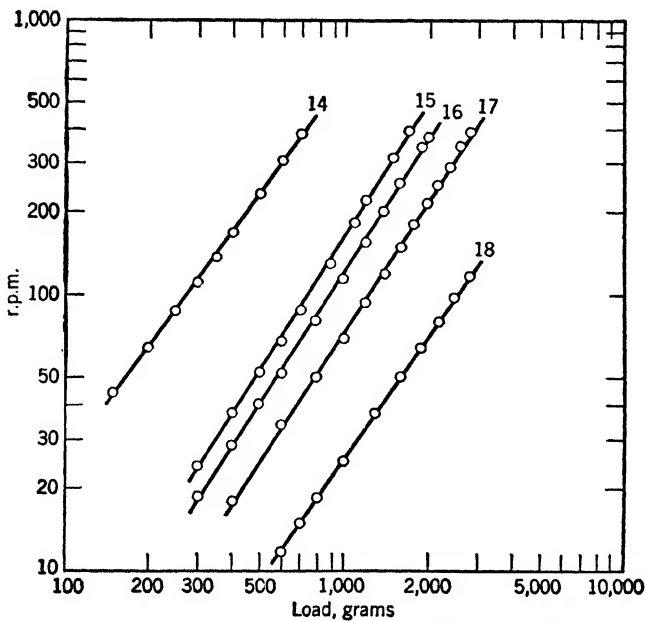


FIGURE 22. Log-log plots of the data for methyl cellulose sols shown in Figure 21.

term has been extended to various kinds of non-Newtonian flow, without discrimination. The terms *pseudoplastic flow* and *pseudoplasticity* have had fairly wide use for materials such as those we are discussing.<sup>63</sup> One characteristic of an ideally pseudoplastic material is flow that begins at a very small shearing stress, the curve meeting the stress axis at the origin. There may, indeed, be some question about the appropriateness of the term pseudoplastic,<sup>64</sup> but it is useful since it distinguishes this kind of flow from plastic, Newtonian, and dilatant flow.

The implications, as well as the difficulties, in experimental measurements of pseudoplastic flow have been pointed out by Freundlich<sup>65</sup> and McBain.<sup>66</sup> Hatschek<sup>67</sup> emphasized the necessity of considering the rate of shear (velocity gradient) in studies on colloidal sols and used the rotational viscometer to advantage. More recently, Conrad<sup>68</sup> and Lyons,<sup>69</sup> with reference particularly to cuprammonium sols of cellulose, showed that the viscosity-concentration relationship depends on the rate of shear and that failure to take this factor into account has been a serious defect in numerous measurements reported in the literature. They point out, further, that the assumption of Newtonian flow at low concentrations is untenable.

Starch and methyl cellulose form typical pseudoplastic colloidal sols.<sup>70</sup> In all cases studied the apparent viscosities decreased as the rate of shear became greater (Table VIII and Figure 21). There was no evidence for linearity in any of the curves, nor was there any indication of an intercept corresponding to a yield value. The data, when plotted on log-log coordinates, resulted in straight lines: any linear portion would appear as deviations toward the stress axis (Figure 22). In the starch pastes the change of calculated apparent viscosity with rate of shear was different for various starches, and this variation could, perhaps, be taken as an indication of the resistance of the colloidal particles to deformation by shearing.<sup>71</sup>

<sup>63</sup> The term *pseudoplastic* is evidently attributable to R. V. Williamson, *Ind. Eng. Chem.*, **21**, 1108-11 (1929).

<sup>64</sup> *Quasi-viscous flow* is an alternative term sometimes used.

<sup>65</sup> H. Freundlich, *Colloid and Capillary Chemistry*, H. S. Hatfield, Translator, Methuen & Co., Ltd., London, 1926; pp. 539-44.

<sup>66</sup> J. W. McBain, *J. Phys. Chem.*, **30**, 239-47 (1926).

<sup>67</sup> E. Hatschek, *The Viscosity of Liquids*, pp. 190-229.

<sup>68</sup> C. M. Conrad, *Ind. Eng. Chem., Anal. Ed.*, **13**, 526-33 (1941); C. M. Conrad and V. W. Tripp, *Textile Research J.*, **16**, 275-83 (1946).

<sup>69</sup> W. J. Lyons, *J. Applied Phys.*, **13**, 43-52 (1945).

<sup>70</sup> E. K. Fischer and C. H. Lindsley; *J. Colloid Sci.*, **3**, 111-28 (1948); W. G. Bechtel and E. K. Fischer, *ibid.*, **4**, 265-82 (1949).

<sup>71</sup> The reader is referred to the original papers for experimental details. See also D. K. Farrow, G. M. Lowe, and S. M. Neale, *J. Textile Inst.*, **19**, T18-T31 (1928).

TABLE VIII. CHANGE IN APPARENT VISCOSITY WITH RATE OF SHEAR

(Starch pastes, 10% dry basis.)

No.	Starch Cooking time (hours)	Apparent Viscosity (poises)		
		Rate of shear (sec. <sup>-1</sup> )		
		3.6	18	300
10A	1.0	22.0	9.7	1.4
9D	1.0	9.7	4.2	1.2
5	0.5	9.5	3.7	1.0
5	1.0	7.5	3.2	1.0
3	1.0	6.2	4.1	...
1	0.5	1.4	1.2	0.65

The question whether thixotropy occurs in pseudoplastic materials is sometimes raised, but difficulties in the measurement and analysis of the flow properties have prevented a definite answer. De Waele<sup>72</sup> has discussed the possibility. Heymann<sup>73</sup> in his study of the sol-gel transformation of methyl cellulose solutions found evidence for thixotropy in the transition region. Starch pastes are sometimes described as thixotropic. If a loop in the flow curve is taken as the criterion of thixotropy, the materials examined by the author and co-workers<sup>70</sup> cannot be regarded as showing this behavior when measured at temperatures where gelation does not occur. (Starch pastes gel on cooling, and methyl cellulose solutions gel when heated above the gelation temperature.) Near the gel point, a structure is formed that is broken down on shearing, and the curves obtained at increasing and decreasing rates of shear do not then coincide. At present, however, there is no evidence that the essential conditions for thixotropy (an isothermal, reversible transition) are met. If these materials are used as vehicles for pigments, as in textile coloring pastes, then flocculation of the pigment particles can occur with the development of plastic and thixotropic flow properties.

In the most common examples of pseudoplasticity, the dispersed phase is lyophilic, i.e., capable of absorbing and swelling in the liquid phase. The particles thus are appreciably solvated and may be pictured as surrounded by an envelope of the colloid-liquid complex. In a material that is capable of forming a gel, the boundaries of one particle merge with those of adjacent particles. As the mixture is sheared, the particles are disturbed from an equilibrium condition and are deformed and

<sup>72</sup> A. De Waele, *J. Am. Chem. Soc.*, **48**, 2760 (1926); *J. Rheol.*, **1**, 139-48 (1930); *ibid.*, **2**, 141-62 (1931).

<sup>73</sup> E. Heymann, *Trans. Faraday Soc.*, **31**, 846-64 (1935).

oriented to some extent in the direction of flow. Some of the liquid associated with the particles may be separated, with the result that the particles themselves are effectively smaller; consequently, interaction during shearing is reduced and hence there is a decrease in resistance to shear. As the rate of shear increases, the extent of such change in effective particle size becomes greater and, as a consequence, the apparent viscosity falls off. If a point were reached at which no further change in particle size occurred, then the relationship between stress and rate of shear would become linear. It is doubtful, however, if this condition could be met experimentally without the complicating effects of turbulence. This explanation appears to account adequately for the experimental observations.

### Dilatant flow

Certain highly concentrated suspensions of finely divided solids appear to become more viscous on agitation and to revert to a flowing state when the agitation is stopped. Comparatively few experimental studies have been made of this phenomenon despite its importance in elucidating the colloidal properties of pigment dispersions, bituminous compositions, and some types of resinous masses.

In 1885 Reynolds<sup>74</sup> introduced the term *dilatancy* to describe the dilation and increase in rigidity of closely packed masses of fine particles, such as sand, when disturbed. The explanation offered by Reynolds was that the particles of a dilatant system settle to a state of minimum voids and that any disturbance causes rearrangement of the particles with a greater void volume. As a consequence the total (bulk) volume of the suspension appears to increase or dilate. In a closely packed suspension, an increase in the space between particles causes the suspending liquid to be drawn into the mass. A familiar example is moist sea sand: when the sand is disturbed by stepping on it, surface moisture is withdrawn, and the sand appears to dry off.

Dilatancy may be defined as the property of a material causing the resistance to flow to increase as the rate of shear increases. This definition is not entirely adequate, and there has been considerable discussion regarding the validity of the term in its more general rheological meaning. There may be materials, for example, that do not dilate on shearing but exhibit the type of flow characterized by a curve concave to the shearing stress axis. Treloar<sup>74a</sup> recommends "shear-hardening" or

<sup>74</sup> O. Reynolds, *Phil. Mag.*, **20**, 469-80 (1885); *Papers on Mechanical and Physical Subjects*, Vol. 2, Cambridge University Press, 1901, pp. 203-16. See also H. Freundlich and F. Juliusburger, *Trans. Faraday Soc.*, **30**, 333-38 (1934).

<sup>74a</sup> L. R. G. Treloar, in *The Principles of Rheological Measurement*, Thomas Nelson & Sons, Ltd., Edinburgh and New York, 1949, p. 197.

"stress-hardening" as more specific alternatives for dilatancy. Burgers and Scott Blair <sup>74b</sup> suggest "shear-rate thickening." Despite the difficulty of precise definition, the term dilatancy is fairly well established, and it will be used in the discussion following.

Interest in the measurement of dilatant suspensions dates from about 1930. Williamson and Heckert <sup>75</sup> described experiments on dilatant systems prepared from starches suspended in water. These investigators referred to the property as "inverted plasticity," an inadequate designation which has since been dropped. Their measurements were performed on a paddle-type rotor affixed to a Stormer viscometer. When starch was suspended in alcohol, plastic flow rather than dilatant flow was observed. When the same starch was suspended in water, however, dilatant flow was observed over a concentration range of 35 to 44 volume percent. Williamson and Heckert found that the rate of stirring with their apparatus was of importance in detecting the phenomenon, but they made no effort to obtain quantitative information from their curves.

Freundlich and Röder <sup>76</sup> studied the dilatant flow of starch and silica suspensions by means of a "snow-plow" type of instrument. They showed that at a fairly critical volume concentration (42 to 45 percent) dilatancy was observable by the increased "pull" on the instrument. At low rates of shear the particles in front of a moving paddle have sufficient opportunity to slip over each other. At a certain critical rate of shear, however, the flowing process may become so rapid that the particles are no longer able "to make way" but are piled up in front of the moving object and create a considerable resistance. The local accumulation of solid particles on one side and the gathering of liquid in cavities on the back of the blade cause a suspension of this type to behave like a solid system. Freundlich states that dilatancy is observable only if the particles are deflocculated and infers that the two requirements for dilatant flow are close packing and deflocculation. Röder observed that relatively large particles (1 to 5 microns in size) showed marked dilatancy and that smaller particles produced less evident dilatant behavior. In contrast to these results, Sheets <sup>77</sup> examined clay suspensions and found that clays of large particle size resulted in "weakly" dilatant behavior over a wide concentration range, whereas a clay with small particle size

<sup>74b</sup> *Proceedings International Rheological Congress, Holland, 1948*, Section V, p. 27.

<sup>75</sup> R. V. Williamson and W. W. Heckert, *Ind. Eng. Chem.*, **23**, 667-73 (1931); *Paint, Oil, Chem. Rev.*, **89**, No. 22, pp. 9-11 (1930).

<sup>76</sup> H. Freundlich and H. L. Röder, *Trans. Faraday Soc.*, **34**, 308-16 (1938); H. L. Röder, *Rheology of Suspensions*, H. J. Paris, Amsterdam, 1939; pp. 29-37. Cf. also H. Freundlich and A. D. Jones, *J. Phys. Chem.*, **40**, 1217-36 (1936).

<sup>77</sup> G. H. Sheets, *Paper Trade J.*, **116**, No. 3, 28-36 (January 21, 1943).

was "strongly" dilatant over a narrow concentration range. Suspensions were prepared that exhibited both thixotropy and dilatancy. Arnold<sup>78</sup> extended this work and noted that clays with lower hydration capacity showed marked dilatancy but clays that were highly hydrated could not be converted into dilatant suspensions.

Gallay and Puddington<sup>79</sup> worked with aqueous starch suspensions and concluded that reversible hydration takes place up to the gelatinization point. Dilatancy they found was most marked at the freezing point and decreased markedly with rise of temperature. The same investigators<sup>80</sup> noted that a 25 percent dispersion of calcium stearate in mineral oil was strongly dilatant at 140° C. Some resins are markedly dilatant, exhibiting cold flow, but shattering into small fragments when struck sharply. "Bouncing putty" is a dispersion of a powdered solid in one of the silicone polymers. The material is free flowing, assuming the shape of the container, and may be drawn into threads, but when rolled into a ball it rebounds to 85 percent of the distance through which it is dropped. A silica gel with similar properties has been described by Cole.<sup>81</sup> An interesting paper by Mead<sup>82</sup> shows the far-reaching consequences of dilatant flow in geological processes. He suggests that dilatancy is important in the production of faults, jointing in sediments, movement of fluids (oil, gas, water) in rock, masses, etc. Scott Blair,<sup>83</sup> in noting additional examples of a different kind (flour doughs during extension, butter during compression, work hardening of metals), pointed out that these phenomena have certain features suggestive of dilatancy, but he hesitated to designate them as such. Mention should be made also of difficulties in oil-well drilling: when the mud that forms during drilling is dilatant, seizure of the drill pipe ensues.<sup>84</sup>

Pigment dispersions frequently exhibit dilatancy. The writer has observed that filter press cakes of certain pigments are strongly dilatant; they are invariably deflocculated suspensions to which some protective colloid or phosphate compound has been added during processing. There is evidently a thixotropic component present, for the filter cakes may retain their form until disturbed. Pryce-Jones<sup>85</sup> has discussed dilatancy

<sup>78</sup> K. A. Arnold, *Paper Trade J.*, **117**, No. 9, 28-34 (August 26, 1943).

<sup>79</sup> W. Gallay and I. E. Puddington, *Can. J. Research*, **21B**, 179-85 (1943).

<sup>80</sup> W. Gallay and I. E. Puddington, *ibid.*, **22B**, 161-72 (1944).

<sup>81</sup> J. W. Cole, *J. Chem. Education*, **23**, 97 (1946).

<sup>82</sup> W. J. Mead, *J. Geol.*, **33**, 685-98 (1925).

<sup>83</sup> G. W. Scott Blair, *A Survey of General and Applied Rheology*, pp. 65-73.

<sup>84</sup> D. H. Larsen, *Colloid Chemistry*, Vol. VI, J. Alexander, Editor, Reinhold Publishing Corp., New York, 1946; p. 516.

<sup>85</sup> J. Pryce-Jones, *J. Oil & Colour Chemists' Assoc.*, **26**, 3-13 (1943).

of pigment dispersions in relation to other types of flow. Daniel <sup>86</sup> described dilatancy of aqueous zinc oxide dispersions and used the criterion of dilatant flow as a comparative measure of the deflocculating action of various protective colloids.

Dilatant flow can be demonstrated by a simple experiment. Ordinary household starch is stirred into water in small additions until approximately a 50 percent (by weight) suspension is obtained. This suspension will pour from one container to another, but, if vigorous stirring is attempted, the paste seems to solidify and break into large granules. When agitation is stopped, the mass will flow again.

For dispersions the primary conditions establishing dilatant flow are (1) volume concentration of the suspended phase, (2) age of the dispersion, (3) quantity and nature of the deflocculating agents added, and (4) particle size and shape of the dispersed solid. Experiments designed to elucidate these factors were performed with A. Renold and are briefly described in the following section.

Volume concentrations for different pigments and other powdered solids are shown in Table IX. In these experiments, the powder was

TABLE IX. CONCENTRATION OF DISPERSED SOLIDS AT WHICH DILATANT FLOW RESULTED

Solid	Concentration of Dispersed Solid at Which Dilatancy Observed (vol. %)		
	Water *	Formamide *	Carbon Tetrachloride †
Starch (slight acid modification)	38	..	59
Starch (gum type)	35	..	62
Calcium carbonate	55	43	50
Lithol toner	53	43	..
Barium sulfate	39	32	..
Carbon black, Molacco	33	33	..
Chrome yellow, medium	31	29	31
Zinc oxide	30	..	33
Zinc oxide, acicular	18	..	..
Iron oxide, red	12	14	18

\* Contained 10% of sulfonated lignin.

† Contained 10% of Aerosol OT.

stirred into the liquid, and the onset of dilatant flow was noted by the increasing resistance to agitation and the tendency to form a granular mass when a spatula was withdrawn quickly from the suspension. The

<sup>86</sup> F. K. Daniel, *India Rubber World*, **101**, No. 3, 50-2 (December, 1939); **102**, No. 4, 33-37 (January, 1940); F. K. Daniel and P. Goldman, *Ind. Eng. Chem., Anal. Ed.*, **18**, 26-31 (1946).



data are of interest in showing the wide range of materials that can be suspended at concentrations sufficiently high to exhibit dilatant flow. The volume concentrations noted are, of course, only approximate. Other liquids were also used; these included toluene, xylene, octyl alcohol, light mineral oil, and ethylene glycol. Most pigment-type powders could be dispersed to provide dilatant suspensions, but the powders of finest particle size (e.g., carbon blacks) produced plastic suspensions. In all instances, however, a large concentration of a protective colloid was dissolved in the liquid vehicle. For water, alcohols, and glycols, several types of sulfonated lignins were effective; for hydrocarbons, Aerosol OT was used.

Viscometric data were also obtained using the modified Stormer viscometer at 30° C. It was necessary to employ a rather large clearance between the cup and bob: at small clearance (e.g., 2 mm.) the suspension became granular during shearing and climbed out of the cup. The best results were obtained with a cup and bob combination with 7.8 mm. clearance. Flow curves obtained are shown in Figures 10, 23, 25, 26, and 27. Since the relationship between rate of shear (r.p.m.) and shearing stress (weight) is non-linear in the dilatant region, the computation of viscosity can be made only at a specified rate of shear. Such an apparent viscosity value characterizes the system as it exists at the time of the measurement.

When unmodified cornstarch was suspended in water at volume concentrations to about 30 percent, the resulting suspensions exhibited Newtonian flow, i.e., the curve for any given suspension was a straight line starting at the origin. As the concentration was increased, however, dilatant flow became evident (at about 35 volume percent); and, with very small further increments, the apparent viscosity became very high. In an aqueous suspension, however, hydration of the starch takes place rapidly, and the swelling of the granules which occurs during a single measurement is sufficient to invalidate the results. For this reason, ethylene glycol was used in place of water. This system swells to a much smaller extent, and viscometric measurements are then feasible.

The change in viscosity with concentration of a modified cornstarch (British gum type) in ethylene glycol suspensions is shown graphically in Figure 23, and computed values for apparent viscosity are given in Table X. When plotted on log-log coordinates, straight lines resulted for the suspensions of different concentrations (Figure 24). From 42.4 to 50.8 percent volume concentration, the flow properties changed markedly, from "slightly dilatant" to an extreme that is approximately the upper working limit for the viscometer. When the same starch was suspended in a solution of Aerosol OT in xylene, higher concentrations, up to 60.8

TABLE X. APPARENT VISCOSITY OF SUSPENSIONS OF STARCH IN ETHYLENE GLYCOL AS A FUNCTION OF CONCENTRATION AND RATE OF SHEAR

Concentration (vol. %)	Apparent Viscosity (poises)	Rate of Shear ( $\text{sec.}^{-1}$ )
42.4	2.4	10
44.7	4.2	10
46.9	12.	10
48.9	47.	10
42.4	2.8	20
44.7	6.2	20
46.9	18.	20
42.4	3.6	50
44.7	8.8	50
46.9	24.	50

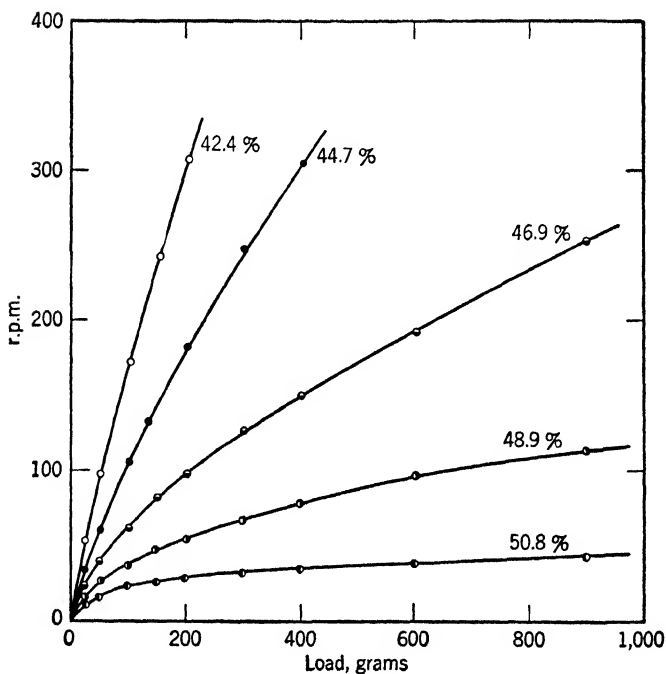


FIGURE 23. Dilatant flow of a series of starch suspensions in ethylene glycol. (Volume concentrations noted on curves.  $T = 30^{\circ} \text{C.}$ )

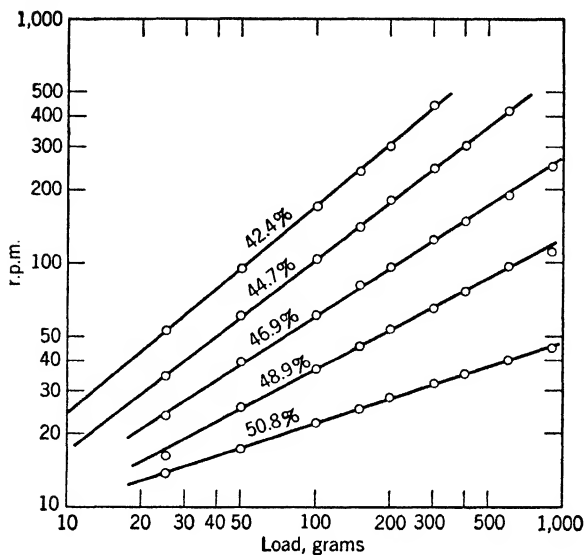


FIGURE 24. Log-log plots of the data for starch suspensions shown in Figure 23.

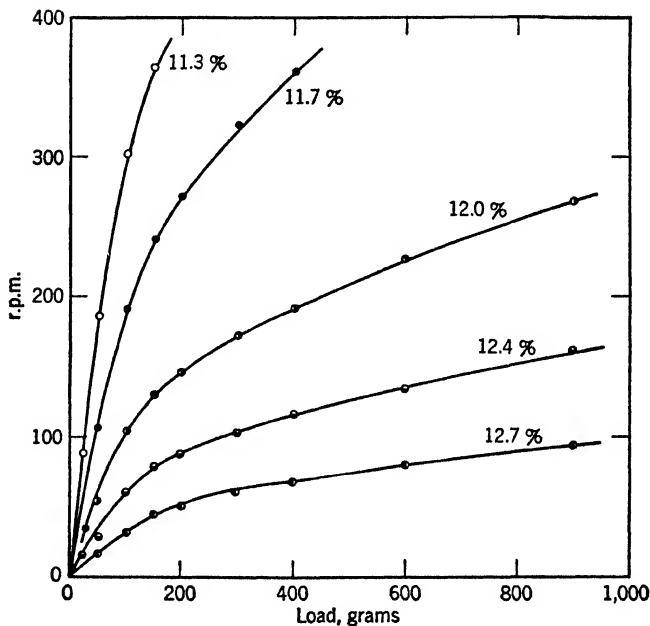


FIGURE 25. Dilatant flow of a series of suspensions of red iron oxide in a 10% solution of sodium lignin sulfonate. (Volume concentrations noted on curves.  $T = 30^{\circ}\text{C}.$ )

percent, were measurable. Xylene suspensions of starch without a surface-active agent were plastic, rather than dilatant. The addition of the surface-active agent or protective colloid produces deflocculation, which allows high volume concentrations of the suspended phase.

Iron oxide suspensions were dilatant at a much lower volume concentration, as shown by the curves in Figure 25. Over a relatively small concentration range, 11.3 to 12.4 percent, the calculated apparent viscosity increased from 2.3 poises to 76 poises for the freshly prepared suspension measured at a low rate of shear.

Suspensions of modified starch and inorganic powdered solids showed a rapid change in dilatancy with time. For starch suspensions the first measurements, made within an hour, invariably showed lower dilatancy than the same suspensions after standing for several hours. With the higher starch concentrations the suspensions set to a rigid gel, but low concentrations were measurable for a longer period. Swelling of the starch granules resulted in an increase in the volume of the suspended phase. With starch suspended in ethylene glycol, only a very small volume change was observed in the course of a week.

Inorganic solids (iron oxide, barium sulfate, carbon black, and zinc oxide) decreased in dilatancy on aging. This result is opposite to the effect for starch and is shown clearly in iron oxide suspensions (Figure 26 and Table XI). It could be assumed, of course, that hydration of the iron oxide particles occurred and that this would increase the volume of

TABLE XI. CHANGE IN APPARENT VISCOSITY OF IRON OXIDE SUSPENSIONS ON AGING

(Suspension in 10% aqueous solution of sodium lignin sulfonate; calculation of apparent viscosity at rate of shear of 20 sec.<sup>-1</sup>.)

Age of Suspension	Concentration (vol. %)	Apparent Viscosity
		Calculated (poises)
1 hour	11.34	2.3
1 hour	11.63	3.6
1 hour	12.05	16.
1 hour	12.39	76.
1 day	11.34	1.2
1 day	11.63	2.4
1 day	12.05	6.5
1 day	12.39	35.
1 week	11.34	0.69
1 week	11.63	2.1
1 week	12.05	4.7
1 week	12.39	39.

the suspended phase, at least to some small extent. This explanation is not sufficient, however, for the decrease in apparent viscosity would obviously call for a corresponding decrease in the total volume of suspended material. Further, dilatant suspensions of iron oxide were successfully prepared in carbon tetrachloride and xylene solutions. The maximum volume concentration noted was 18 percent. In these liquids

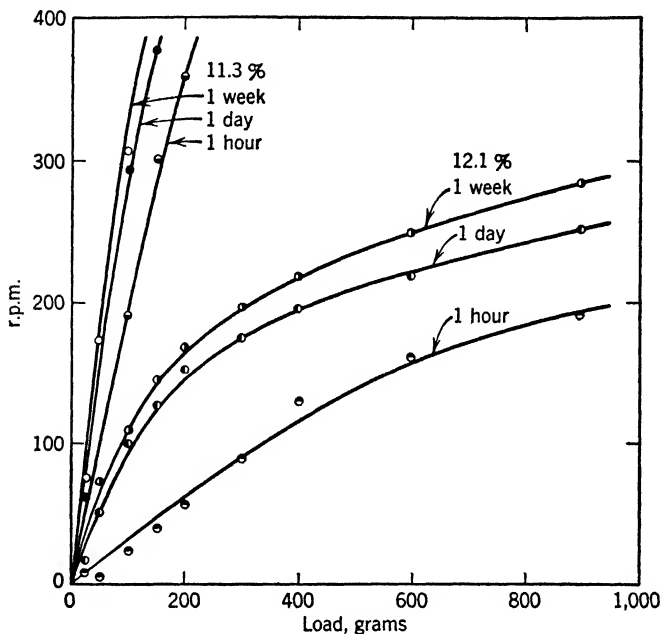


FIGURE 26. Effect of aging on dilatant flow of a series of red iron oxide suspensions in a 10% solution of sodium lignin sulfonate.

hydration is impossible, and swelling of the iron oxide particles by a non-polar hydrocarbon is improbable. Another explanation is possible. As the iron oxide particles are stirred into the liquid, an appreciable volume of air is entrained in the system; the iron oxide particles, although small individually (approximately 0.08 micron in equivalent  $d_3$  diameter, determined by adsorption), are formed into aggregates by the entrained air; each aggregate then functions rheologically as if it were a larger volume of iron oxide; on aging, the air is gradually displaced from the aggregate, and, as wetting of more and more of the individual particles occurs, they are dispersed in the liquid, and the effective volume of the iron oxide thus decreases. Similar aging effects were observed in the barium sulfate, zinc oxide, and carbon-black suspensions. This explanation is supported by experience in the manufacture of paint where the

pigment dispersion is sometimes allowed to stand for several days before final packaging; during this aging period the air displaced from the solid-liquid interface rises and forms bubbles on the surface.

The function of a protective colloid in these dispersions is to deflocculate the suspended particles. When the particles are flocculated, a suspension with plastic flow properties results, and dilatancy cannot be easily observed. Some investigators, notably Freundlich, emphasize the necessity for deflocculating the suspended phase; but there is no theoretical reason to rule out the possibility of dilatancy when flocculation is present. This criterion is pertinent when dilatant flow is observed by hand stirring or other simple means. Several of the compositions measured in this series appeared to show a small yield value. The presence of a flocculated structure will modify the observation of dilatant flow since the stresses applied to the system then are partially transmitted through the floccules, rather than through masses of particles in close proximity. When the concentration of a suspended phase is sufficiently high and flocculation exists, the material will appear solid, i.e., it will not deform under low shearing stresses, such as obtain when gravity is acting on a mass of the material, but will deform and exhibit dilatancy when subjected to the high shearing stresses possible, for example, on a roll mill.

Dilatancy is frequently confused with thixotropy, but the mechanisms responsible for the two types of flow are quite different. There is experimental evidence that dilatant compositions have thixotropic properties. Some suspensions exhibit a loop in the flow curve when they are measured at both increasing and decreasing rates of shear, and the only explanation is that a structure is present in the suspension that breaks down on shearing. Aqueous suspensions of carbon black, zinc oxide, and iron oxide show this property.<sup>87</sup>

In the theoretical discussion of dilatancy, the packing of spheres was taken as a model for distortion of the mass during shearing. In the closest packing (rhombohedral), the voids represent 26 percent of the mass, and each sphere is in contact with 12 neighboring spheres. In cubic packing the voids are 47.6 percent and each sphere touches six adjacent spheres. Various other kinds of packing have been calculated in which the voids are larger. For example, an arrangement of spheres can be made in which the voids are 63 percent and each sphere is also in contact with six other spheres.<sup>87a</sup> Corresponding concentrations are 74 and

<sup>87</sup> Quicksands are designated as either thixotropic or dilatant. Popular descriptions of the behavior of quicksand would suggest that it is both thixotropic and dilatant, breaking down when agitated slowly but acting like a solid under impact.

<sup>87a</sup> S. Melmore, *Nature*, **154**, 708 (1944).

37 percent. These are, then, the extremes of packing that would be approximated by the suspensions of starch grains, and, if the packing volume could be taken as the criterion for dilatant flow, the first intimations of dilatancy should become evident at about 37 percent volume concentration. This corresponds roughly with the lower concentration for starch suspended in water. If the opportunity for change in packing at the higher limit (74 percent) were eliminated, then any stress applied to the suspension would result in deformation of the solid. Actually, as we have seen, the particles when unconfined do change to a more open packing, and the resultant increase in voids is shown by drawing in the surface liquid.

In this connection the packing volumes of sand, lead shot, and other materials are of interest. This subject has been extensively studied from both theoretical and practical points of view.<sup>88</sup> Fraser found that wet sea sand in a loose state contained 53 to 57 percent solids and compacted sand, 61 to 65 percent.<sup>89</sup> Other data for round particles are as follows: round beans, 63 percent; poppy seeds, 60 percent; lead shot, 56 to 63 percent; steel bearing balls, 61 percent. The writer has determined the voids in grinding balls: the range is from 38 to 42 percent (a density of 62 to 58 percent) or a volume that falls in the same range as the other materials noted. Starch consists of granules that are closer to spheres than any other powdered material used in the experiments described above, and it is thus probably beyond coincidence that the highest volumes found for starch granules in dilatant suspensions were about 60 percent. On the other hand, the iron oxide particle shape is that of a parallelepiped, and it will be recalled that dilatancy became evident at much lower concentrations than those of the starch suspensions. It may be inferred that the iron oxide particle because of its asymmetry would sweep out a larger sphere of action as its orientation is disturbed by agitation.

It is possible to visualize the manner in which dilatant flow occurs in the following way. Particles initially suspended settle in close proximity with each other (if not acted on by forces causing them to link together in a network), and only the minimum of liquid is then required to fill the spaces between particles. Such a settled system will flow if poured from one container to another, for the liquid present is sufficient to allow the particles to slide, one over the other, as if lubricated. If, now, such a

<sup>88</sup> An excellent review is by L. C. Gratton and H. J. Fraser, *J. Geol.*, **43**, 785-909 (1935). See also D. R. Hudson, *Machinery (British)*, **70**, 617-22, 681-83 (1947); *J. Applied Phys.*, **20**, 154-62 (1949); *Proc. Leeds Phil. Lit. Soc., Sci. Sect.*, **5**, Part 1, pp. 65-74 (1947).

<sup>89</sup> H. J. Fraser, *J. Geol.*, **43**, 910-1010 (1935).

mass is stirred more vigorously, the particles are forced into new arrangements, with a larger total volume between particles; the liquid present is now no longer sufficient to fill the spaces between particles. As a consequence, the lubricating effect of the liquid is lost to a degree that corresponds to the dilation of the mass of particles, and the particles then appear to pile up, acting like a solid mass. In Figure 27 a diagrammatic

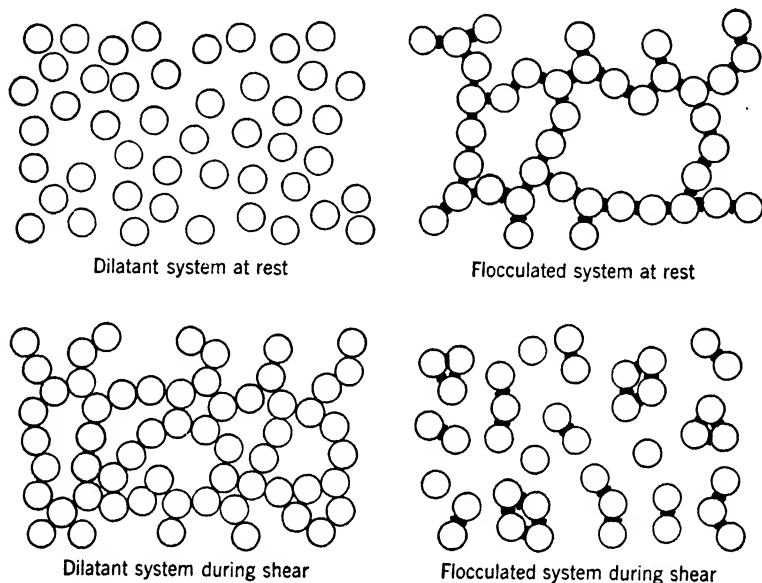


FIGURE 27. Diagram illustrating mechanism of dilatant flow (left) and of plastic and thixotropic flow (right).

scheme is shown to illustrate the difference between plastic flow, resulting from flocculation of dispersed particles, and the crowding and interference of particles in a dilatant system.

The implications of dilatancy are important and seemingly have been given scant attention. Some applications of this property of suspensions have been noted, and the effect of dilatant flow during mechanical dispersion will be found in Chapters 9 and 11.

### Applications of Rheological Data

In the discussion of rheological measurements thus far, the more general features of the subject have been covered. It will be appropriate now to examine the application of rheological information in connection with various products derived from dispersions.



## Oils

Oils, both mineral and vegetable, have long been considered the best examples of Newtonian flow. They are suitable for viscosity standards, if certain limitations arising from thixotropic flow characteristics in the more viscous varieties are considered. Measurements of viscosity can be made with a great variety of standardized instruments, and the data can be converted from one system to another.

The oils available from the National Bureau of Standards have been described by Swindells.<sup>90</sup> These oils are, of course, a primary reference in precision viscometry. Other standard oils are available from the American Petroleum Institute.

Many industrial users of oils and resin solutions at present specify oil viscosities in units traditional within an industry, rather than in absolute units. Bodied vegetable oils used in the paint and the printing ink industries are described in the Gardner-Holdt system,<sup>91</sup> which uses rising air bubbles in tubes of oils for comparison of oils of standard and unknown viscosities. The "bubble viscometer," so-called, is widely used. In Table XII, viscosities of oils in poises, approximating the letter standards, are given. The viscosities are given in poises, but they should be in stokes.<sup>92, 93</sup>

Lithographic varnishes used in the printing ink industry have not been standardized although several systems have been recommended. The varnishes are coded in numbers. Designation of viscosities by number or letter is, of course, purely arbitrary, but the method may be advantageous in manufacturing operations. A survey by the New York Printing Ink Production Club<sup>94</sup> showed extreme variations for varnishes of the same number (and hence presumably of the same "body"), obtained from 12 different users and suppliers. Recommendations of this group are given in Table XIII. These values were considered a practical compromise between previous recommendations, current practice in the

<sup>90</sup> J. F. Swindells, *J. Colloid Sci.*, **2**, 177-84 (1947).

<sup>91</sup> H. A. Gardner and G. G. Sward, *Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors*, Tenth edition, Henry A. Gardner Laboratory, Bethesda, Md., 1950; pp. 299-303.

<sup>92</sup> The stoke,  $\nu$ , is  $\eta/\rho$  where  $\rho$  is the density; dimensionally [ $L^2T^{-1}$ ]. The values in poises would be correct only when  $\rho = 1$ . See W. T. Harvey, *Official Digest Federation Paint & Varnish Production Clubs*, No. 274, pp. 616-18 (1947).

<sup>93</sup> Charts for approximate conversion of readings on the Gardner Mobilometer, the Ford Cup, A.S.T.M. Cup, and one version of the modified Stormer viscometer have been given by G. G. Sward and J. D. Garber, *Nat. Paint, Varnish Lacquer Assoc., Sci. Sect., Circ. 644 and 646*, August, 1942.

<sup>94</sup> P. W. Greubel, E. K. Fischer, H. J. Wolfe, and J. Zimmerman, *Am. Ink Maker*, **18**, No. 8, pp. 25-26 (August, 1940).

TABLE XII. GARDNER-HOLDT BUBBLE-VISCOMETER STANDARDS  
(Temperature 25° C.)

Varnish Series		Heavy-Bodied Oil Series		Lithographic Varnish Series	
Tube	Viscosity (poises)	Tube	Viscosity (poises)	Tube	Viscosity (poises)
A	0.50	U	6.2	L-000	1.8
B	0.65	V	8.8	L-00	4.8
C	0.85	W	10.7	L-0	8.0
D	1.00	X	12.9	L-1	14.4
E	1.25	Y	17.6	L-2	23.5
F	1.40	Z	22.7	L-3	34.0
G	1.65	Z-1	27.0	L-4	62.1
H	2.00	Z-2	36.2	L-5	120.
I	2.25	Z-3	46.3	L-6	200.
J	2.50	Z-4	63.4	L-8	1250.
K	2.75	Z-5	98.5		
L	3.00	Z-6	148.		
M	3.20	Z-7	388.		
N	3.40	Z-8	590.		
O	3.70	Z-9	855.		
P	4.00	Z-10	1066.		
Q	4.35				
R	4.70				
S	5.00				
T	5.50				

Courtesy of Henry A. Gardner Laboratory, Inc., Bethesda, Md.

TABLE XIII. LITHOGRAPHIC VARNISH STANDARDS  
(Temperature 25° C.)

Varnish Number	Printing Ink Standard * (poises)	Gardner-Holdt Standard (poises)
00000	2.0	.....
0000	3.0	.....
000	4.5	1.8
00	7.0	4.8
0	12.0	8.0
1	20.0	14.4
2	30.0	23.5
3	60.0	34.0
4	100.	62.1
5	150.	120.
6	200.	200.

\* New York Printing Ink Production Club recommendations. (Allowable variation  $\pm 5\%$ .)

industry, and a useful spacing of viscosity differences. The Gardner-Holdt standards are also listed in Table XIII.

Although oils of all types have long been considered liquids exhibiting Newtonian flow, convincing evidence has accumulated that the more viscous oils have complex rheological properties. Neale<sup>95</sup> observed that the coefficient of viscosity of lubricating oils decreased markedly at high rates of shear. The most extended investigation is that of Weltmann,<sup>96</sup> who studied a variety of oils (mineral, linseed, castor, isobutylene, and varnishes) ranging in viscosity from 1 to 780 poises (computed at low rates of shear). Up to a "limiting rate of shear," these oils exhibited Newtonian flow, but above this limit thixotropic flow was encountered. The value of the limiting rate of shear for each oil is not sharply defined, but, generally, the higher the viscosity of the oil the lower we find the limiting rate of shear. Thus for oils with viscosities below 5 poises, rates of shear in excess of 1000 sec.<sup>-1</sup> are required to reveal anomalous flow. At the other extreme, a mineral oil of 780 poises exhibited anomalous flow above 9 sec.<sup>-1</sup>. When this barrier has been exceeded, the oils behave like thixotropic plastics. Careful investigation demonstrated that the thixotropic properties of oils are independent of complications of temperature rise.<sup>97</sup> Other investigators have reported comparable results. Wachholtz<sup>98</sup> and Tollenaar and Bolthof<sup>99</sup> describe the change in bodied linseed oils at high rates of shear, and the dependence of computed values for the coefficient of viscosity at high rates of shear for ordinary liquids has been considered by Grunberg and Nissan.<sup>100</sup>

That very viscous oils should behave as non-Newtonian liquids is not unexpected, once the effect has been demonstrated experimentally. The implications of this fact deserve consideration. Weltmann points out, for example, that the oils used as reference standards should not be subjected to shearing above their limiting rates of shear, for, if they are, errors in standardization are inevitable. It means, also, that the viscosity of an oil under shear, as in a journal bearing, is not the same as that determined instrumentally at lower rates of shear.

### Paints and lacquers

Paint technologists are well aware of the importance of the rheological properties of paints, and the literature contains numerous references to

<sup>95</sup> S. M. Neale, *Chem. & Ind.*, **19** (56), 140-1 (1937).

<sup>96</sup> R. N. Weltmann, *Ind. Eng. Chem., Anal. Ed.*, **15**, 424-29 (1943).

<sup>97</sup> R. N. Weltmann, *Ind. Eng. Chem.*, **40**, 372-80 (1948).

<sup>98</sup> F. Wachholtz, *Fette u. Seifen*, **48**, 423-26 (1941); *Chem. Abs.*, **37**, 2595 (1943).

<sup>99</sup> D. Tollenaar and H. Bolthof, *Ind. Eng. Chem.*, **38**, 851-53 (1946).

<sup>100</sup> L. Grunberg and A. H. Nissan, *Nature*, **156**, 241 (1945)

testing methods. Gamble<sup>101</sup> has reviewed, in general terms, the methods in use. Paints are, perhaps, the most frequently encountered examples of plastic flow. Gloss enamels, with a low pigment content, show the least plasticity and thixotropy; outside house paints and semi-gloss enamels are intermediate; flat paints exhibit the highest plasticity. The consistency is controlled empirically by vehicle components, pigment volume, and ingredients that induce flocculation of the pigment particles. Paints are often described as having "false body," a term implying thixotropic flow in which the time for restoration of high consistency after agitation is very short.

The early investigations of Bingham and Green<sup>102</sup> demonstrated the essential fact that paints exhibited plastic flow properties and established, for the first time, magnitudes for plastic viscosity (expressed as the reciprocal, mobility) and yield value. One paint investigated, for example, had a plastic viscosity of 5 poises and a yield value of 87 dynes per sq. cm. This work was considerably extended a few years later by the co-operative effort of several laboratories.<sup>103</sup> Measurements on a selected variety of paint samples by different investigators showed fairly good reproducibility, and variations in the values could be attributed partly to actual differences in the samples as a consequence of mixing, aging, evaporation, etc. The yield value for the paint samples was less than 500 dynes per sq. cm., except for a flat white which had a yield value in excess of 1,300 dynes per sq. cm. The plastic viscosities for all except one sample were included between 0.9 poise and 5 poises. Perhaps the most important conclusion drawn from the data was the linearity of the curve of efflux volume vs. shearing stress. It became evident at this time to many discerning investigators that a single numerical definition of consistency, based on some combination or ratio of the two flow factors, was a futile endeavor.

Various other investigations have been made on the flow properties of paints in an effort to correlate rheological data with brushing and spraying properties. Williamson and co-workers<sup>104</sup> measured a series of paints and correlated the rheological data with ratings of experienced painters. They estimated that brushing produces a rate of shear ranging from 100 to 200 sec.<sup>-1</sup> The plastic viscosities of paints with acceptable

<sup>101</sup> D. L. Gamble, "Symposium on Consistency," American Society for Testing Materials, Philadelphia, Pa., 1938; pp. 15-22.

<sup>102</sup> E. C. Bingham and H. Green, *Am. Soc. Testing Materials, Proc.*, II, **19**, 640-75 (1919).

<sup>103</sup> J. E. Booge, E. C. Bingham, and H. D. Bruce, *ibid.*, II, **22**, 420-63 (1922). Cf. also E. C. Bingham, *Fluidity and Plasticity*, p. 220 ff.

<sup>104</sup> R. V. Williamson, G. D. Patterson, and J. K. Hunt, *Ind. Eng. Chem.*, **21**, 1111-15 (1929).

brushing properties were between 2 and 5 poises. Droste<sup>105</sup> considers that paint has good brushing properties when the plastic viscosity is in the range of 3.5 to 4.0 poises and the yield value lies between 400 and 1,400 dynes per sq. cm. Nitrocellulose lacquers are said to have good brushing properties if the viscosity is 0.16 to 0.18 poise.<sup>106</sup>

Waring<sup>107</sup> presented an interesting analysis of the leveling of paint films as a rheological process, deriving the following expression:

$$h = \frac{w^2 f}{8\gamma} \quad (32)$$

where  $h$  is the height of the brush mark and  $w$  the width,  $f$  is the yield value, and  $\gamma$  is the surface tension. Assuming that typical brush marks have a width of 0.1 cm., that the surface tension is 35 dynes per cm., and that the surface appears level when  $h$  is less than 0.0001 cm., Waring concluded that a yield value of less than 3 dynes per sq. cm. will result in perfect leveling. This value appears unreasonably low. It means that a yield value lower than that measurable with certainty would result in brush marking. It may be inferred that the analysis presumes extremely low viscosity and film thickness. A further defect is failure to consider the effects of thixotropy. McMillen<sup>108</sup> has developed a more complicated expression in which thixotropic buildup is considered. The actual conditions during paint application cannot be fully included in measurements made on the bulk composition, however, because the important factor of solvent evaporation is not considered.

The writer<sup>108a</sup> has measured the rheological properties of a number of commercial paints, enamels, and varnishes by means of the modified Stormer viscometer. The samples were purchased locally in retail packages. Fifteen different manufacturers were represented. Although a sampling taken in this way does not take into account such factors as age, conditions of storage, formula variations, etc., it indicates the range of flow properties encountered by the consumer of "ready-mix" products at the time of use. Data summarizing these measurements are given in Table XIV.

<sup>105</sup> W. H. Droste, *Farben-Z.*, **37**, 619-20; 655-57; 694-95 (1932); *Chem. Fabrik*, **7**, 249-50 (1934); noted also by R. Houwink, *Elasticity, Plasticity, and Structure of Matter*, p. 314 *et seq.*, and J. E. Arnold, *Paint Technol.*, **9**, 163-66 (1944).

<sup>106</sup> J. J. Coughlin and R. F. Wint, *Official Digest Federation of Paint & Varnish Production Clubs*, No. 263, pp. 694-96 (1946).

<sup>107</sup> R. K. Waring, *J. Rheology*, **2**, 307-14 (1931).

<sup>108</sup> E. L. McMillen, *J. Rheology*, **3**, 163-78 (1932).

<sup>108a</sup> E. K. Fischer, *J. Colloid Sci.*, **5**, 271-81 (1950).

TABLE XIV. RHEOLOGICAL DATA ON COMMERCIAL PAINTS

Product	Plastic Viscosity (poises)	Yield Value (dynes/cm <sup>2</sup> )	Thixotropy Rating
Enamels, gloss	1.4-3.9	0-30	Nil to slight
Enamel, semi-gloss	1.0-3.5	50-120	Slight
Flat or matte paints	0.6-1.	20-100	Slight to marked
Wall, water-dispersible *	0.2-1.4	10-100	Slight to marked
Primers, metal	0.3-1.2	0-100	Nil to marked
Varnishes	0.9-2.9	0	Nil

\* Diluted as recommended by manufacturer.

With only an occasional exception, all the samples examined had a plastic viscosity less than 4 poises. High-gloss enamels exhibited very low or zero yield values and thixotropy was absent or of low magnitude. Outside house, flat, and emulsion paints had the highest yield values (with a maximum about 200 dynes per sq. cm.) and the most evident thixotropic properties.

The viscosity of lacquers for spray-gun application is usually adjusted to fall within the range of 0.4 poise to 1.2 poises by appropriate solvent additions. The dilution serves two main purposes: to allow efficient atomizing in the spray gun and to leave sufficient solvent in the applied film for adequate flowout.

Aldrich<sup>109</sup> states that hot plastic paints, applied at temperatures in the range of 275° to 300°F., should have a viscosity of less than 1.5 poises. Higher viscosities produce an uneven spray. Viscosities of gel lacquers have been described by Malm and Smith.<sup>110</sup> These compositions are applied by dipping, and each coat may be as thick as 0.015 inch, as contrasted with the usual dip-lacquer finish which is approximately one-tenth this thickness. The usual range for application is 20 to 40 poises.

Measurements on a recording viscometer by means of a specially designed paddle have been reported by Wicker and Geddes.<sup>111</sup> This test procedure is rapid and perhaps convenient for industrial control, but complex curves are obtained that affect the accuracy and precision of the measurement.

The rheological behavior of a finish at various stages during and after application determines to a large extent the final smoothness of the film and the freedom from surface imperfections. Irregularities in the surface

<sup>109</sup> H. L. Aldrich, *Paint, Oil Chem. Rev.*, **110**, No. 2, pp. 8, 30, 31, 34 (January 23, 1947).

<sup>110</sup> C. J. Malm and H. L. Smith, *Ind. Eng. Chem.*, **38**, 937-41 (1946).

<sup>111</sup> C. R. Wicker and J. A. Geddes, *ASTM Bull.*, No. 120, 11-18 (1943).

of many types of decorative and protective coatings are so common as to be considered almost unavoidable. Although these defects do not appreciably impair the service of a coating, the appearance is usually considered marred, and elaborate buffing and polishing means are employed to achieve uniformly smooth surfaces. Familiar examples are the following.

Sag marks and "curtains" may result from any method of application if the film has been applied in a layer too thick to prevent excessive flow before the composition sets. Brush marks are parallel ridges and valleys

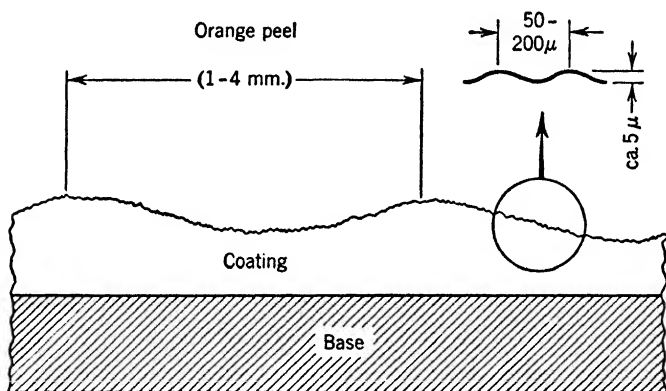


FIGURE 28. Cross-sectional diagram of a sprayed paint film giving approximate dimensions of the orange-peel texture and a finer texture superimposed on the former.

where the matted hairs of a paint brush leave an imprint. Surface ripples, usually termed "orange peel" by analogy with the skin of an orange, result from spray-gun application of lacquers and enamels.

A close examination of the orange-peel texture shows that it is analogous to the peneplain of the geologist in which low hills or undulations rise from a nearly level plain. The orange-peel topography is visible to the unaided eye at small viewing angles and is characterized by low elevations, commonly 1 to 4 mm. apart (Figure 28).

Another and finer texture of more complex shape, superimposed on orange peel or brush marks, is visible under low-power magnification in all finishes containing volatile solvents, regardless of the method of application. This defect is associated with the evaporation of solvents from the wet film and in some examples shows small elevations (about 5 microns high) with the distance between them of the order of 100 microns. The fine structure appears to be a mass of microscopic valleys, and, when viewed perpendicularly to the surface, a network of "cells," sometimes hexagonal in shape, can be observed. The dimensions of the

cells vary greatly, but they are often in the range of 50 to 200 microns in diameter. Often these cells are clearly visible in finishes formulated with a mixture of pigments by the concentration of one pigment at the boundaries or centers of the cells. Bartell and Van Loo<sup>112</sup> have described this effect.

Application of a finish in such a way as to avoid surface imperfections is, of course, highly desirable. Efforts to achieve this result are based largely on a balance of formula ingredients to assure flowout during application, but the large number of variables that need consideration preclude any simple answer. The control of initial viscosity is essential for proper standardization. This measurement, however, cannot compensate for variations during application and in the interval before setting or drying of the film. The importance of rheological information has been emphasized by Bogin<sup>113</sup> and others,<sup>114</sup> who observe, further, that there are virtually no data connecting the variables involved. At least part of the difficulty in assaying the results of different investigators is the use of methods of measurement that yield data expressed in arbitrary units.

The requirements for complete leveling of an applied finish have been stated by several investigators.<sup>115</sup> The general conditions are the following: surface forces tend to produce flow on the applied film, smoothing the surface irregularities incidental to application by brushing or spraying; thixotropic buildup of the pigment structure within the film tends to reduce the rate of leveling; solvent evaporation increases the plastic viscosity and yield value, thus slowing down flowout of the film. With these factors in mind, it will be helpful to consider available data for typical varnishes, paints, and lacquers.

The effect of viscosity and film thickness on flowout may be readily demonstrated by brushing or spraying oils of different viscosities onto a non-porous surface and then observing the time for leveling. An oil with a viscosity of less than 0.5 poise levels in less than a minute at film thicknesses from 0.5 mil to 5 mils. An oil of 2 poises requires about 5 minutes to flow to a smooth film if the film thickness is about 0.5 mil, but at higher film thicknesses leveling proceeds more rapidly and with

<sup>112</sup> F. E. Bartell and M. Van Loo, *Ind. Eng. Chem.*, **17**, 925-29; 1051-56 (1925).

<sup>113</sup> C. D. Bogin, Chapter 22, pp. 641-736, in *Protective and Decorative Coatings*, Vol. 1, J. J. Mattiello, Editor, John Wiley & Sons, Inc., New York, 1941.

<sup>114</sup> Anon., *Paint Technol.*, **8**, No. 89, p. 68 (1943).

<sup>115</sup> E. L. McMillen, *Ind. Eng. Chem.*, **23**, 676-79 (1931); R. V. Williamson, G. D. Patterson, and J. K. Hunt, *ibid.*, **21**, 1111-15 (1929); G. S. Haslam and L. D. Grady, Jr., *Ind. Eng. Chem., Anal. Ed.*, **2**, 66-69 (1930); D. L. Gamble, *Ind. Eng. Chem.*, **28**, 1204-10 (1936); C. Bogin and H. L. Wampner, *ibid.*, **29**, 1012-18 (1937); R. W. Kewish and D. F. Wilcock, *ibid.*, **31**, 76-83 (1939).



thick films is complete in less than 30 seconds. When the viscosity reaches 10 poises, thin films do not flow out in less than several hours and thick films require about 10 minutes. These simple experiments suggest that flowout should occur in a film in a relatively short time, perhaps 2 minutes, to level completely. If any thixotropic buildup occurs, it should not be complete in the flowout time. Brush marks and orange peel are inevitable if yield value of any appreciable magnitude is observed in the paint film.

The actual change in flow properties is rapid, of course, when volatile solvents are present. Within 5 minutes after application, the plastic viscosity of an enamel may increase to 10 or more poises and the yield value builds up proportionately.

A thorough analysis of the application factors that influence the flow of lacquers has been made by Bogin.<sup>116</sup> The usual distance between the spray gun and the object varies and is difficult to control, but 8 to 12 inches may be considered the average range. The ratio of air to fluid delivery for commercial spray guns is very great, from 5 to 15 cubic feet per minute being required for adequate atomization. Bogin found that 47 to 74 percent of the solvents present initially were lost, during spraying, at distances between gun and object from 8 to 18 inches.

The solvent loss and high air velocity are of considerable importance in analyzing flowout since they account for the important rheological changes that occur during atomization. There is, first, the effect of cooling: the composition as applied is at a lower temperature than the bulk material as a consequence of solvent evaporation, and the plastic viscosity of the film is accordingly higher. The solvent loss also results in a rapid increase in plastic viscosity. The change for a typical material is from 0.5 poise to 3 poises for normal spraying distance. Even higher values have been observed at greater spraying distances, and one black baking enamel increased to more than 30 poises. The yield value of the applied composition increases with solvent loss. Finally, the turbulent spray fan or cone impinging on the film as applied sets up ripples and waves.

A cause of orange peel frequently listed is the moisture in the composition or a high humidity during spraying. Hochwalt and Marling<sup>117</sup> consider removal of water, present in the lacquer solvent, a vital condition. In the author's experience, however, the presence of water has small effect on orange peel with many compositions, if the pigment combination is not flocculated. When water-sensitive pigments are

<sup>116</sup> C. Bogin, *Paint, Oil, Chem. Rev.*, **103**, No. 15, p. 7, and No. 16, p. 16 (July 19 and 31, 1941).

<sup>117</sup> C. A. Hochwalt and P. E. Marling, *Ind. Eng. Chem.*, **27**, 190-2 (1935).

present, then orange peel, reduced gloss, and numerous other defects become prominent.

During application by brush, the paint is subjected to a moderate amount of shearing, and the thixotropic structure often present is broken down momentarily. After the brush has left the layer of paint on the surface, several competing processes start: the paint layer begins to flow and the dispersed pigment particles begin to rebuild the original thixotropic structure. If rebuilding takes place quickly, leveling and flowout cease and brush marks are formed. On the other hand, if the development of structure is protracted, flowout continues and the applied paint film forms sag marks, particularly on vertical surfaces. The balance between these properties establishes the performance of the paint. Saunders <sup>118</sup> obtained fair correlation of leveling and rheological data and states that paints that are considerably reduced in consistency on agitation and show a slow rate of thixotropic recovery exhibit the best leveling. On the other hand, when the thixotropic recovery is rapid, poor leveling results.

An over-all picture of the formation of an orange-peel surface pattern from spray application may be theorized as follows. The clearest source of imperfections is a spray gun in which the atomization of the liquid is imperfect and particles of abnormal size are projected toward the panel, resulting in a very uneven application. With spray equipment in good condition, however, the likelihood of imperfect atomizing of the liquid is much smaller. Nevertheless, the liquid particles from the gun coalesce to some extent after leaving the spray nozzle, particularly at the center of the spray cone, and to some extent also by deposition of successive droplets adjacent to each other, forming relatively large irregularly shaped lakes of the composition. In addition, at the time of deposition, the surface is subjected to an air blast of extremely high velocity and turbulence which sets up ripples on the layer of viscous material deposited.

After deposition of the coating, the surface is left momentarily with irregularities, and the related processes of continued evaporation of solvent, leveling under the surface forces at the interface, and the gradual increase of viscosity begin. If the composition immediately after deposition exhibits yield value (or rapid thixotropic buildup), the structure is set by the low mobility of the composition. If the flow properties are those of a Newtonian or pseudoplastic type, then, at the low shearing stresses operating under the conditions of leveling, the initial viscosity and the solvent volatility at the time determine entirely whether or not

<sup>118</sup> B. Saunders, *J. Oil & Colour Chemists' Assoc.*, **31**, 95-106 (1948). This subject has also been discussed by M. E. D. Jarrett, *ibid.*, **31**, 357-78 (1948).

the surface will level to perfect smoothness. In thin layers (less than 25 microns) the time for oils to flow to a smooth layer becomes excessively long if the viscosity exceeds 2 to 3 poises, although thick films level quickly—within a fraction of a minute. The flowout time for films of greater thickness is much more rapid.

For most commercial types of finishes, however, the evaporation of solvent proceeds with concomitant increase of plastic viscosity. If the viscosity for 1 minute after spraying is less than 1 poise, the flowout will be complete, even for very thin films. This result is accomplished in practice by considerable dilution of the composition with solvents. Most compositions, however, are applied with a higher total solid content, and, as a consequence, the viscosity of the deposited film is considerably greater, requiring correspondingly greater flowout time.

### Printing inks

Although we are accustomed to thinking of printing inks as a class of very viscous dispersions, actually they range from less than 1 poise, as typified by gravure inks, to several thousand poises, as represented by certain offset inks. Printing inks have a great range in formulation, but with few exceptions they are suspensions of finely divided pigments in vehicles that contain some binding resin or oil. For satisfactory printing the ink has to meet an impressive list of requirements. The ink must, first of all, "work" properly on the press, that is, it must distribute evenly, transfer to the printing plate or type surface, and transfer again to the paper without picking, smearing, or crawling.<sup>119</sup> It should not "dry" on the press, but, once applied to paper, it should dry with dispatch. The dried ink film should be opaque, in order to confer maximum legibility for typeset matter, and it should not smudge onto the reader's hands.<sup>120</sup>

The performance of an ink for a given purpose is established in large measure by its rheological properties, and since 1940 notable advances have been made in methods of measurement and in application of rheo-

<sup>119</sup> "Picking" is the printer's term for the lifting of the paper surface; when the ink is too viscous, it acts as an adhesive and, instead of transferring to the paper, stays on the type and picks up parts of the paper surface. "Crawling" is a defect caused by the withdrawing or retracting of the ink from the printed area, leaving portions of the surface deficient in ink.

<sup>120</sup> For a comprehensive treatment of the subject of printing inks the reader is referred to the following references: H. J. Wolfe, *Printing and Litho Inks*, MacNair-Dorland Co., Fourth edition, New York, 1949; C. Ellis, *Printing Inks*, Reinhold Publishing Corp., New York, 1940. A general review with historical notes is by E. K. Fischer, *Am. Ink Maker*, **26**, No. 8, pp. 21-23, 47, 49 (August, 1948), No. 9, pp. 59, 61, 87 (September, 1948).

logical information to standardization of printing inks and to more effective adaptation of inks to printing processes.

There are three processes that constitute the bulk of commercial printing.

Printing by letterpress is the oldest and still the most widely used process; it is classified as typographic. The printing surface is raised above the non-printing areas. Ink is applied by rollers, and, when paper is pressed into contact, most of the ink transfers to the paper. Some of the ink remains on the type surface, in amounts varying from about 35 to 75 per cent, depending on the pressure applied during impression.

Offset printing is an outgrowth of the early lithographic process. Lithography depends on the principle that oil and water do not mix, and that a dampened surface will reject ink, whereas a waxy or oily area will accept ink. Lithography, as the name implies, uses a fine-grained stone. Offset printing is really highly mechanized lithography, with the stone replaced by a fine-grained zinc, aluminum, or chromium-surfaced plate. The ink-receptive areas are produced photographically. The offset press has three cylinders: the plate, blanket, and impression cylinders. For press operation, the plate is curved around the first cylinder; a dilute water solution of gum arabic and other reagents is applied by a dampening roller to the plate as it rotates; ink is applied from another roller. The printing areas accept the ink and transfer it (hence, offset) to the rubber-covered blanket cylinder which in turn applies the ink to the paper as it passes between the blanket and impression cylinders. Since offset printing is performed from a surface that is essentially flat, it is classified, generically, as a planographic process. This method allows printing on relatively coarse or textured papers because the ink is applied from an elastic rubber surface.

Unlike typographic and offset printing, gravure depends on very fluid inks that fill small depressions in the printing cylinder or plate and transfer to the paper by spreading and penetrating. The printing surface consists of countless wells or cells. These cells pick up the ink directly from a fountain; excess is removed by a flexible knife in contact with the cylinder. When the paper is pressed against the cylinder, the ink is considered by most authorities to penetrate instantly into the capillaries of the paper. It appears more likely, however, that the ink first spreads over the fibers of the paper and subsequently penetrates by capillary (or wick) action.

Approximate ranges of plastic viscosity for different printing inks are given in Table XV. In general, the fast printing rates require inks of low plastic viscosity. This adjustment is required to allow adequate

TABLE XV. APPROXIMATE PLASTIC VISCOSITY RANGES OF DIFFERENT PRINTING INKS

Class of Ink	Poises
Rotogravure	0.4-5
Letterpress	
Newspaper	1-50
Magazine	10-500
Offset	100-1,000

feeding of the ink from the fountain to the distributing system and is established primarily by the construction of the press. Buchdahl and Thimm<sup>121</sup> and Voet<sup>122</sup> have described flow requirements of printing inks at various stages of the printing process. In letterpress printing, the ink in the fountain should flow toward the slowly turning fountain roller; low yield value and slow thixotropic buildup are necessary. On the distribution system composed of a series of rollers, the ink is transferred from one roller to the next until it is in a uniform layer. If the viscosity of the ink is too high, insufficient spreading occurs, and, if the viscosity is too low, uneven spreading with resultant streaking is likely to take place. When the ink is transferred to the raised printing surface, it should remain on these surfaces and not flow to the sides; thixotropic buildup assists at this stage. Finally the critical transfer to the paper surface occurs. When the ink film is broken by separation of the printing surface from the paper, the rate of shear is certain to be very high. The pull on the paper surface increases with press speed, and, if a balance is attained between the plastic viscosity of the ink and mechanical strength of the paper, printing takes place without picking of the paper surface.

No systematic survey of the measured rheological properties of printing inks and the actual requirements during press operation has been published. The data in the table serve as approximations. In manufacture, base inks are usually made; these contain the maximum amount of the pigments and extenders. The plastic viscosity is, in consequence, higher than that of the inks intended for use on printing presses and, according to Buchdahl and Thimm,<sup>121</sup> may reach 100,000 poises. The yield value of printing inks covers a range comparable to the plastic viscosity. For base inks the yield value becomes, in a few instances, immeasurably high, but more commonly it is of the order of 5,000 to 10,000 dynes per sq. cm. When the base inks are extended with additional vehicle, both the plastic viscosity and the yield value are decreased. A typical rotary press ink has a viscosity of 450 poises and

<sup>121</sup> R. Buchdahl and J. E. Thimm, *J. Applied Phys.*, **16**, 344-50 (1945).

<sup>122</sup> A. Voet, *Am. Ink Maker*, **27**, No. 2, pp. 27-30, 41 (February, 1949).

yield value of 4,000 dynes per sq. cm. A representative black news ink has a plastic viscosity of 3 poises and yield value of 200 dynes per sq. cm. Gravure inks, on the other hand, show low or immeasurably small yield values and plastic viscosities of the order of 0.4 to 1 poise.

Offset printing is adapted for high-viscosity inks, since a thinner ink film is carried and the concentration of pigment in the ink is consequently greater.

Although the plastic viscosity of a printing ink would seem to be the primary measure of flow properties, the tack or tackiness of the ink has been the chief method of rating ink. The pressman has long relied on a subjective measure of tack obtained by tapping a thin film of ink on the surface of glass or paper with the index finger. The sensation of resistance to pull is described as tackiness.

More than a century ago Stefan<sup>123</sup> attempted to measure the forces required to separate two parallel plates immersed in viscous liquids. Evidently the analysis was inadequate, but Stefan concluded that tackiness was proportional to viscosity. Subsequent investigators sought to bring higher precision to the measurement, specifically for printing inks. Bekk<sup>124</sup> determined the compressive and tensile stresses on commercial printing inks confined in a small, hemispherical cell. An improved version of these instruments was described by Green,<sup>125</sup> who also offered an analysis of the concept of tack.

The instrument, a parallel plate viscometer, consists of two circular plates approximately 0.5 inch in diameter, the lower one affixed to a constant-temperature water bath and the upper plate connected to a lever system. It is intended to simulate the action of the finger tap-out test. Separation of the plates is adjusted by means of a micrometer screw. Measurements are made by taking the time for the film to separate at different initial film thicknesses and with different loadings. The curve connecting rate of pull with pull resistance (weight) is, ordinarily, a straight line, comparable to the curve of shearing stress vs. rate of shear obtained on a rotational viscometer. This instrument has a potential range of 1 to 30,000,000 poises at film thicknesses between 5 and 1,200 microns.

After surveying a variety of printing inks and other materials, Green concluded that for Newtonian liquids the tack or pull resistance is di-

<sup>123</sup> See the "Discussion on the Measurement of Tack," British Rheologists' Club, *Paint Technol.*, **9**, 211-21 (1944), in particular the papers by N. A. deBruyne (pp. 211-13) and R. F. Bowles (pp. 213-14); also, J. J. Bikerman, *Surface Chemistry for Industrial Research*, Academic Press, New York, 1947; pp. 358-60.

<sup>124</sup> J. Bekk, *Deutsche Drucker*, No. 526, pp. 450 ff. (July, 1938).

<sup>125</sup> H. Green, *Ind. Eng. Chem., Anal. Ed.*, **13**, 632-39 (1941); U. S. Patent 2,345,968 (April 4, 1944). Cf. also *Paper Trade J.*, **114**, No. 6, 39-42 (February 5, 1942); *Interchem. Rev.*, **1**, 7-10 (1942).

rectly proportional to the rate of break if the pulling area and initial film thickness are constant. For plastics, when measured under the same conditions, the pull resistance in excess of the yield value is proportional to the rate of pull. For rapidly separating surfaces, the tackiness was found to be directly proportional to viscosity, in confirmation of Stefan's early work.<sup>126</sup>

In theory, the subject is still clouded with uncertainty and controversy. None of the measurements described have been made at time intervals corresponding to actual printing-press speeds, of the order certainly of less than 0.01 second. Voet<sup>127</sup> emphasizes the possibility of rupture of the ink film on separation, rather than flow into thin threads with subsequent breaking of the threads into droplets. Experiments with adhesive tapes showed appreciable differences in removal force as a function of the rate of stripping.<sup>128</sup> It should be noted, however, that the separation of an ink film on rollers or between paper and the printing surface is different from that of a coherent adhesive from a non-yielding surface. In Green's analysis, the ink film is considered essentially fluid and breaking of the film takes place by liquid flow and "necking" of the ink into a thin string; each of the two separating surfaces retains a thin film of ink. The breaking of the adhesive bond between a tacky surface, such as milled rubber, and a non-yielding surface leaves the latter clean, and some elastic recovery of the tacky substance occurs. With inks that show appreciable flocculation, continued flow without rupture cannot be assumed, nor can the possibility be entirely ruled out that dilatant flow with highly pigmented inks occurs at the high rates of shear that exist during printing. Plastic flow (with high yield value) and dilatant flow would lead to rupture of the filament of ink. This is an important point that must await further experimental work.

A practical instrument for measuring the rheological properties of printing inks, which simulates the roller system on a press, has been described by Opp<sup>129</sup> and Reed.<sup>130</sup> Called an Inkometer, this device

<sup>126</sup> The mathematical derivation of Stefan's relationship has been described by J. J. Bikerman, *J. Colloid Sci.*, **2**, 163-75 (1947). For experimental details on a parallel plate viscometer see G. J. Dienes and H. F. Klemm, *J. Applied Phys.*, **17**, 458-71 (1946).

<sup>127</sup> A. Voet, *Am. Ink Maker*, **23**, No. 9, pp. 65-67, 69, 71, 91 (September, 1945).

<sup>128</sup> W. F. Busse, J. M. Lambert, and R. B. Verdery, *J. Applied Phys.*, **17**, 376-85 (1946).

<sup>129</sup> C. J. Opp, *Am. Ink Maker*, **12**, No. 3, 9-11 (March, 1934); *ibid.*, **13**, No. 3, 17, 19 (March, 1935).

<sup>130</sup> R. F. Reed, U. S. Patent 2,101,322 (December 7, 1937); *Am. Ink Maker*, **16**, No. 2, 37 (February, 1938); *Technical Bulletin 2*, Research Series No. 4, Lithographic Technical Foundation, Inc., Chicago, 1939; Thwing-Albert Instrument Co., *Inkometer Instruction Book*, Philadelphia (n.d.).

measures the torque on an ink-covered roller when rotating at speeds approximating those of printing press rolls. Three commercial models are available with peripheral roll speeds ranging from 470 to 1,570 feet per minute. The ink-film thickness is controllable: a standard procedure depends on a film thickness of 0.0005 inch (approximately 13 microns). Tack is taken as the torque measurement at a given speed. A series of four-color process inks, for example, gave the following instrumental readings (in gram-meters): yellow, 31; red, 23; blue, 18; black, 11. The plastic viscosities of the inks are generally in the same order.<sup>131</sup> Process inks are graded in this way to ensure proper printing, for the ink of highest viscosity and tack is printed first, and, since the inks are printed successively, one onto the other, they must have progressively lower viscosities in order to "trap" or print properly. The way in which plastic viscosities and tack ratings can be used for the practical testing of printing qualities of both ink and paper has been described by Berberich, Englehart, and Zucker.<sup>132</sup>

### Highly viscous and plastic compounds

Asphalt, plastic, and rubber compositions are characterized by extremely high consistency. In most compositions of this type a solid is dispersed in the highly polymeric material, and the flow properties become complicated and difficult to measure. Expressed in viscometric terms (at best only an approximation) the range for materials in this category is roughly  $10^4$  to  $10^8$  poises. Rheological measurements are made with a variety of instruments including the following: parallel plate plastometer, penetrometer, and falling-ball, capillary, and rotational viscometers. In general most data have been obtained at low rates of shear (usually less than  $1 \text{ sec.}^{-1}$ ), but some investigators have used higher shear rates.

Several aspects of high-consistency measurements are pertinent to our main discussion and will be noted briefly.

Asphalts have been extensively investigated by Traxler and co-workers.<sup>133</sup> These materials, obtained from still residues in petroleum refining and natural deposits, exhibit all types of flow. Newtonian, plastic, pseudoplastic, and thixotropic flow properties have been observed. Many show a visco-elastic behavior, and age-hardening (or increase in consistency on standing) is common. Rheological data on a

<sup>131</sup> Buchdahl and Thimm<sup>121</sup> give the following plastic viscosities in poises for a set of process inks: yellow, 550; red, 250; blue, 125; black, 110.

<sup>132</sup> O. P. Berberich, L. F. Englehart, and M. Zucker, *Am. Ink Maker*, **6**, No. 7, pp. 26-28, 59 (July, 1948) and No. 8, pp. 26-28, 51 (August, 1948); *Paper Trade J.*, **127**, No. 7, pp. 53-57 (August 12, 1948) and No. 9, pp. 53-54 (August 26, 1949).

<sup>133</sup> Cf. the review by R. N. Traxler, *J. Colloid Sci.*, **2**, 49-68 (1947).



variety of asphalts, determined with a rotational viscometer, have been reported.<sup>134</sup> Dispersion of solids in asphaltic materials provides many important industrial products, such as paving mixtures, flooring compounds, and roofing materials. Such "filled" compositions exhibit plastic flow. Traxler noted apparent viscosities as high as  $3 \times 10^7$  poises for bitumen-pumice mixtures. Yield values of the order of  $5 \times 10^5$  dynes per sq. cm. were recorded for silica-asphalt and black slate-asphalt mixtures. It is probable that dilatant flow occurs in such dispersions.

Rubber compounds have been extensively investigated, but an adequate rheological description awaits further research. Dillon and Cooper<sup>135</sup> have summarized the status of consistency measurements on rubber and rubber compounds. Crude and milled rubber show pseudoplastic flow. When reinforcing solids (carbon black) are incorporated by milling in increasing concentrations, the compound then becomes plastic and the curves approach straight lines with a clearly defined yield value.<sup>136</sup> Thixotropy is evident in uncompounded rubbers.

Special instruments used in the rubber industry, including the widely used Mooney and Williams plastometers, are described by Gallay.<sup>137</sup>

Plastics present many rheological features similar to those of rubber and asphalt.<sup>138</sup> One of the difficulties in these measurements is in separating the elastic from the viscous shear component. Many high polymers when subjected to a constant stress exhibit in sequence (1) a small, instantaneous deformation, (2) a slower deformation exponentially related with time, (3) a deformation which is approximately linearly related to time. The first two stages are considered elastic, and the third is considered viscous deformation. Considerable progress is being made in the rheology of high polymers, and correlation of physical properties with processing conditions will doubtless be forthcoming.

The rheological properties of highly concentrated dispersions or stiff pastes, as they are often designated, present special problems. Many industrial compositions fall into this category: stock pigment dispersions, clay bodies, mortar, plasters, putty, and asphalt mixtures. Experiments and the design of suitable measuring instruments have been de-

<sup>134</sup> R. N. Traxler, J. W. Romberg, and H. E. Schweyer, *Ind. Eng. Chem., Anal. Ed.*, **14**, 340-3 (1942); *Ind. Eng. Chem.*, **36**, 823-29 (1944).

<sup>135</sup> J. H. Dillon and L. V. Cooper, American Society for Testing Materials, "Symposium on Consistency," Philadelphia, 1938; pp. 52-63.

<sup>136</sup> J. H. Dillon and N. Johnston, *Physics*, **4**, 225-35 (1933).

<sup>137</sup> W. Gallay, Chapter IV, pp. 150-80 in *The Chemistry and Technology of Rubber*, C. C. Davis and J. T. Blake, Editors, Reinhold Publishing Corp., New York, 1937.

<sup>138</sup> An excellent review is by R. Buchdahl and H. K. Nason, *Ind. Eng. Chem.*, **40**, 642-51 (1948).

scribed by Ward and Westbrook.<sup>139</sup> These investigators find that mastics of the type used for caulking compounds behave as plastics, in the Bingham sense, when they are sheared above a critical stress. At lower stresses, however, the rate of shear decreases with time. This result is attributed to shear hardening or a "locking" of the dispersed components into a rigid mass. Many of the pastes showed evidence of thixotropic flow.

Our discussion of the rheological properties of dispersions has been concerned largely with materials in which the relationship between deformation and applied stresses can be readily measured and systematized. There are, however, many additional aspects of flow that are not relevant to our central topic: viz., rheological properties of fibers, of metals, and, in general, systems in which deformation occurs only on the application of very high stresses and then takes place at relatively slow rates.

<sup>139</sup> A. G. Ward and E. L. E. Westbrook, *J. Soc. Chem. Ind.*, **67**, 389-98 (1948); A. G. Ward and P. R. Freeman, *J. Sci. Instruments*, **25**, 387-96 (1948).

## 6. Surface-Active Agents

The addition of small quantities of a reagent to modify the working properties of a pigment dispersion is an expedient that has had long use. Commonly used materials include soaps, tallow, stearin pitches, waxes, gilsonite, etc. Since 1930 a variety of synthetic compounds have become commercially available. These materials greatly augment the number of reagents of possible utility.

Although the function of many of these additives is not clearly defined, one important result of their incorporation into a pigment-vehicle system is a change in flow properties. Other results may be of equal or greater importance, particularly in assessing the requirements for special uses to which the products may be put, but these can often be traced to the extent of comminution and deflocculation of the pigment. With this point of view it is possible to examine the numerous examples that have been presented in both the technical and the patent literature and to bring a measure of system into an admittedly confused subject.

The practical objectives in the use of surface-active materials and protective colloids are varied and can be stated as follows.

*Control of particle size during precipitation of pigments.* The addition of these reagents is usually intended to aid in keeping the size of the primary particles small.

*Control of pigment aggregates and wetting qualities.* Pigments that disperse with the minimum of mechanical work have been the objective of many pigment-manufacturing processes. Such "soft-grinding" pigments depend, often, on the presence of reagents that not only prevent the growth of hard aggregates but also modify the wetting qualities of the product and the properties associated with lower oil absorption. A shortened mixing cycle is a frequent objective.

*Control of consistency.* It is often desirable to decrease the yield value of a pigment dispersion or alternatively to increase the pigment content without greatly increasing the yield value. This result can be accomplished by deflocculating reagents.

*Control of settling.* For products in which hard pigment settling is likely, as in ready-mix paints, some flocculation of the suspended pigment is desirable. This requirement is frequently met by formulating the product with reagents that confer thixotropic flow properties.

*Derived properties.* Numerous secondary properties are frequently sought: higher gloss in enamels, control of flooding or floating of pigment mixtures, simpler handling in the factory, etc.

*Flushing from aqueous to oil dispersion.* The direct transfer of a pigment from an aqueous suspension to dispersion in oil frequently necessitates the use of surface-active agents. This topic is discussed in Chapter 12.

### Terminology

The nomenclature associated with surface-active agents needs some discussion because these compounds find many and varied applications, and terms with different connotations are now used. *Surface-active agent* is a general term applicable to the greatest variety of compounds and uses. *Wetting agent* implies that the substance produces improved spreading qualities for a liquid on a repellent surface. *Penetrating agent* suggests that the compound effects more rapid passage of a liquid into a porous solid. *Dispersing agent* is a term often applied to compounds that are added to suspensions and dispersions with the purpose of causing breakdown of aggregates or floccules. Where a process is primarily cleaning or removal of soiling materials, *detergent* is the appropriate term. *Emulsifying agent* is a compound that stabilizes the dispersion of one liquid in another where the two are immiscible. Since most of these compounds produce a temporarily stable mixture of air with a liquid, they may be called *foaming agents* when this property is the primary function.<sup>1</sup>

The theories for the action of surface-active compounds have led to other terms that have found their way into the patent and technical literature. Most commonly used, perhaps, is *polar* compound to designate a molecule that is capable of orientation or symmetrical arrangement at a surface in a definite direction as though under the action of a force. For complex molecules, composed of an inert or non-orienting portion in addition to a polar part, the hybrid term *polar-non-polar* is frequently used. With a somewhat different meaning the nearly unpronounceable term *amphipathic* molecule is suggested by Hartley.<sup>2</sup> An

<sup>1</sup> E. K. Fischer, *Soap Sanit. Chemicals*, **19**, No. 12, pp. 25-29, 53 (1943); **20**, No. 1, pp. 28-31, 67, 69 (1944).

<sup>2</sup> G. S. Hartley, *Aqueous Solutions of Paraffin-Chain Salts*, Herman & Cie, Paris, 1936.

amphipathic substance is one that has an affinity for two different materials (oil and water, for example) or phases. There is, in addition to these terms, the well-established designation *protective colloid*, used to describe substances that assist in stabilizing suspensions against coagulation or flocculation.

From the definitions noted above, it may be seen that there are two types of terms: one refers to the process in which a surface-active agent finds utility; the other pictures the role that the reagent assumes.

### Classes of Surface-Active Agents

Chemical compounds of great variety are included in the class of surface-active agents. Usually they are organic compounds. It is perhaps inevitable that the commercial products should range from clear-cut chemical compounds with known physical and chemical properties to materials or mixtures of completely unknown or undisclosed character. Many are extended with inert materials formed either as an incident in their manufacture or added as diluents to facilitate use.

Good lists of these compounds with trade names and, for a large number, an indication of the chemical composition are to be found in the literature.<sup>3</sup> The chemistry of surface-active agents has been discussed by various authorities,<sup>4</sup> and the whole field has been the subject of important symposia.<sup>5</sup> The monograph by Schwartz and Perry<sup>6</sup> is especially useful.

Any classification of surface-active compounds suffers, of course, from lack of precise information, but it is helpful to group the compounds commercially available as shown below.

1. Alcohols.
2. Fatty acids.
3. Ethers; ether-alcohols.
4. Esters.
5. Fatty alcohol sulfates.

<sup>3</sup> H. L. Cupples, *U. S. Dept. Agr., Bur. Entomol. Plant Quarantine, Bull.* E-504 (June, 1940); F. J. Van Antwerpen, *Ind. Eng. Chem.*, **35**, 126-30 (1943); J. W. McCutcheon, *Chem. Inds.*, November, 1947. See also, C. B. F. Young and K. W. Coons, *Surface-Active Agents*, Chemical Publishing Co., Brooklyn, N. Y., 1945.

<sup>4</sup> D. Price, *Ann. N. Y. Acad. Sci.*, **46**, 407-26 (1946); F. D. Snell, *Soap and Sanit. Chemicals*, **19**, No. 10, pp. 27-30, 31-33, 73 (1943); *Ind. Eng. Chem.*, **35**, 107-17 (1943).

<sup>5</sup> *Wetting and Detergency*, A. Harvey, London, 1937; "Conference on Surface-Active Agents," *Ann. N. Y. Acad. Sci.*, **46**, 347-530 (1946).

<sup>6</sup> A. M. Schwartz and J. W. Perry, *Surface Active Agents. Their Chemistry and Technology*, Interscience Publishers, Inc., New York, 1949.

6. Sulfonates: oils; aliphatic and aromatic compounds.
7. Nitrogen derivatives: amines, amides, quaternary ammonium salts.
8. Plant and animal extracts.
9. Inorganic compounds.
10. Unidentified; proprietary mixtures.

### Theory

The mode by which surface-active substances function cannot easily be generalized. Some of the conditions that determine the state of a suspended solid have been noted in previous chapters. In aqueous suspensions, a lowering of the surface tension facilitates wetting of the solid by water and, as a consequence, the displacement of entrained or sorbed gases on the solid surface is facilitated. For some pigments, particularly the organic toners, low surface tension is prerequisite, and without a suitable reagent the pigment masses into clumps which resist all efforts of mechanical dispersion, reforming again after mixing or grinding, but forming a uniform, fluid dispersion upon the addition of a surface-tension depressant.

Some of the reagents, however, do not appreciably lower the surface tension of water, and their action is probably more nearly that usually associated with the function of a protective colloid. A protective colloid functions, according to accepted colloid theories, because of its lyophilic or solvent-binding properties: the solvent-colloid combination is adsorbed on the particles, forming an envelope which serves as a bridge between the continuous phase and the particle, conferring stability by shielding the particle against flocculating influences such as electrolytes. The suspended particles may be considered as having assumed the properties of the colloidal substance. This concept has been highly fruitful in understanding many complex compositions.<sup>7</sup>

The role of micelles, formed by colloidal electrolytes, has been of great assistance in explaining the enhanced solubility of dyes in water. This view assumes that the particles enter the micellar structure, probably as molecules, reaggregating within the micelle in which they then remain suspended. It is difficult to extend the hypothesis of micelle

<sup>7</sup> The reader is referred to standard references on colloid chemistry for a more detailed discussion of protective colloid action. An early review by J. Alexander [*J. Soc. Chem. Ind.*, **28**, 280-5 (1909)] mentions numerous applications of protective colloids, and summaries of the experiments of many investigators may be found in H. Freundlich, *Kapillarchemie*, Leipzig, 1932; E. A. Hauser, *Colloidal Phenomena*, McGraw-Hill Book Co., Inc., New York, 1939; A. W. Thomas, *Colloid Chemistry*, McGraw-Hill Book Co., New York, 1934.

structures on solubilization to the deflocculation of pigment particles. However, the sizes of some particles are so small as to come within the realm of micellar dimensions, and the hypothesis should not be dismissed because of the present lack of experimental evidence.

There is, finally, the matter of the electric charges assumed by particles suspended in an aqueous system and the ion-exchange reactions that have been observed with materials such as carbon black in solutions of certain alkyl-aryl sulfonates. Particles carrying electric charges form stable suspensions partly because they are kept in a state of vigorous Brownian motion and the probability of collision and adhesion is minimized. When polyvalent ions of opposite charge are introduced, flocculation results. Ion-sequestering substances, such as sodium hexametaphosphate, are known to hold polyvalent ions and to prevent or inhibit their agglomerating effect on suspended particles.<sup>8</sup>

In dispersions of pigments in non-aqueous media the possibility of ionic reactions is largely excluded, and the explanation for the effect of surface-active agents requires consideration of other factors. The role of water in causing flocculation by forming a bridge between particles has already been noted. The explanation advanced is based on a lowering of the interfacial tension between the continuous phase and the water which forms the bond between particles. The evidence adduced, drawn from the properties of hydrophilic solids in non-aqueous media, lends some support for this view. It is possible, also, that the concept of a protective colloid may be applied. There is some evidence, further, for the existence of micellar structures in non-aqueous systems.<sup>9</sup>

The distinction between one substance that is designated as a protective colloid and another that is considered a wetting agent is not to be sharply drawn. Several arbitrary criteria can, however, be adduced; these may serve to clarify the function of the reagents. Protective colloids of the type of soluble gums (gum arabic, tragacanth, etc.), proteins (gelatin, casein, albumin, glue, etc.), glucosides (saponin) ordinarily show only a small reduction in surface tension of water and are, moreover, used in relatively large concentrations. Many surface-active agents, on the other hand, embody molecular structures, empirically selected, which are markedly effective in lowering the surface tension of water when added in very small quantities.

The quantity of reagent estimated as sufficient to form a monomolecular film at the pigment-vehicle interface has been considered the minimum required to cause a change in the flow properties of a dis-

<sup>8</sup> G. B. Hatch and O. Rice, *Ind. Eng. Chem.*, **31**, 51-57 (1939).

<sup>9</sup> A. S. C. Lawrence, *Trans. Faraday Soc.*, **34**, 660, 1938.

persion. Calculations of this quantity for commercial pigments have been published. These figures are based on a number of arbitrary assumptions including estimated specific surface values for the pigments and areas for the sorbed molecules. A further assumption is that all the active material is present at the pigment-vehicle interface and that none is present in solution in the continuous or vehicle phase. The computed figures are, accordingly, little more than a rough guide; they have the support, however, of some practical experience. Thus for most pigments less than 1 percent is an ample quantity; for pigments of fine particle size, such as certain organic toners and carbon black, a quantity up to 5 percent is required. Where protective colloids are employed to obtain maximum stability, quantities considerably greater are used.

The combination of small amounts of various substances with pigments isolated as dry powders is usually considered to take the form of a coating of the particles. This conception is widely held, but it should be recognized that there is no clear evidence that the reagent forms such a uniform envelope or shell around each pigment particle. In some cases, merely mixing the dry ingredients—pigment and reagent—gives essentially the same final result, and the pigment thus merely serves as a carrier for the reagent. Since the quantities of reagent are often quite large, exceeding by many times the amount theoretically required to form a monomolecular film, it is possible that a portion of the reagent is sorbed onto the pigment surface and the remainder precipitates in association with the particles. Where the treated pigment is used in an oil system, and an oil-soluble reagent has been used with the pigment, the final composition will undoubtedly contain some of the reagent in the continuous or vehicle phase and the amount at the pigment-vehicle interface will assume an equilibrium concentration. It should, therefore, be of small consequence whether a reagent forms a uniform envelope on the particle or whether the pigment serves as the medium by which a suitable surface-active material is introduced into the system.

## Experimental Studies

### Colloidal graphite

Graphite dispersions, prepared by Acheson's processes, have become widely known through their numerous applications.<sup>10</sup> The observations and experiments that led Acheson to the successful dispersion of graphite

<sup>10</sup> The term "Dag" associated with the commercial products is derived from "deflocculated Acheson graphite."



in water and in oil have been told by the inventor and by Szymanowitz.<sup>11</sup>

In an attempt to use clay as a binder for graphite in making crucibles, Acheson found that certain imported clays gave higher-strength crucibles, and he deduced that organic matter present in the clays changed the plastic flow properties. This was the explanation for the historic use of straw in brick making: extracts of straw produced a marked deflocculating action when clay was pugged in water. Acheson reasoned that sedimentary clays, which provided the best results, contained organic material, such as tannins, from the water that had seeped through forest and farm lands. This idea suggested the type of substances to use, and a variety of materials was found effective for the deflocculation of graphite in water, including straw, nutgalls, tea leaves, sumac, hemlock and oak bark, gallotannic acid, and catechu gum. Some of these are described in patents and will be found in the next section.

Acheson referred to the process of dispersion as deflocculation. He pictured the action of a deflocculating agent as follows: particulate solids are considered to be formed of colloidal units, held together with "surface forces," and to be highly porous, with capillaries and "submicro-capillaries" extending throughout; when immersed in a solution of a protective colloid, which is, in addition, surface active, the reagent will concentrate at the solid-liquid interfaces, and the solution will penetrate throughout the mass of capillaries, surrounding the colloidal aggregates, and imparting to them like electric charges; the component particles then are forced apart (presumably by the action of the solution) and, separated by the electric charges, remain suspended in the water.

Acheson states that the dispersion of a mass of powdered graphite by means of aqueous tannin solutions can be carried on with successive decantations of dispersed material and retreatments of the tailings until the entire mass of graphite has been suspended. No grinding is necessary, according to this report.

### Sedimentation phenomena

When a pigment powder is shaken or stirred with a liquid and then allowed to settle, the rate of settling and the final sedimentation volume indicate the extent to which the solid is flocculated. The sedimentation curve can also be used to determine the distribution of particle (aggregate)

<sup>11</sup> E. G. Acheson, *J. Ind. Eng. Chem.*, **4**, 62-64 (1912); "Deflocculated Graphite," Chapter 37, pp. 547-54, in *Colloid Chemistry*, Vol. III, J. Alexander, Editor, Chemical Catalog Co. (Reinhold Publishing Corp.), New York, 1931; R. Szymanowitz, *J. Chem. Ed.*, **16**, 413-21 (1939); "Colloidal Graphite," Chapter 19, pp. 436-58, in *Colloid Chemistry*, Vol. VI, J. Alexander, Editor, Reinhold Publishing Corp., New York, 1946.

sizes of the suspended particles. These methods have been used by a number of workers in analyzing pigment suspensions.

The experiments of Ryan, Harkins, and Gans<sup>12</sup> were performed with titanium dioxide, extended titanium dioxide pigments, zinc oxide, and zinc sulfide. Settling volumes were at the minimum when oleic acid or various metal soaps were present in benzene. The method was found sufficiently sensitive to compute the interfacial area of oleic acid, and this value corresponded with that of a monomolecular film. The final volume of 1 cc. of titanium dioxide in a flocculated suspension was 20 cc. in pure, dried benzene; when oleic acid, in quantity sufficient to form a monomolecular film was present, the sedimentation volume was 5 cc. Above a limiting minimum the molecules in the adsorbed film were judged to be in a tightly packed condition, oriented with the carboxyl groups toward the pigment surface and the hydrocarbon groups toward the benzene. Other non-polar liquids gave similar results. These investigators concluded that any chemically active pigment forms a monomolecular film of a soap when the pigment is immersed in a liquid that contains fatty acids. A non-reactive pigment adsorbs from solution whatever surface-active material is present to form a monomolecular film at the surface. The presence of water profoundly affected the sedimentation volume. Quantities of water of the order of 0.05 percent on the pigment caused flocculation which was not appreciably affected by the oleic acid. The concept of "wettability" is questioned by these authors.

Experiments by Damerell<sup>13</sup> and co-workers have contributed further information on sedimentation. Carbon black was found to adsorb lecithin, copper oleate, cobalt naphthenate, and sodium dioctyl sulfosuccinate. Oleic acid, however, was not adsorbed from xylene solution. For calcium sulfate and silica suspensions in hydrocarbons, the metal sulfosuccinates, naphthenates, and lecithin were found most effective. Damerell suggests that surface-active compounds facilitate dispersion by actual disruption of aggregates. The experimental evidence presented is taken from size analyses on suspensions in xylene.

### Rheological properties

A survey designed to explore more quantitatively the effect of surface-active agents on the flow properties of pigment dispersions has been

<sup>12</sup> L. W. Ryan, W. D. Harkins, and D. M. Gans, *Ind. Eng. Chem.*, **24**, 1288 (1932); W. D. Harkins and D. M. Gans, *Jour. Phys. Chem.*, **36**, 86-97 (1932).

<sup>13</sup> V. R. Damerell and A. Urbanic, *Jour. Phys. Chem.*, **48**, 125-33 (1944); V. R. Damerell and R. Mattson, *ibid.*, **48**, 134-41 (1944); V. R. Damerell, K. Gayer, and H. Laudenslager, *ibid.*, **49**, 436-42 (1945); V. R. Damerell and M. J. Vogt, *J. Phys. & Colloid Chem.*, **52**, 363-67 (1948).

made by the author in collaboration with C. W. Jerome.<sup>14</sup> In these tests, experiments were performed with a group of pigments, vehicles, and surface-active agents selected to represent types or representatives of each class of material. The pigments included titanium dioxide, ultramarine blue, carbon black, iron blue, toluidine toner, barium lithol toner. The vehicles included mineral oil, bodied linseed oil, an oil-modified phenolic resin in mineral solvent, and glycerol. Surface-active agents were selected to include at least one specimen from each major class. The dispersions were prepared by grinding on a roll mill, and rheological measurements were made on a rotational viscometer. The plan of the experiment was to scan the countless combinations of these ingredients in a feasible survey. The data are given in Tables I to V. (Plastic viscosity  $U$  is expressed in poises and yield value  $f$  in dynes per sq. cm.).

TABLE I. RHEOLOGICAL PROPERTIES OF ULTRAMARINE BLUE DISPERSIONS

Reagent	Ultramarine Blue					
	39.7% by volume in glycerol		32.0% by volume in mineral oil		43% by volume in linseed varnish	
	$U$	$f$	$U$	$f$	$U$	$f$
None (control)	41	0	46	1,900	100	580
Octyl ester sulfosuccinic acid (Na salt)	20	0	28	530	160	890
Dibutyl phenyl phenol sulfonate (Na salt)	41	0	46	6,700	130	890
Alkyl-aryl sulfonic acid (Na salt)	32	0	..	.....	131	880
Lauryl alcohol sulfate (Na salt)	51	0	50	7,200	130	2,300
Lecithin	65	7,700	23	74	110	3,500
Alkyl aryl sulfonate (Na salt)	37	0	..	.....	161	1,370
Secondary fatty alcohol sulfate (Na salt)	30	0	90	1,400	110	960
Zinc naphthenate	60	1,970	35	180	145	590
Water	..	.....	*	*	*	*

\* Too high to measure.

<sup>14</sup> E. K. Fischer and C. W. Jerome, *Ind. Eng. Chem.*, **35**, 336-43 (1943); E. K. Fischer, *Am. Ink Maker*, **21**, No. 3, pp. 23, 25-27; No. 4, pp. 19-23, 45 (1943).

TABLE II. RHEOLOGICAL PROPERTIES OF IRON-BLUE DISPERSIONS

Reagent	Iron Blue					
	29.8% by volume in glycerol		20% by volume in mineral oil		28% by volume in linseed varnish	
	<i>U</i>	<i>f</i>	<i>U</i>	<i>f</i>	<i>U</i>	<i>f</i>
None (control)	8.3	37	106	6,900	90	2,600
Octyl ester sulfosuccinic acid (Na salt)	8.3	260	32	5,500	78	2,200
Dibutyl phenyl phenol sulfon- ate (Na salt)	8.6	830	81	6,350	98	2,200
Alkyl aryl sulfonic acid (Na salt)	14 *	0	61	9,000	92	2,400
Lauryl alcohol sulfate (Na salt)	8.8	130	38	2,700	83	2,300
Lecithin	57	1,400	23	410	85	2,400
Alkyl aryl sulfonate (Na salt) <i>A</i>	8.8	130	74	6,600	84	1,800
Alkyl aryl sulfonate (Na salt) <i>B</i>	9.9	350	69	5,200	81	1,700
Diethyl amino ethyl stearyl acid amide	70	8,000	77	4,400	81	2,300
Secondary fatty alcohol sulfate (Na salt)	7.3	300	89	9,300	114	1,700
Zinc naphthenate	†	†	47	4,400	78	2,200
Water	.....	.....	†	†	†	†

\* Calculated at r.p.m. < 100; dilatant at higher speeds.

† Too high to measure.

TABLE III. RHEOLOGICAL PROPERTIES OF BARIUM LITHOL TONER DISPERSIONS

Reagent	Barium Lithol Toner					
	19.8% by volume in glycerol		34.2% by volume in linseed varnish		20.8% by volume in mineral oil	
	<i>U</i>	<i>f</i>	<i>U</i>	<i>f</i>	<i>U</i>	<i>f</i>
None (control)	31	1,120	90	3,080	40	2,100
Octyl ester sulfosuccinic acid (Na salt)	38	6,050	110	6,800	39	1,680
Dibutyl phenyl phenol sulfonate (Na salt)	13	4,380	120	5,310	37	2,640
Alkyl aryl sulfonic acid (Na salt)	27	865	105	7,080	42	2,880
Lauryl alcohol sulfate (Na salt)	7.3	220	110	7,520	43	2,600
Lecithin	44	8,260	79	2,690	35	1,100
Alkyl aryl sulfonate (Na salt) <i>A</i>	22	4,380	116	5,020	42	2,840
Alkyl aryl sulfonate (Na salt) <i>B</i>	6.1	0	127	2,060	41	2,450
Diethyl amino ethyl stearyl acid amide	69	12,700	63	4,370	45	2,550
Secondary fatty alcohol sulfate (Na salt)	43	7,120	.....	.....	41	1,780
Zinc naphthenate	95	19,100	66.8	8,400	48	2,260
Water	....	.....	168	7,360	56	6,540

TABLE IV. RHEOLOGICAL PROPERTIES OF CARBON BLACK DISPERSIONS

Reagent	Carbon Black					
	9.7% by volume in glycerol		11.6% by volume in mineral oil		15.3% by volume in linseed varnish	
	<i>U</i>	<i>f</i>	<i>U</i>	<i>f</i>	<i>U</i>	<i>f</i>
None (control)	3.0	3,800	45	7,300	57	10,400
Octyl ester sulfosuccinic acid (Na salt)	3.1	2,000	48	6,000	55	8,650
Dibutyl phenyl phenol sulfonate (Na salt)	8.4	1,550	44	7,100	69	8,260
Benzidine	17.0	5,870	47	7,700	53	770
Copper oleate	4.8	2,600	41	4,230	64	2,500
Alkyl aryl sulfonate (Na salt)	6.2	1,780	37	6,300	56	10,900
Lauryl alcohol sulfate (Na salt)	5.6	1,200	44	8,650	75	9,880
Gilsonite	....	. .	46	3,760	63	7,300
Petroleum residue	14.0	3,080	43	6,060	55	7,930
Lecithin	12.0	6,640	34	6,250	68	6,000
Alkyl aryl sulfonate (Na salt) <i>A</i>	6.1	1,390	40	7,500	66	7,200
Alkyl aryl sulfonate (Na salt) <i>B</i>	6.9	1,250	42	7,020	53	9,620
Secondary fatty alcohol sulfate (Na salt)	4.4	820	40	7,100	65	10,700
Zinc naphthenate	21.0	4,100	38	5,960	69	8,060
Water	....	.....	..	.....	70	8,850

TABLE V. CHANGE IN FLOW PROPERTIES OF PIGMENT DISPERSIONS ON ADDITION OF WATER

Reagent	Before Water Addition		After Water Addition	
	<i>U</i> (poises)	<i>f</i> (dynes/sq.cm.)	<i>U</i> (poises)	<i>f</i> (dynes/sq.cm.)
26% Titanium Dioxide by Volume in Mineral Oil				
None (control)	*	*	*	*
Zinc naphthenate	35	2,900	53	4,400
Lecithin	22	1,300	18	1,500
Octyl ester sulfosuccinic acid (Na salt)	40	3,600	31	3,200
31% Titanium Dioxide by Volume in Bodied Linseed Oil				
None (control)	58	740	*	*
Zinc naphthenate	44	780	60	1,440
Lecithin	68	8,200	50	10,000
Octyl ester sulfosuccinic acid (Na salt)	61	3,400	55	6,400
27% Ultramarine Blue by Volume in Bodied Linseed Oil				
None (control)	33	1,000	*	*
Lecithin	24	0	25	90
Octyl ester sulfosuccinic acid (Zn salt)	19	220	170	4,100

\* Too high to measure.

A number of conclusions were drawn from these experiments. The greatest reduction in yield value was observed where the pigment and the vehicle were of different wetting characteristics. Thus when titanium dioxide and ultramarine blue (as examples of pigments that could be easily dispersed in water) were ground in mineral oil, rather high yield values resulted. The addition of zinc naphthenate and lecithin produced a marked lowering of yield value. In glycerol, on the other hand, ultramarine blue was deflocculated and the addition of these same reagents caused an increase in consistency. Other surface-active agents of the water-soluble type caused, in general, no change in properties of this dispersion. Carbon black in lithographic varnish was markedly changed by the addition of benzidine base and copper oleate. This pigment in glycerol dispersion was more effectively deflocculated by several of the water-soluble surface-active agents.

The effect of water on the flow properties of these pigment dispersions is shown. Only with carbon black is there a slight decrease of yield value. The manner in which surface-active agents can protect a dispersion against the flocculating effect of water is shown in Table V.

Tinting-strength determinations were made on most of the dispersions. In general it was found that no appreciable difference in strength could be attributed directly to the use of a surface-active agent or protective colloid. However, the change in flow properties, by affecting the efficiency of mill operation, could alter the final strength values (Table VI). That surface-active agents increase the rate of dispersion and lead,

TABLE VI. RELATION OF PIGMENT STRENGTH TO PLASTIC VISCOSITY (THREE-ROLL MILL DISPERSIONS)

	Number of Experiments	
	Colors *	Carbon black †
Increase in plastic viscosity	76	64
Increase in strength	74	104
Decreased or unchanged plastic viscosity	87	152
Decrease or no change in strength	89	112

\* Includes toluidine toner, iron blue, ultramarine blue.

† Includes "long" and "short" carbon blacks.

in addition, to a higher final tinting strength is a claim sometimes presented. The complexity of the dispersion process excludes any simple generalization. Evaluation must be based on a consideration of (1) the type of dispersion operation, (2) the rate of output as compared with a control dispersion, and (3) the rheological properties of the dispersion.

### Mechanical dispersion

Several laboratory studies of the effect of surface-active agents on pigment dispersions in paint vehicles have been reported. One of the first reports on this subject dealt primarily with 15 pigments and 5 vehicles of interest in paint manufacture.<sup>15</sup> Zinc naphthenate, lecithin, and a sulfonated mineral oil proved generally most useful in ratings that included lowering of consistency, grinding, and several paint-application factors. Titanium dioxide exhibited the greatest changes, and the majority of surface-active materials were useful with this pigment. On the other hand, organic pigments—lithol, toluidine, and para reds—were unaffected by the reagents. All the results obtained on different mills were comparable, indicating that the method of dispersion was of secondary importance. Further work along similar lines was reported somewhat later.<sup>16</sup> It was observed that the major effect on the dispersion was deflocculation of the pigment. The time for comminution

<sup>15</sup> New York Club, *Nat. Paint Varnish Lacquer Assoc., Sci. Sect., Circ.* 495, pp. 376-87 (1935).

<sup>16</sup> Detroit Club, *ibid.*, *Circ.* 604, 303-13 (1940).



of pigments on different mills was not appreciably affected, although the actual grinding time on roll mills was increased when the reagent caused a marked reduction in consistency. It was emphasized that no reagent acted as a "dispersing" agent, with the implication that the amount of mechanical work was decreased because of its presence: fineness was the same as the control for all the dispersions. Finally, hard settling of the dispersed material was observed when the pigment was deflocculated. These results are concordant and consistent.

Additional information and recommendations on the mechanical aspects of this subject are given in the paper cited previously.<sup>14</sup> For roll-mill dispersion, as typified by the three-roll mill, disintegration of aggregates is accomplished first by an actual crushing of particles, 10 microns and larger in size, at the start of a batch grinding operation, and finally by shearing within the plastic mixture; shearing reduces the aggregate size to the dimensions of ultimate pigment particles less than 1 micron in diameter. Internal friction resulting from flocculation of the pigment particles is of small comparative magnitude and may be considered negligible. The output of a roll mill is directly proportional to the viscosity of the mix when roll clearance and operating speeds remain constant. Surface-active agents that increase the plastic viscosity, act to increase mill output rates, and the addition of these reagents is a useful production device. Essentially the same result may be obtained, however, by formulation with higher viscosity oils, by increase in the pigment content, or both, using preferably a deflocculating combination of vehicles and reagents. When the dispersion is satisfactory, the product can be extended with additional vehicle to give the desired pigment-vehicle ratio.

Somewhat different considerations apply to colloid-mill and to ball-and pebble-mill operation. The mixture introduced into gravity-feed colloid mills should be fluid, since any appreciable yield value will markedly reduce the rate at which the dispersion will flow into the mill. In ball and pebble mills the mixture should allow cascading of the grinding medium, and if the yield value is excessively high the balls or pebbles will pack, especially in small mills, with consequent reduction in attrition.

It is evident that an improved dispersion rate resulting from an increase in mill efficiency by the addition of surface-active agents is a secondary effect of such reagents. Final pigment tinting strength appears to be directly related to the change in plastic viscosity of the mixture produced by the addition of surface-active agents. This is shown by the statistical data in Table VI. The strength differences in this series were in the range of 2 to 10 percent, sufficiently large to be outside

the errors of the measurement. Although no direct experimental evidence has been obtained to show that surface-active agents facilitate the breakdown of pigment aggregates during milling, such a result is, nevertheless, not unlikely. The data for carbon black suggest that with this pigment at least a favorable effect is found, and the statement of Acheson for graphite dispersion noted above lends credence to this possibility.

### Methods of addition

The several methods by which surface-active agents may be incorporated are of considerable practical interest. The most common procedure is to mix all ingredients, including surface-active agents, by means of a dough mixer or change-can mixer. This procedure, designated *A*, follows manufacturing practice in the paint and printing ink industries. Other methods include the following: *B*, solution or dispersion of the reagent in the vehicle; *C*, addition of the reagent to a pigment dispersion already prepared; and *D*, treatment of the pigment, either during processing or after separation as a dry powder, to incorporate the reagent with the pigment. The last method is often considered "coating" the pigment. All these methods and numerous variations are used. Experiments illustrating the four procedures noted above are described in Table VII. All methods give results that are comparable, but the effects differ in degree. Reagents oxidized by exposure to air will yield products whose properties depend to a greater extent on the method of addition.

### Practice

The practice of the application of surface-active agents and protective colloids in pigment dispersion is shown in a large group of patents. Illustrations are given in the patents cited below, and, although this survey is probably incomplete (since relevant information may be included, for example, in patents on the synthesis of certain reagents), it will serve to show the variety of substances that are claimed. The reader is urged to consult the original patents for details, particularly if some legal interpretation is to be made. Patents covering reagents for the transfer of pigments from dispersion in water to oil are described in Chapter 12 on flushed colors and are not repeated in the discussion immediately following.

### Soaps and fatty acids

Various organic compounds and particularly the fatty substances have long been used in preparing pigments with modified properties. The

TABLE VII. METHOD OF INCORPORATING SURFACE-ACTIVE AGENTS

Pigment	Pigment Concentration (vol. %)	Vehicle	Reagent	Yield Value in Dynes/Sq. Cm. *					
				Control	Method A	Method B	Method C	Method D	
Ultramarine	20.8	Mineral oil	Zinc naphthenate †	3,000	120	90	100	0	
Ultramarine	37.0	Phenolic resin varnish	Alkyl aryl sulfonate †	3,800	120	0	240	710	
Toluidine toner	22.0	Glycerol	Alkyl aryl sulfonate †	620	0	0	0	0	
Toluidine toner	27.3	Mineral oil	Lecithin †	1,150	550	660	560	220	
Iron blue	24.3	Mineral oil	Lecithin †	10,000	2,580	1,770	2,600	770	
Carbon black									
Short	13.7	Linseed varnish	Benzidine †	1,100	330	260	400	430	
Long or flow	9.0	Phenolic resin varnish	Lecithin †	620	160	160	140	500	
Short	9.8	Mineral oil	Gilsonite †	970	660	430	770	970	
Long or flow	13.7	Linseed varnish	Zinc naphthenate †	350	290	290	260	660	

\* A, all ingredients mixed and ground; B, reagent in vehicle; C, reagent added to dispersion after grinding; D, coating pigment.

† 3% on pigment by weight.

‡ 5% on pigment by weight.

variety of compounds specified in patents is great, and there is, moreover, considerable overlapping. Johnson<sup>17</sup> describes a procedure for treating pigments for distemper colors in which the pigment is merely ground in an aqueous suspension with glue or gums, dried in shallow pans, and pulverized. A more complicated process is given by Breinig<sup>18</sup> in which a rosin-soap solution is used to emulsify a typical paint vehicle (linseed oil plus resins). Pigment is then added, the mixture boiled, and finally the composite dried. In another early patent, Ramage<sup>19</sup> causes lead oxide to react with soaps (e.g., sodium stearate) or stearic acid by fusion.

Rosin has long been used with pigments, particularly with some of the organic toners. The advantages are numerous, as has been pointed out by Campbell.<sup>20</sup> The rosin is added as a soluble soap and in this form assists materially in the solution of the intermediates. During laking with calcium or barium salts, water-insoluble resinate is formed, causing flocculation of the pigment in the aqueous suspension and assisting in rapid filtration and washing. Drying proceeds without the formation of hard aggregates, so that the product is readily dispersed in film-forming vehicles and provides dried films of high gloss. The use of resins with pigments has been discussed at greater length by Weisberg<sup>21</sup> who criticizes the concept of a "coated" pigment particle, pointing out that adsorption of the colloiddally dispersed rosin soap begins at the earliest stages of precipitation and that the rosin is associated with the character of the aggregates that form during processing.

Resinated pigments, as they are generally termed in the pigment trade, exhibit reduced bronziness and are usually of cleaner hue. They often appear more transparent and produce glossier films when formulated in printing ink vehicles. The advantages of the resin treatment are most apparent with lithol, red lake C, and phloxine toners. Numerous other organic pigments are resinated and the process has been applied, as will be noted below, to some inorganic pigments.

The amount of rosin and soaps formed by reaction with the abietic acid present varies from quantities of the order of 1 percent or less to about 20 percent. Allen and Siegel,<sup>22</sup> for example, mention very high concentrations (to 50 percent) in order to obtain colors free of optical bronz-

<sup>17</sup> H. M. Johnson, U. S. Patent 99,907 (February 15, 1870); Reissue 5,510 (July 29, 1873).

<sup>18</sup> R. M. Breinig, U. S. Patent 304,902 (September 9, 1884).

<sup>19</sup> A. S. Ramage, U. S. Patent 982,992 (January 31, 1911).

<sup>20</sup> G. A. Campbell, "The Wetting of Pigments," pp. 107-16, in *Wetting and Detergency*, A. Harvey, London, 1937.

<sup>21</sup> H. E. Weisberg, *Am. Ink Maker*, **18**, No. 12, pp. 24-26, 33 (1940).

<sup>22</sup> E. R. Allen and A. Siegel, U. S. Patent 1,772,300 (August 5, 1930); Reissue 18,590 (September 6, 1932).

ing effects. In a later disclosure, Siegel<sup>23</sup> observes that the flow properties of phthalocyanine pigments when dispersed in lithographic varnishes are changed from a "buttery" to a more fluid condition when the pigment is intimately mixed with a metallic resinate (barium resinate).

Insoluble rosin derivatives are mentioned in a series of patents by Siegel<sup>24</sup> for treating azo lakes and pigments. These include oxidized, chlorinated, nitrated, "arylated," and hydrogenated rosins. Natural gums and balsams are noted for the same purpose.<sup>25</sup> Combinations of abietic and fatty acid soaps, detailed by O'Neal,<sup>26</sup> are prepared and mixed with pigment powders before dispersion in oleoresinous vehicles. Because of the availability and low cost of fatty acids, these materials have been fully exploited. The superior wetting properties of paint vehicles containing some free fatty acid is shown in the early disclosures of Blakeman<sup>27</sup> in which vegetable oils are hydrolysed for this purpose. O'Brien<sup>28</sup> mentioned oleic, stearic, and palmitic acids, as well as alginates for lithopone and other pigments to provide soft, non-aggregated powders. It is entirely probable that part of the zinc in the lithopone reacts to form a zinc soap *in situ*. Processes designed to facilitate reaction of lithopone with fatty acids are described by Baldwin.<sup>29</sup> Zinc oxide can be processed by spraying with coconut fatty acids at an elevated temperature.<sup>30</sup>

Stearic acid is used as a leafing agent to coat flake metallic pigments such as aluminum, bronze, and lead powders. Application of stearic acid by condensation of the vapor on metallized mica flakes is described by Castor.<sup>31</sup> Various reagents to stabilize metal-paste dispersions are described by McMahan<sup>32</sup> and Wampner.<sup>33</sup> For the dispersion of zinc

<sup>23</sup> A. Siegel, U. S. Patent 2,173,699 (September 19, 1939).

<sup>24</sup> A. Siegel, U. S. Patents 2,013,074; 2,013,075; 2,013,076; 2,013,077 (September 3, 1935); A. M. Erskine and A. Siegel, U. S. Patent 2,013,090 (September 3, 1935); E. R. Allen, W. N. Headley, and A. Siegel, U. S. Patent 2,013,084 (September 3, 1935).

<sup>25</sup> W. N. Headley and A. Siegel, U. S. Patents 2,013,099 and 2,013,100 (September 3, 1935).

<sup>26</sup> G. M. O'Neal, U. S. Patent 2,350,525 (June 6, 1944).

<sup>27</sup> W. N. Blakeman, U. S. Patents 883,514; 883,515; 883,516 (March 31, 1908).

<sup>28</sup> W. J. O'Brien, U. S. Patents 1,832,416; 1,832,417; 1,832,418 (November 17, 1931); 2,068,066 (January 19, 1937).

<sup>29</sup> J. T. Baldwin, U. S. Patents 1,946,052; 1,946,053; 1,946,054; 1,946,055 (February 6, 1934).

<sup>30</sup> F. B. Gearhart and F. A. Steele, U. S. Patent 2,065,687 (December 29, 1936).

<sup>31</sup> W. W. Castor, U. S. Patent 2,387,243 (October 23, 1945).

<sup>32</sup> E. L. McMahan, U. S. Patents 2,178,179; 2,178,180; 2,178,181 (October 31, 1939).

<sup>33</sup> H. L. Wampner, U. S. Patents 2,240,151 (April 29, 1941); 2,340,280 (January 25, 1944); 2,345,956 (April 4, 1944).

oxide in rubber, "coatings" of zinc acetate<sup>34</sup> and zinc propionate<sup>35</sup> are said to be advantageous. Fatty, naphthenic, abietic and other acids, as well as soaps of these acids are mentioned in various other disclosures.<sup>36-44</sup>

A water-soluble soap is used to treat calcined lithopone in the disclosure of Booge and Hanahan<sup>45</sup> for the purpose of improving the mixing and dispersing properties of the pigment in paint vehicles. A somewhat more involved procedure, patented by Oppermann,<sup>46</sup> is based on deflocculation of a pigment such as lithopone or titanium dioxide by grinding in an aqueous slurry with 0.01 to 0.5 percent soluble phosphate (e.g., sodium pyrophosphate) as a deflocculant, addition of 0.1 to 2.0 percent of a soap such as sodium naphthenate or sodium soap of coconut fatty acids, acidification of the slurry, and drying.

The compounds listed by Meister<sup>47</sup> include stearates of aluminum, lead, and zinc and fatty esters of ethylene glycol, all of which are miscible with paint vehicles. These compounds are dissolved in a suitable organic solvent which is added to the pigment slurry.

A somewhat different insoluble soap is described by Auer<sup>48</sup> for use as a flattening agent. For this product the melting point of rosin is raised by hydrogenation or condensation with maleic anhydride, and it is then used to form soaps of aluminum, zinc, magnesium, and the alkaline-earth metals. The soaps so formed are finely divided and "coated" with methyl cellulose, casein gums, etc. As flattening agents these products are reported to be quite transparent and to remain in suspension in nitrocellulose lacquer compositions.

Other soaps are mentioned in patent disclosures for specific purposes. Chromium naphthenate is used to improve the chalk resistance of ti-

<sup>34</sup> H. M. Cyr, U. S. Patent 2,348,883 (May 16, 1944).

<sup>35</sup> B. R. Silver and E. R. Bridgwater, U. S. Patent 2,303,330 (December 1, 1942).

<sup>36</sup> F. Risse, H. E. Wohlers, M. Paquin, U. S. Patent 1,832,242 (November 17, 1931).

<sup>37</sup> J. W. Lang, U. S. Patent 2,365,479 (December 19, 1944).

<sup>38</sup> H. A. Toulmin, Jr., U. S. Patent 2,408,353 (September 24, 1946).

<sup>39</sup> C. M. Dann, U. S. Patent 2,287,416 (June 23, 1942).

<sup>40</sup> V. Giambalvo, U. S. Patent 2,262,229 (November 11, 1941).

<sup>41</sup> C. E. Berry, U. S. Patent 2,274,521 (February 24, 1942).

<sup>42</sup> M. A. Dahlen and S. R. Detrick, U. S. Patent 2,291,452 (July 28, 1942).

<sup>43</sup> H. A. Endres, U. S. Patents 1,919,714 and 1,919,715 (July 25, 1933).

<sup>44</sup> A. M. Erskine and A. Siegel, U. S. Patent 2,013,092 (September 3, 1935).

<sup>45</sup> J. E. Booge and M. L. Hanahan, U. S. Patent 1,722,174 (July 23, 1929).

<sup>46</sup> C. F. Oppermann, U. S. Patent 2,266,793 (December 23, 1941).

<sup>47</sup> W. F. Meister, U. S. Patent 2,113,539 (April 5, 1938).

<sup>48</sup> L. Auer, U. S. Patents 2,363,489 (November 28, 1944) and 2,364,611 (December 12, 1944).

tanium dioxide.<sup>49</sup> Other naphthenates mentioned for improved pigment texture are ammonium naphthenate,<sup>50</sup> various salts of naphthenic acid<sup>51,52</sup> and the esters and amides of naphthenic acid.<sup>53</sup>

Water-repellent ultramarine blue is prepared by precipitating a soap of a polyvalent metal on the pigment.<sup>54</sup>

Lead, zinc, and calcium soaps are also used to render aluminum powder non-leafing.<sup>55</sup> To facilitate the dispersion of carbon black, organic compounds of copper,<sup>56,57</sup> and nickel, cobalt, and iron<sup>58</sup> are efficacious. The compounds mentioned are oleates, naphthenates, and salicylates. The alkaline-earth metal soaps are also specified for cellulose-ether dispersions of carbon black.<sup>59</sup> Lead and zinc naphthenates, zinc resinate, and synthetic surface-active agents are used for deflocculation of pigments in the vehicles, composed of waxes and thermoplastic resins, used in formulating heat-set printing inks.<sup>60</sup>

### Oils

Various oils are mentioned for modifying pigments. Booge<sup>61</sup> specified sulfonated castor oil. Oils in quantities computed to form a monomolecular film are specified by Crouet,<sup>62</sup> and inert mineral oils, sufficient to confer hydrophobic properties, are mentioned by Greubel.<sup>63</sup> For calcium carbonate, tall oil, added before filtration of the pigment at elevated temperatures, is used by Gage.<sup>64</sup> For fine-particle-size calcium carbonate and silicate intended for rubber reinforcing, coconut oil and tall oil are used.<sup>65</sup> To confer chalk-resistant properties on titanium dioxide, phthalic anhydride<sup>66</sup> and the dimethyl, diethyl, and diphenyl esters of phthalic acid are mentioned.<sup>67</sup>

<sup>49</sup> G. F. New, U. S. Patent 2,242,320 (May 20, 1941).

<sup>50</sup> H. E. Burdick, U. S. Patent 2,294,381 (September 1, 1942).

<sup>51</sup> R. W. Sullivan, U. S. Patent 2,254,630 (September 2, 1941).

<sup>52</sup> A. A. Brizzolara, U. S. Patent 2,062,159 (November 24, 1936).

<sup>53</sup> A. M. Erskine and B. H. Perkins, U. S. Patent 2,294,394 (September 1, 1942).

<sup>54</sup> H. F. Dieterle, U. S. Patent 2,323,748 (July 6, 1943).

<sup>55</sup> G. R. Babcock, U. S. Patent 2,309,377 (January 26, 1943).

<sup>56</sup> C. W. Sweitzer, U. S. Patent 1,987,980 (January 15, 1935).

<sup>57</sup> H. E. Stone, U. S. Patent 2,021,949 (November 26, 1935).

<sup>58</sup> R. L. Zapp, U. S. Patent 2,173,444 (September 19, 1939).

<sup>59</sup> R. L. Zapp, U. S. Patent 2,173,445 (September 19, 1945). Brit. Patent 517,640.

<sup>60</sup> J. K. Boggs, U. S. Patent 2,361,740 (October 31, 1944).

<sup>61</sup> J. E. Booge, U. S. Patent 1,722,174 (July 23, 1929).

<sup>62</sup> J. Crouet, U. S. Patent 2,077,167 (April 13, 1937).

<sup>63</sup> P. W. Greubel, U. S. Patent 2,245,104 (June 10, 1941).

<sup>64</sup> F. Gage, U. S. Patent 2,345,191 (March 28, 1944).

<sup>65</sup> A. E. Boss, *Chem. Eng. News*, **27**, 677-79 (1949).

<sup>66</sup> H. A. Gardner, U. S. Patent 2,172,505 (September 12, 1939).

<sup>67</sup> J. M. Jarmus and W. W. Flechner, U. S. Patent 2,291,082 (July 28, 1942).

### Insoluble resins

Resin coatings offer, perhaps, one of the most promising methods for modifying pigment properties. Widmer<sup>68</sup> precipitates resins of the urea-formaldehyde type in the pigment slurry, and, after thermo-setting of the resin, the product is reduced to a fine powder. Such processes usually result in a rather large increase in particle size, and the claim that the pigments are rendered insoluble in organic solvents is never fully realized, for the pigment-resin matrix so formed is sufficiently porous to allow the solvent to reach the pigment. The idea of a resin-treated pigment, nevertheless, is of considerable value in cementing two pigments of dissimilar properties into a unit, with the result that the pigment matrix greatly reduces flooding.

The idea of a matrix pigment is used by Randolph<sup>69</sup> who describes a procedure in which the mixed pigments are dispersed in a cellulose nitrate solution and, after evaporation of solvents, the mixture is pulverized. When the matrix pigment is incorporated into a paint vehicle in which the cellulose nitrate binder is insoluble, flooding is minimized.

Zinc oxide treated with a polymerized, insoluble alkyd resin is described by Depew;<sup>70</sup> pigments of the phosphotungstate acid lake type are treated with rosin or terpene hydrocarbon resins in order to make them suitable for dispersion in moisture-set printing inks.<sup>71</sup>

The idea of coating a bronze powder is described in an earlier patent by Oeser.<sup>72</sup> The pulverized material is mixed with a rapidly drying varnish, and the suspension is then spray-dried. By coating a metal powder with urea-formaldehyde resin, resistance to tarnishing is improved.<sup>73</sup> Cellulosic compounds can be used as materials for coating. Hanahan<sup>74</sup> uses an alkaline cellulose solution (e.g., xanthate) which is precipitated by acidifying. The gel-like precipitate is said to give enhanced hiding power to white pigments.

### Nitrogen compounds

Various amines, amides, and quaternary ammonium salts are listed for treating pigments.

Amines are singularly effective reagents for the deflocculation of car-

<sup>68</sup> G. Widmer, U. S. Patent 2,119,189 (May 31, 1938).

<sup>69</sup> W. G. Randolph, U. S. Patent 1,942,491 (January 9, 1934).

<sup>70</sup> H. A. Depew, U. S. Patent 2,277,393 (March 24, 1942).

<sup>71</sup> D. R. Erickson and P. J. Thoma, U. S. Patents 2,327,595; 2,327,596; 2,327,597 (August 24, 1943).

<sup>72</sup> E. Oeser, U. S. Patent 976,594 (November 22, 1910).

<sup>73</sup> C. J. Ryan, U. S. Patent 2,303,504 (December 1, 1942).

<sup>74</sup> M. L. Hanahan, U. S. Patents 2,321,467 and 2,321,468 (February 11, 1941).



bon black in cellulose esters and oleoresinous vehicles. They are, moreover, among the few compounds that are useful as deflocculants for this pigment. Wiegand<sup>75</sup> lists the following as useful amines: triethanolamine, diphenyl guanidine, diorthotolyl guanidine, phenyl orthotolyl guanidine, and combinations of these amines with fatty or resin acids. Several methods for treating the pigment may be used: (1) mixing a solution of the amine with the pigment and evaporating the solvent; (2) spraying the pigment with a solution of the amine; (3) distributing the amine by mixing a small portion of pigment with the amine and then extending the concentrate so prepared with the whole quantity of pigment. From 1 to 5 percent of the reagent is the range in which satisfactory results may be expected. Amines mentioned by Vogel,<sup>76</sup> also for treating carbon black intended for dispersion in oleoresinous vehicles, are triethylenetetramine, metaphenylenediamine, diethylene triamine, ethylene diamine, and benzidine. Vogel combines copper soaps with aromatic polyamines for dispersion in nitrocellulose. For this purpose the aromatic amines are preferred. Several well-known dye intermediates are effective: rosaniline base, Bismarck brown, induline and chrysoidin bases.

Deflocculation of carbon black in wax vehicles, intended for carbon-paper coatings, is accomplished in similar fashion by the addition of induline base and methyl violet dye.<sup>77</sup>

Amines are useful as deflocculating reagents for pigments other than carbon black. A variety of compounds, formed by the action of alkylene diamines on fatty acids or fats, is specified by Friedrich and Droste.<sup>78</sup> For calcium sulfate pigments, Kingsbury and Schultz<sup>79</sup> treat the pigment with aliphatic amines such as tetraethylene pentamine, diethylene triamine, diethylaminoethanol, and triethylene tetramine. Free amines are mentioned by Sloan and Patterson<sup>80</sup> chiefly for phosphotungstic acid lakes and lead pigments. The term free amine is rather broadly interpreted to include any compound with one amino nitrogen group capable of forming salts with acids. The quantities required range from 1 to 8 percent, computed on the pigment, for phosphotungstic acid pigments and about one-fourth of this quantity for lead pigments. Polyhydroxy amines derived from reducing sugars are also mentioned

<sup>75</sup> W. B. Wiegand, U. S. Patent 1,848,213 (March 8, 1932).

<sup>76</sup> M. R. Vogel, U. S. Patents 2,173,430 (September 19, 1939) and 2,190,461 (February 13, 1940).

<sup>77</sup> W. F. Goepfert, U. S. Patents 2,392,657 and 2,392,658 (January 8, 1946).

<sup>78</sup> H. Friedrich and W. Droste, U. S. Patent 1,927,117 (September 19, 1933).

<sup>79</sup> F. L. Kingsbury and F. J. Schultz, U. S. Patents 2,341,994 (February 15, 1944); 2,365,560 (December 19, 1944).

<sup>80</sup> C. K. Sloan and G. D. Patterson, U. S. Patent 2,192,955 (March 12, 1940).

by the same inventors.<sup>81</sup> These compounds are typified by glucamine which is prepared by reacting glucose, ammonia, and hydrogen under pressure with the aid of catalysts.

Polyalkanol amines, reacted with fatty acids, are used in conjunction with emulsified hydrocarbons (e.g., toluene) to produce soft-process pigments by Detrick and Lang.<sup>82</sup> Phthalocyanine and vat-dye pigments produced by this method contain a residue of the amine soap which facilitates dispersion in oily media. Morrison and Perkins<sup>83</sup> mention a petroleum nitrogen base for a comparable process. Cationic reagents are mentioned also for soft-grinding pigments.<sup>84</sup> These reagents include quaternary ammonium, sulfonium, and phosphonium compounds containing an aliphatic radical of at least 8 carbon atoms. An extension of this idea is to be found in a further disclosure of Sloan<sup>85</sup> in which a long-chain alkylammonium halide is added to an aqueous pigment slurry and, after agitation, this reagent is followed by a sodium soap and barium hydroxide. This process is said to be particularly well adapted for white pigments that can be dispersed into paint vehicles by mixing.

The gloss of titanium dioxide paints is said to be improved when the pigment contains about 0.5 percent trialkylphenyl or trialkylphenylene ammonium hydroxide.<sup>86</sup>

Free amines present in pigment dispersions that are intended for air-dry finishes may seriously prolong drying times because of the inhibiting action of the amine. Adjustment of the drier content in the final formulation is necessary.

### Protective colloids

The materials forming this class of substances are extremely varied. In most respects they may be classed as lyophilic colloids, and many natural products are used. Hoffman<sup>87</sup> has listed substances of demonstrated utility. More recently, additional materials that have become available are methyl cellulose, carboxy methyl cellulose, polyvinyl alcohol, etc. These substances are usually employed in conjunction with highly surface-active materials when a high degree of water dispersibility is required.

In the manufacture of colored pigments, protective colloids aid in

<sup>81</sup> C. K. Sloan and G. D. Patterson, U. S. Patent 2,192,953 (March 12, 1940).

<sup>82</sup> S. R. Detrick and J. W. Lang, U. S. Patent 2,305,379 (December 15, 1942).

<sup>83</sup> J. O. Morrison and B. H. Perkins, U. S. Patent 2,282,303 (May 12, 1942).

<sup>84</sup> C. K. Sloan and G. D. Patterson, U. S. Patent 2,192,956 (March 12, 1940);

C. K. Sloan, U. S. Patent 2,282,006 (May 5, 1942).

<sup>85</sup> C. K. Sloan, U. S. Patent 2,296,066 (September 15, 1942).

<sup>86</sup> J. B. Sutton, U. S. Patent 2,226,147 (December 24, 1940).

<sup>87</sup> E. Hoffman, *Kolloid-Z.*, **83**, 221-29; 324-31 (1938).

keeping the particle size small. Alexander<sup>88</sup> mentions glue, gelatin, and gum arabic for this purpose, adding the protective colloid to all the solutions used in precipitating the pigment. Jones<sup>89</sup> uses protective colloids during the precipitation of lead carbonate, and the combination of a surface-active agent with the protective colloid is the subject of an extension of this idea.<sup>90</sup>

To obtain a finely divided pigment powder Allen and Kaufmann<sup>91</sup> prepare a froth of the aqueous pigment suspension by adding licorice, saponin, soap-bark extracts, or soap and beating the mixture until a uniform foam results. When the foam is dried a powder is obtained which disperses in water. Bishop and Thompson<sup>92</sup> disperse a pigment in a foam produced by agitating a solution of soap, dextrin, and sucrose; where the pigment is dried it can be dispersed in water by stirring. Simpler procedures are described by Crossley, Kienle, and Royer.<sup>93</sup> Protective colloids such as dextrin and surface-active agents, such as sulfonated naphthalene derivatives, are mixed with pigment suspensions in a dough mixer; after a uniform distribution of the components has been accomplished, the mixture is dried, preferably in a vacuum, until about 95 percent of the total water has been removed. Hygroscopic substances (e.g., glycerine, ethyl ether of diethylene glycol) are added in small quantities to reduce dusting. Relatively large proportions of dextrin are specified. For example, the phosphotungstic acid lake of methyl violet is combined with an equal weight of dextrin. Water-dispersible sulfur is prepared in a similar way by mixing an aqueous slurry of sulfur with polythionic acid in conjunction with sugars (sucrose, maltose, dextrose) or polyhydric alcohols (glycerine, propylene glycol). Lactose, brown sugar, and similar substances in combination with surface-active agents are mentioned by O'Brien.<sup>94</sup> Various types of surface-active agents are specified by other inventors for water-dispersible pigments.<sup>95, 96, 97</sup>

<sup>88</sup> J. Alexander, U. S. Patent 1,259,708 (March 19, 1918).

<sup>89</sup> L. D. Jones, U. S. Patent 1,854,744 (April 19, 1932).

<sup>90</sup> F. Gunther, F. Teller, C. Immerheiser, and B. Zschimmer, U. S. Patent 1,802,174 (April 21, 1931).

<sup>91</sup> E. R. Allen and W. E. Kaufmann, U. S. Patent 1,665,945 (April 10, 1928).

<sup>92</sup> O. M. Bishop and M. S. Thompson, U. S. Patent 1,659,131 (February 14, 1928).

<sup>93</sup> M. L. Crossley, R. H. Kienle, and G. L. Royer, U. S. Patents 2,079,548 (May 4, 1937); 2,090,511 (August 17, 1937); reissue 21,402 (March 19, 1937); and M. L. Crossley, R. H. Kienle, and A. L. Peiker, 2,181,800 (November 28, 1939).

<sup>94</sup> R. J. O'Brien, U. S. Patent 2,155,326 (August 18, 1939).

<sup>95</sup> J. E. Clapham and A. J. Hailwood, Brit. Patent 399,497 (October 2, 1933).

<sup>96</sup> J. Davies, A. Hailwood, and W. Todd, U. S. Patent 2,213,693 (September 3, 1940).

<sup>97</sup> J. G. Kern, U. S. Patent 2,230,353 (February 4, 1941).

The comparative dispersibility of different pigments in water may be measured by a procedure described by Crossley, Kienle, and Royer.<sup>93</sup> A cotton cloth, 4 inches square, is placed over a wide-mouth 8-ounce bottle and fastened with a rubber band. One gram of the treated pigment is placed on the cloth and 25 cc. of water is impinged onto the pigment from a pipette or burette at a rate such that it takes 80 seconds for the water to carry through the cloth. The undispersed pigment remains on the cloth and may be determined by drying and weighing. The ratio of weight pigment dispersed by this test to the original weight is expressed as "percent autodispersibility."

The art of making aqueous dispersions of various classes of pigments that have not been treated for easy dispersibility in water depends largely on the use of reagents to effect deflocculation of the pigment. For many purposes, apparently, fine comminution of the pigments suspended in an aqueous system is not a prerequisite; it is equally, or more, important to have a rather high pigment content. There are several reasons that probably account for this situation, and these are related to the end use of aqueous dispersions. For distemper paints, for example, a matte or egg-shell finish is desired, and an aqueous dispersion of the pigment components can tolerate and perhaps be benefited by oversize particles which would be deleterious in a gloss finish. Oversize particles may be readily removed in a deflocculated dispersion by centrifuging or settling.

Because the viscosity of water is too low to impart shearing forces through the liquid, comminution of aggregates of a hard pigment presents difficult problems. One method is to use slurries or filter-press cakes of the pigment which are ordinarily free from aggregates. When dry pigments are to be processed, however, the most effective method is to grind the pigment in glycerine, diethylene glycol, sugar syrups, or similar water-soluble vehicles by means of a roll mill and to dilute the pigment paste so formed with the requisite amount of water. This expedient introduces a non-volatile, hygroscopic binding material which may be objectionable in some formulations, but it permits efficient dispersion. Surface-active materials and protective colloids can be added to the mill paste.

This procedure is described by Böhner, Wendt, and Eggert<sup>98</sup> who describe a process of kneading the pigment with polyhydric alcohols of the type of 1,3,5 trihydroxyhexane together with protective colloids (e.g., gelatin) by means of a dough mixer.

Graphite dispersions in water are prepared by the use of tannic acid.

<sup>98</sup> G. Böhner, B. Wendt, and J. Eggert, U. S. Patent 2,316,535 (April 13, 1943).

These are the original disclosures of Acheson.<sup>99</sup> In addition to tannic acid as a protective colloid Acheson mentions dextrans and infusions of vegetable matter. Gelatin is mentioned for the same purpose.<sup>100</sup> Burger<sup>101</sup> adds a substantive dye as a stabilizer to the graphite suspension.

Alcohol and ketone dispersions of titanium dioxide may be prepared by the aid of tannic acid derivatives.<sup>102</sup> Another disclosure for alcohol dispersions of titanium pigments is described by Nelson<sup>103</sup> in which an "acid reacting salt" is used. Halides of aluminum, iron, thorium, titanium, zirconium, cerium, and thallium are mentioned.

Aqueous dispersions of carbon black can be successfully prepared by the use of a reagent and process described by Tucker.<sup>104</sup> The protective colloid is prepared by condensing sulfonic acids of naphthalene with formaldehyde. The carbon-black content of dispersions so prepared may approach 50 percent (by weight) and are quite likely to be markedly dilatant. Rather large quantities of the protective colloid are required: 10 percent or greater, computed on the weight of pigment.

The wetting of the pigment by the aqueous phase proceeds for some time, and it is advisable to allow the pigment to "wet out" for a period of several days in a vessel or container that can be vented. The gases displaced from the pigment build sufficient pressure in a sealed container to cause spattering on opening.

A carbon-black pigment with water-dispersing properties is prepared, according to Tuley,<sup>105</sup> by boiling an aqueous slurry of the black with sulfites of the alkali metals. As an example, 10 parts of the pigment with 1 part of sodium sulfite, are slurried in 100 parts of water and boiled for one hour.

For the preparation of non-aqueous dispersions that have thixotropic flow properties, pigments are treated with hydrophilic substances, such as gum arabic, Irish moss, agar-agar, gum tragacanth, and dextrin. The quantity required is less than 1 percent computed on the weight of pigment. Water is added to the composition to obtain maximum thixotropic properties.<sup>106</sup> Proteins, including glue, gelatin, and casein, when

<sup>99</sup> F. G. Acheson, U. S. Patents 843,426 (February 5, 1907); 844,989 (February 19, 1907); 911,358 (February 2, 1909); 964,478 (July 19, 1910).

<sup>100</sup> P. G. Pigache, U. S. Patent 1,854,061 (April 12, 1932).

<sup>101</sup> P. J. Burger, Brit. Patent 571,164 (August 9, 1945); *Chem. Abs.*, **41**, 874 (1947).

<sup>102</sup> Brit. Patent 483,694 (April 25, 1938).

<sup>103</sup> W. K. Nelson, U. S. Patent 2,084,918 (June 22, 1937).

<sup>104</sup> G. R. Tucker, U. S. Patents 1,972,208 (September 4, 1934); 2,046,757 and 2,046,758 (July 7, 1936).

<sup>105</sup> W. F. Tuley, U. S. Patent 1,818,770 (August 11, 1931).

<sup>106</sup> D. L. Gamble and L. D. Grady, U. S. Patent 2,135,936 (November 8, 1938). Cf. also A. D. Wilson, U. S. Patents 2,345,311 (March 28, 1944) and 2,346,243 (April 11, 1944); Brit. Patent 467,875.

applied to lithopone are said to improve the gloss of finishes formulated with the treated pigments.<sup>107</sup> Zinc oxide is treated with casein, egg albumin, hemoglobin, or glue to give improved properties in rubber dispersion.<sup>108</sup> Proteins are added to a slurry of pigment and then coagulated by the addition of aluminum or barium salts or acids to accelerate the settling of pigments during manufacture.<sup>109</sup>

*Dispersion of acetate dyes.* When cellulose acetate, spun into fibers, was first used in textiles, difficulty was experienced in dyeing the finished fabrics. It was found that many dyes would color the fiber if they were present in the form of a suspension in water, rather than in solution, and indeed it has been stated by Mullin<sup>110</sup> that the affinity of the dyestuff is greater if the particles are relatively coarse in comparison with the more conventional dye bath. The so-called dispersol dyes are aqueous dispersions of insoluble dyes, stabilized by various protective colloids. A series of patents, issuing from 1922 on, abstracted by Mullin<sup>110</sup> describe the early work in this field.

Dyes that are insoluble in water but capable of dyeing cellulose acetate are treated with various solubilizing agents, and the product then colors the fiber.<sup>111</sup> Among the solubilizing reagents are sulforicnoleic, oleic, stearic, or palmitic acid or their alkali or ammonium salts. Other materials used as protective colloids which are mentioned in the early processes are casein, glue, gelatin, dextrin, glucose, and waste sulfite liquor. The last is of considerable interest; in crude form the liquor contains sodium lignin sulfonate, resinous materials, sugars, salts, etc. Sodium lignin sulfonate, the chief ingredient, is currently in extensive use, under various trade names, for it is one of the most effective solubilizing and protective agents.

Manufacture of the pastes is accomplished by grinding the dyes in an aqueous solution of the protective materials by means of a ball mill or by mixing the dye paste with a protective colloid and a surface-active agent. When a dry dispersible powder is required, the resulting paste is dried at low temperatures, as in a vacuum drier, and subsequently pulverized to a fine powder.

### Inorganic compounds

Various pigments, particularly the white oxides, are frequently modified by precipitating inorganic compounds in the pigment slurry before

<sup>107</sup> K. S. Mowlds, U. S. Patent 2,134,198 (October 25, 1938).

<sup>108</sup> Brit. Patent 460,164.

<sup>109</sup> H. Grossman, U. S. Patent 1,819,462 (August 18, 1931).

<sup>110</sup> C. E. Mullin, *Acetate Silk and Its Dyes*, D. Van Nostrand Co., Inc., New York, 1927.

<sup>111</sup> British Celanese, Ltd., and G. H. Ellis, Brit. Patent 219,349 (1923).

final processing. Titanium dioxide is often modified in this way, and the commercial pigments have from 0.1 to 2.0 percent of aluminum, antimony, or some other oxide present. As an example of this process, aluminum formate or acetate is added to a slurry of titanium dioxide. The suspension is then boiled, and the salt hydrolyzes, depositing the hydrous aluminum oxide on the pigment particles. The acid is volatilized during the boiling. Other metals that deposit a white oxide (tin, bismuth) are also used.<sup>112</sup> A pigment so treated has several improved properties when formulated into dispersions. Resistance to flocculation, as in lithographic printing inks, is usually increased, and some improvement in resistance to chalking and yellowing is frequently claimed. Other patents give variations on this process. A trivalent titanium compound when precipitated on titanium dioxide is used for a blue tint.<sup>113</sup> The hydrous tetravalent oxide, when precipitated on the titanium dioxide after calcination in a quantity range of 0.2 to 2 percent and dried at temperatures below 200° C., confers stability of the pigment in lithographic printing inks. Generally, it is stated, elements in the first subgroup of group IV and group V of the periodic table are suitable for this purpose.<sup>114</sup> Similarly, improvement in lead chromate can be effected.<sup>115</sup>

Silicates are claimed in a number of patents. Titanium dioxide, treated with barium silicate, is said to have improved resistance to yellowing.<sup>116</sup> The hiding power of various white and extender pigments in paint vehicles is reported to be improved by precipitation of aluminum or zinc silicate,<sup>117</sup> or other insoluble silicates.<sup>118</sup> Precipitation of silicates on other pigments is claimed in several additional patents,<sup>119-121</sup> and Marcot<sup>122</sup> utilizes a soluble silicate (e.g., 0.05 to 0.5 percent sodium silicate) in combination with oleic acid to obtain controlled thixotropic flow properties in paints. A brief review of the treatment of white pig-

<sup>112</sup> B. W. Allan and W. E. Land, U. S. Patent 2,297,523 (September 29, 1942); K. W. Peterson, U. S. Patent 2,161,975 (June 13, 1939).

<sup>113</sup> C. R. Hager, U. S. Patent 2,214,132 (September 10, 1940).

<sup>114</sup> A. M. Erskine, U. S. Patent 2,218,704 (October 22, 1940).

<sup>115</sup> S. C. Horning, U. S. Patent 2,212,917 (August 27, 1940).

<sup>116</sup> G. D. Patterson, U. S. Patent 2,296,618 (September 22, 1942).

<sup>117</sup> K. S. Mowlds, U. S. Patents 2,269,470 (January 13, 1942); 2,259,481 and 2,259,482 (October 21, 1941).

<sup>118</sup> M. L. Hanahan, U. S. Patent 2,296,639 (September 22, 1942); cf. also U. S. Patents 2,296,636; 2,296,637; 2,296,638 (September 22, 1942).

<sup>119</sup> N. F. Livingston, U. S. Patent 2,237,104 (April 1, 1941).

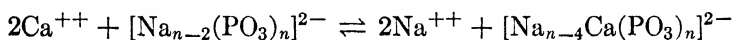
<sup>120</sup> B. W. Allan, U. S. Patent 2,357,721 (September 5, 1944).

<sup>121</sup> W. H. Daiger and G. R. Scidel, U. S. Patent 2,357,089 (August 29, 1944).

<sup>122</sup> G. C. Marcot, U. S. Patent 2,255,263 (September 9, 1941).

ments, particularly with inorganic substances, has been given by Sawyer.<sup>123</sup>

Soluble phosphates have utility in preparing aqueous dispersions of a number of inorganic pigments. Their use in the process described by Oppermann<sup>46</sup> has been noted. Booge<sup>124</sup> prepares a water-dispersible zinc sulfide by mixing sodium pyrophosphate in a concentration of 0.18 to 0.36 percent with the pigment, and Sawyer<sup>125</sup> mentions sodium pyrophosphate and hexametaphosphate as deflocculants for lithopone, titanium dioxide, and other pigments. The action of the soluble phosphates has been termed ion sequestration by Hall<sup>126</sup> and is based on the idea of a polyvalent metallic ion forming a soluble complex according to the following equation:



Other compounds act as sequestering compounds; among these is sodium phytate (inositol hexaphoric acid). The polyvalent cation which could cause flocculation of negatively charged particles in aqueous suspensions is effectively removed by formation of the complex ion.

### Miscellaneous substances

Numerous other substances are used to modify pigment properties. Waxes are mentioned<sup>127</sup> for the purpose of preventing hard settling of pigments in lacquer and paint vehicles. The waxes include carnauba, montan, beeswax. These inventors also mention stearine pitch and an "acid sulfonation product." Brill<sup>128</sup> uses a salt of a sulfonated aromatic petroleum.

Salicylic acid has been used as a deflocculant in paint manufacture. This compound was also included in the 1935 study by the New York Paint and Varnish Production Clubs<sup>15</sup> where it was found of some value. Bernard<sup>129</sup> describes the use of similar compounds (2-methoxybenzoic, 2,3-hydroxynaphthoic) for the purpose of increasing pigment content.

<sup>123</sup> R. H. Sawyer, "Surface Coatings of Opaque Pigments," American Society for Testing Materials, "Symposium on Paint," pp. 3-9 (1943).

<sup>124</sup> J. E. Booge, U. S. Patent 2,178,334 (October 31, 1939).

<sup>125</sup> R. H. Sawyer, U. S. Patent 2,260,871 (October 28, 1941).

<sup>126</sup> R. E. Hall, U. S. Patent 1,956,515 (April 24, 1934). See also H. W. Zussman, *Soap and Sanit. Chemicals*, **24**, No. 2, pp. 57-59, 171, 173, 189 (1949).

<sup>127</sup> C. Coolidge and H. S. Holt, U. S. Patents 2,009,436 and 2,009,437 (July 30, 1935).

<sup>128</sup> H. C. Brill, U. S. Patent 2,220,952 (November 12, 1940).

<sup>129</sup> H. Bernard, U. S. Patent 1,879,045 (September 27, 1932).



Salicylic acid derivatives are also mentioned by Stutz and Elm<sup>130</sup> for the purpose of improving the dispersing properties of pigments.

Aluminum benzoate in large quantity (30 to 70 percent) is specified by Vesce<sup>131</sup> for phthalocyanine pigments. This compound is formed in an aqueous paste or slurry of the pigment by the addition of sodium benzoate and aluminum sulfate. Aluminum benzoate is thus used in a manner comparable to that described by Siegel<sup>23</sup> for barium resinate.

Terpene derivatives, including the alcohols (e.g., fenchyl alcohol, borneol), hydrocarbons (e.g., dipentene), esters (e.g., ethyl abietate), as well as abietic acid, are listed by Pickett<sup>132</sup> as effective deflocculants for pigments dispersed in rubber and in paint and lacquer vehicles.

The idea of treating a pigment with salts that will impart drying properties to a paint formulated with such pigments is elaborated in a series of patents by Blakeman. For this purpose various metal salts are dissolved in a suitable solvent, mixed with the pigment, and the composite dried. Lead, manganese, zinc, and other metals are specified.<sup>133</sup> Carbon-black finishes frequently exhibit a progressive increase in drying time, a phenomenon attributed to adsorption and inactivation of the driers added to the composition. Treating the carbon black with ferric, cobaltic, cupric, or lead acetate is said to make the carbon black less reactive toward the metals present in the catalysts. The pigments are treated with an aqueous solution of the salt and dried. Chromates and bichromates are also specified for this purpose.<sup>134</sup>

An attempt to use silanes for the treatment of hydrophilic pigments in order to improve durability of water-base paints has been described.<sup>135</sup> For this purpose ditertiary butoxy diamine silane,  $(C_4H_9O)_2Si(NH_2)_2$ , was mixed with the pigment and heated at 110° C. overnight.

### Summary

The reader who has followed this maze of seemingly unrelated empirical data may well inquire if there are any generalizations that can be used as a guide in formulating pigment dispersions with surface-active agents and protective colloids. The answer must necessarily be given in

<sup>130</sup> G. F. A. Stutz and A. C. Elm, U. S. Patent 1,978,727 (October 30, 1934).

<sup>131</sup> V. Vesce, U. S. Patent 2,327,472 (August 24, 1943).

<sup>132</sup> O. A. Pickett, U. S. Patent 2,070,177 (February 9, 1937).

<sup>133</sup> W. N. Blakeman, U. S. Patents 702,173; 702,176; 702,177; 702,178 (June 10, 1902); 726,623 (April 28, 1903).

<sup>134</sup> M. R. Vogel and J. W. Snyder, U. S. Patents 2,266,104 (December 16, 1941) and 2,350,846 (June 6, 1944).

<sup>135</sup> Northwestern Paint and Varnish Production Club, *Paint, Oil, Chem. Rev.*, **110**, No. 25, pp. 32-34, 36, 38 (December 11, 1947).

rather broad terms, for most authorities agree that a measure of specific action is associated with the use of these compounds. Accordingly it is advisable to survey the several classes of reagents, selecting one or more from each class for this purpose and, on the basis of preliminary results so obtained, to study, experimentally, species related to the most effective compounds. For example, if one commercial variety of sodium do-decyl sulfate is found suitable, more extended experiments can be performed with the same compound from other manufacturers as well as similar compounds derived from oleyl, palmityl, or other alcohols. The compounds listed in Tables I to IV and VIII will serve as a guide in such an initial survey.

TABLE VIII. GENERALIZED LISTING OF REAGENTS FOR PIGMENT DISPERSION

Pigment	Reagent
	Water as Vehicle
Titanium dioxide pigments, zinc oxide, calcium carbonate, lithopone, etc.	Soluble gums (e.g., gum arabic) Methyl cellulose; carboxymethylcellulose
Ultramarine blue	Fatty alcohol sulfates Alkyl aryl sulfonates Sodium pyrophosphate; sodium hexametaphosphate
Carbon black and Organic toners	Tannins, sulfonated lignins, sulfonated condensation alkyl aryl compounds Water-soluble surface-active agents
	Oleoresinous Vehicles
Titanium dioxide, zinc oxide, calcium carbonate, lithopone, etc.	Metal soaps (e.g., zinc naphthenate) Amine soaps
Ultramarine blue	Fatty acids Lecithin
Carbon black	Amines (e.g., benzidine) Copper oleate
Organic toners and Phthalocyanine colors	Resinates (e.g., barium resinate)

The work reported, however, may be summarized as follows.

1. An extremely wide variety of compounds has been found of utility. The largest group, which is also the oldest, comprises soaps and fatty acids. Comparable or superior results are obtainable from amines combined with fatty acids.

2. For dispersions in water, alcohol, glycerol, and for water-miscible vehicles in general, many of the synthetic surface-active agents are quite effective. These can be combined to advantage with protective colloids

such as glue, gelatin, soluble gums, and cellulose ethers for aqueous dispersions.

3. Various inorganic pigments are readily deflocculated in aqueous systems by the use of soluble phosphates (e.g., sodium hexametaphosphate).

4. Non-aqueous dispersions of pigments which may be designated as hydrophilic in wetting properties are greatly benefited by surface-active agents and protective colloids. In addition to the heavy metal and amine soaps, a few commercial surface-active agents are effective. Lecithin and zinc naphthenate have been found of quite general utility. For hydrophobic pigments, surface-active agents have little effect.

5. Carbon black has properties which distinguish it from other pigments. Copper soaps and amines in conjunction with fatty acids (which may be present as a normal component of oleoresinous vehicles) are noteworthy as deflocculants for non-aqueous systems. Sulfonated lignins are effective for aqueous dispersions.

6. Efficiency of preliminary mixing may be increased by the use of these reagents. The mixing time in some instances is appreciably shortened, for the vehicle is caused to wet the pigment (with displacement of entrained and sorbed gases) in a shorter time than with untreated pigment.

7. Dispersion time on standard mill equipment depends on secondary factors. Grinding time on a roll mill may actually be lengthened if the reagent causes an appreciable lowering of plastic viscosity. Feeding into a colloid mill may be facilitated by deflocculating reagents, however; in a ball mill, maximum ball mobility can be maintained.

8. Greater final strength of pigments cannot be expected through the utilization of surface-active agents. For some applications, however, a deflocculated pigment suspension may provide improved coverage. The evidence for increased rate of dispersion by the use of surface-active agents is not clear. Some authorities have observed a more rapid dispersion rate, particularly where the mechanical work done on the system is at the minimum. Where viscous vehicles are used in standard dispersion equipment, however, the mechanical shearing stresses are ordinarily sufficient to disintegrate pigment aggregates and an increased rate of dispersion is difficult to isolate as a controlling factor.

9. Deflocculation of the pigment by means of these reagents may be detected by sedimentation tests, rheological measurements, and microscopic observation. A pigment deflocculated in a low-viscosity medium settles slowly to a hard sediment. In a viscous vehicle and at higher concentrations, yield value measurements provide a measure of deflocculation. These results can be corroborated by microscopic observation.

10. No one theory can be stated to explain the action of surface-active agents for all pigment-vehicle combinations. It is possible that deflocculation is accomplished in some combinations by the effect of a surface-active substance on sorbed moisture. In others, the function of a protective colloid can be presumed.

11. Different methods of addition of the reagents are employed: (a) pre-mix of all ingredients, separately added; (b) solution or dispersion of the reagent in the vehicle; (c) addition of the reagent to a dispersion already prepared, (d) treatment of the pigment, either during processing or as the dry powder, to "coat" the pigment surfaces with the reagent. Numerous variations of these procedures are used commercially. Where accessory reactions are ruled out, comparable results are obtained by the four methods. The magnitude of the changes in properties may differ in degree, however.

12. The concentration of reagent producing the optimum effect on the properties of a pigment dispersion is always greater than that estimated to form a monomolecular film of the pigment-vehicle interface. For most pigments this quantity is estimated as less than 3 percent. However, larger concentrations of the reagents that act as protective colloids may be desirable, particularly for aqueous dispersions.

## 7. The Process of Comminution

The process of dispersion, considered in its entirety, consists of wetting the powdered solid with the liquid of the dispersion medium, the breakdown or comminution of aggregations of particles or, in with some materials, fracturing the primary particles themselves by mechanical means, and adjustment of the formulation to obtain the requisite physical properties. In previous chapters we have scanned the ideas associated with wetting phenomena and the specification of particle size, and we have examined by several experimental means the physical properties of solids dispersed in liquid media. As a preliminary to the engineering aspects of pigment dispersion, which are given in detail in subsequent chapters, a discussion of the process of comminution is appropriate.

### Dry Grinding of Solids

Crushing and grinding of solids provides some insight into the mechanism of comminution, and several important topics will be considered briefly.

The fracture of brittle solids has been pictured by Poncelot<sup>1</sup> as follows: on the application of sufficient force to a solid, stresses are built up and these lead to cracks; compressive pulses with transverse stresses travel through the solid as a result of the initial crack, and the generation and propagation of additional stresses result in the fragmentation of the original solid. The process, it is apparent, is enormously complex.<sup>2</sup>

<sup>1</sup> E. F. Poncelot, *Trans. Am. Inst. Mining Met. Engrs., Inst. Metals Div., Tech. Pub. No. 1684* (1944); *Chem. Abs.*, **38**, 2527 (1944).

<sup>2</sup> Attempts have been made to express the results of comminution in terms of size distribution of the particles. See A. M. Gaudin, *Principles of Mineral Dressing*, McGraw-Hill Book Co., New York, 1939, pp. 132-33; R. Schuhmann, Jr., *Am. Inst. Mining Met. Engrs., Tech. Pub. No. 1189* (1940), *Chem. Abs.*, **34**, 5386 (1940); E. Rammler, *Z. Ver. deut. Ing. Verfahrenstech.*, 1942, No. 4, pp. 103-8, through

Various attempts have been made to correlate work input with new surface developed as a result of crushing. In the processing of minerals, Rittenger's law, first proposed in 1867, seems now fairly well accepted. Rittenger's law states that the energy required to reduce the size of particles is directly proportional to the increase of surface.<sup>3</sup> Several experimental methods have been used to test this law. The most convincing evidence came from an impact crusher on material such as quartz and the ball milling of sand. The efficiencies of these crushing operations were very low.<sup>4</sup>

Although the relationship expressed in Rittenger's law is of great theoretical interest and has incited a large amount of experimentation, it seems to have little practical application in the practice of pigment dispersion. Not only is the estimation of new surface difficult, but the relative amount of energy utilized in the creation of new surface is virtually impossible to determine. It has been estimated, for example, that the ball mill used for crushing minerals is operated at an efficiency of less than 1 percent. Most of the energy is lost in the friction of the ball charge and is converted into heat. Further, in pigment dispersion, crushing is a mere incident in the process, and it is probable that the actual milling efficiency is even lower than that of a process strictly one of crushing.

All practical dispersion processes depend on shearing. When a shear component is combined with high localized pressures, marked changes in crystal structure result. The classic research of Beilby<sup>5</sup> provides some idea of changes occurring in the surface. Mechanical operations such as cutting, filing, grinding, and polishing produce a surface layer which differs from the body of material. Beilby provided evidence showing that the surface layer was in a fluid state at the time of the action. The depth of this layer was estimated as several hundred millimicrons. He observed that the grinding of crystalline substances involves more than merely progressive reduction in size to finer fragments, since it involves also a transformation of part of the substance into a vitreous state. Compression of powders into a cake also implies some flow at points of contact. Support for this conception is afforded by the

*Chem. Abs.*, **38**, 4492 (1944); A. M. Gaudin and R. T. Hukki, *Am. Inst. Mining Met. Engrs., Tech. Pub. No. 1779* (1944). The statistical aspects of fracture have been reviewed by B. Epstein, *J. Applied Phys.*, **19**, 140-7 (1948).

<sup>3</sup> A. M. Gaudin, *Principles of Mineral Dressing*, p. 135; W. H. Coghil and F. D. DeVaney, *Missouri, Univ., School Mines and Met., Bull.* **13**, No. 1, 1938, p. 31.

<sup>4</sup> See also F. A. Henglein, *Chem. Ztg.*, **68**, 23-25 (1944), through *Chem. Abs.*, **38**, 5448 (1944).

<sup>5</sup> G. B. Beilby, *Aggregation and Flow of Solids*, Macmillan & Co., Ltd., London, 1921.

experiments of Bridgman.<sup>6</sup> Under a pressure of 50,000 kg. per sq. cm. and with a shearing stress sufficient to initiate plastic flow, many substances are deformed to a limited extent and then break, self-weld again under the high pressure, and repeat the sequence of flowing, breaking, and self-welding. Eventually a steady state is reached in which the crystalline material has a highly distorted lattice, essentially that of a glass. This effect was experimentally observed by Ray<sup>7</sup> on extended grinding of sand. The change from a crystalline to an amorphous state was determined by the heats of solution in hydrofluoric acid. Ray concluded that approximately 25 percent of the quartz was converted to an amorphous or vitreous state by grinding. Density changes are associated with prolonged grinding. Martin<sup>8</sup> found an initial increase in the density of sand on grinding, a result attributed to the elimination of pores originally present; on further grinding a decrease in density resulted. The theory for some of these physical changes has been examined by Griffith.<sup>9</sup>

When polymeric materials are subjected to grinding, the usual result is a marked depolymerization. Lampitt, Fuller, and Goldenberg<sup>10</sup> subjected wheat starch to extended periods of grinding in a ball mill and estimated that the reduction in molecular weight of certain fractions was from 60,000 to 27,400 after 470 hours' grinding. Extended grinding led to "soluble" starch. It was concluded that the starch retained its typical characteristics but that the lateral linkages in the polymeric structure had been ruptured. Dry grinding of cellulose results in a similar depolymerization.<sup>11</sup> Cotton, for example, when ground for 12 hours decreased in molecular weight (as determined by cuprammonium fluidity) from about 220,000 to 62,000. Other materials studied by Staudinger and his colleagues which showed comparable changes include cellulose nitrate and polystyrene.<sup>12</sup> Natural proteins are decomposed by dry ball-mill grinding. Cohen<sup>13</sup> studied the changes produced in a variety of proteins. Water-insoluble proteins were so modified as to give water-soluble extracts, but the changes observed were extremely complex and

<sup>6</sup> P. W. Bridgman, Chapter 14, pp. 327-37 in *Colloid Chemistry*, Vol. V., J. Alexander, Editor, Reinhold Publishing Corp., New York, 1944; *J. Colloid Sci.*, **2**, 7-16 (1947).

<sup>7</sup> R. C. Ray, *Proc. Roy. Soc. (London)*, **A102**, 640-2 (1923); **A101**, 509-16 (1922).

<sup>8</sup> G. Martin, *Trans. Brit. Ceram. Soc.*, **26**, 45-56 (1927).

<sup>9</sup> A. A. Griffith, *Phil. Trans. Roy. Soc. (London)*, **A221**, 163-98 (1921).

<sup>10</sup> L. H. Lampitt, C. H. Fuller, and N. Goldenberg, *J. Soc. Chem. Ind. (London) (Trans.)*, **60**, 1-6T, 25-9T, 47-50T (1941).

<sup>11</sup> H. Staudinger and E. Dreher, *Ber.*, **79**, 1091-98 (1936).

<sup>12</sup> H. Staudinger and W. Hener, *Ber.*, **67**, 1159-64 (1934).

<sup>13</sup> H. R. Cohen, *Arch. Biochem.*, **2**, 1-8, 345-51, 353-55, 357-61 (1943); **4**, 145-50, 151-54 (1944).

could be generalized only by noting marked disintegration of the protein molecule. Routh<sup>14</sup> observed similar degradation of wool on grinding and found evidence also for oxidative changes.

An attempt has been made by Hess and co-workers<sup>15</sup> to analyze the effect of the grinding process on cellulose and polystyrene. They estimate that the kinetic energy in a "rocking" ball mill is 1,500 ergs per impact and that the work required to rupture a C—C or a C—O linkage is about 0.2 erg per impact. For an impact of  $10^{-5}$  second duration, some  $10^{10}$  bonds are broken.

Any such analysis of the mechanism of grinding necessitates numerous assumptions. During ball-mill grinding considerable heat is developed at the interface between contacting balls, and thermal degradation alone could account for some of the changes observed. In addition, degradation from oxidation can occur. Isolation of the effect of shear or impact is thus virtually impossible.

### Dispersion in Liquid Media

In what manner and to what extent the forces involved in grinding a powdered solid in a viscous liquid can alter the properties of the solid are not known with any certainty. It is probable that the extent of deformation of crystals composing a typical pigment is comparatively small in most grinding operations. There is general agreement that the primary purpose of most dispersion procedures is reduction in aggregate size to some acceptable minimum. Actual breakdown of small compact crystals is not likely. One exception is a powder in the form of needle-shaped crystals. Certain varieties of chrome yellow, zinc oxide, and phthalocyanine blue, to mention a few typical materials, are in this class. Intensive dry pulverization, either in a hammer mill or a ball mill, breaks the crystals into successively smaller lengths. When the same acicular material is dispersed in a vehicle by means of a ball mill where high turbulence exists, there is evidence also for continued breakdown, but on a roll mill the crystals may orient with their long axes parallel with the nip of the rolls. In this event prolonged milling produces only a very gradual decrease in crystal length. Where pigment loading is so high as to result in dilatant flow, direct contact of aggregates and crystals is almost inevitable, and the transmission of momentary shearing stresses

<sup>14</sup> J. I. Routh and H. B. Lewis, *J. Biol. Chem.*, **124**, 725-32 (1938); *ibid.*, **135**, 175-81 (1940).

<sup>15</sup> K. Hess, E. Stener, and H. Fromm, *Kolloid-Z.*, **98**, 290-304 (1942); through *Chem. Abs.*, **36**, 5582 (1942). For a description of the conversion of crystalline cellulose to amorphous by dry grinding, see P. H. Hermans and A. Weidinger, *J. Am. Chem. Soc.*, **68**, 2547-52 (1946).



of high magnitude from one particle to another is highly probable. Fracture of the crystal could then occur. This condition, it may be seen, is certainly the most efficient for pigment dispersion. Isolation of the effect of shear in such a dilatant system is impossible, for the temperature rise during grinding is often sufficiently great to cause reactions and decomposition of the pigment particle quite independent of shear. The possibility for paradoxical changes in the characteristics of pigment particles may be connected both with the effect of high shearing stresses and localized temperature rise.

The dispersion of carbon black presents several problems that may highlight the more general features of changes in particulate substances during dispersion, particularly with respect to the nature of the comminution of aggregates.

Density measurements indicate a porous structure for carbon black. Rossman and Smith<sup>16</sup> computed densities of carbon black from x-ray data and immersion in liquid helium and in water. X-ray diffraction data provided the highest values (2.16-2.18); helium gave intermediate values (1.90-2.13) and water provided the lowest densities (1.79-1.99). If the x-ray values are considered the true densities, then the difference in density obtained by the immersion technique offers a measure of the porosity of the particle. These investigators consider that the aggregate (or ultimate working unit) persists throughout all practical applications and recommend the lower values obtained with water as typical of the *apparent density* of carbon black in dispersed form.

The effect of compaction on the "dispersibility" of carbon black in rubber was considered in the experiments of Schoenfeld and Allen.<sup>17</sup> During the initial mixing of pigment with rubber, part of the carbon black is compacted by the rolls. In an effort to simulate such aggregation, carbon black was passed through the mill rolls and the compacted material was then used for tests on ease of dispersion. In all the tests, a marked decrease in dispersibility was noted. After five compacting passes, the dispersibility was rated as 54 percent in comparison with the original pigment which was rated as 85 percent in the test method used. These writers point out that the variation in shearing stress with temperature (within normal operating limits) outweighs other effects which may be ascribed to temperature changes. Schoenfeld and Allen also observed that one to two percent water present in the black aids dispersion but that higher quantities inhibit dispersion. This effect has been noted repeatedly by other workers.

<sup>16</sup> R. P. Rossman and W. R. Smith, *Ind. Eng. Chem.*, **35**, 972-76 (1943).

<sup>17</sup> F. K. Schoenfeld and R. P. Allen, *Ind. Eng. Chem.*, **25**, 1102-6 (1933).

More recent work on compaction has been described by Dobbin and Rossman.<sup>18</sup> The carbon blacks that are most affected are the so-called structure blacks (e.g., acetylene black). Oil absorption, liquid retention, and electrical resistance were decreased, and, when the blacks were milled into rubber, marked changes in the stock were noted. These investigators concluded that the secondary aggregation of the carbon particles was reduced by mechanical processing.

The persistence of aggregates through most comminution processes seems well established. Clark and Rhodes<sup>19</sup> calculated aggregate sizes from microscopic and x-ray data, finding many primary particles per aggregate (cf. chapter on particle size). They state that only physical dispersion is operative during the rubber dispersion process, since the x-ray diffraction pattern for the dispersion matched that of the combination of patterns for the rubber and carbon black alone. In fluid media, the presence of such aggregates for carbon black has been demonstrated by rheological studies.<sup>20</sup> Note has already been made of measurements of particle size of titanium dioxide after dispersion on rubber.

Adsorption measurements on carbon black recovered from rubber dispersions were made by Amon, Smith, and Thornhill.<sup>21</sup> These studies showed that the surface areas of the black after dispersion were unchanged from those of the original pigments. This result also suggests that reaction of the rubber hydrocarbon with the carbon-black surface is slight or non-existent and lends support to the physical concept of reinforcement of rubber by carbon black.

The fracture of crystals or the disruption of aggregates as a result of shearing is affected to some extent by the constituents of the liquid dispersion medium (see Chapter 6). The experimental results obtained by Rebinder and his associates may be cited in this connection. The plastic deformation of lead, tin, and copper under constant load was greatly facilitated by addition of surface-active materials to the paraffin oil in which the metal was immersed. The compounds found effective were the fatty acids, *n*-valeric, *n*-heptoic, stearic, oleic, and cerotic and cetyl alcohol.<sup>22</sup> Pure single crystals of zinc and tin showed a similar re-

<sup>18</sup> R. E. Dobbin and R. P. Rossman, *Ind. Eng. Chem.*, **38**, 1145-48 (1946). Aggregates formed by compaction during milling have been called impactoids. Cf. I. M. Bernstein, *ibid.*, **42**, 908-16 (1950).

<sup>19</sup> G. L. Clark and H. D. Rhodes, *Ind. Eng. Chem., Anal. Ed.*, **12**, 66-71 (1940).

<sup>20</sup> R. Buchdahl, R. Braddicks, Jr., and P. V. McKinney, Paper at American Chemical Society Meeting, Chicago, 1946, *Abstracts Book*, p. 44P.

<sup>21</sup> F. H. Amon, W. R. Smith, and F. S. Thornhill, *Ind. Eng. Chem., Anal. Ed.*, **15**, 256-58 (1943).

<sup>22</sup> P. A. Rebinder and E. R. Venstrom, *Bull. Acad. Sci., U.R.S.S. Classe sci. mat. nat., Ser. phys.*, 1937, 531-38; through *Chem. Abs.*, **32**, 5676-77 (1938).

sult.<sup>23</sup> The optimum concentration was about 0.2 percent. The action was attributed to the penetration of microscopic cracks by the surface-active material during deformation along the glide planes of the crystal; a kind of lubrication is thus provided. When specimens of copper, aluminum, zinc, and iron were ground on a steel plate with carborundum powder, the work expended was considerably lessened when solutions of fatty acids were used, and there was some indication that the particle sizes of the abraded metals were smaller.<sup>24</sup>

General experience seems to indicate that wet grinding is more economical of the energy expended than dry grinding.

### Dispersion by Ultrasonic Radiation

Considerable publicity has been given the industrial use of high-frequency sound waves as a means of introducing energy into a dispersion. High-intensity sound waves have long been known to produce unusual physical effects, but there are many limitations in the application of frequencies within the audible range. However, when the frequency is increased beyond that perceived by the ear, not only may high intensities be employed without discomfort but the apparatus then becomes of practical dimensions. The first work on ultrasonics was reported by Wood and Loomis.<sup>25</sup> These experiments have been considerably extended by subsequent investigations, and useful summaries have been given by Bergmann<sup>26</sup> and Sollner.<sup>27</sup>

Ultrasonic waves<sup>28</sup> are sound waves of a frequency beyond that perceived by the human ear, or approximately 15,000 cycles per second. The maximum frequency used is of the order of  $10^9$  cycles per second, and the energy input for colloidal studies is somewhat greater than 10 watts per sq. cm. Generation of the ultrasonic radiation depends on a rapidly vibrating element, such as a piezoelectric crystal, and the energy is transmitted through a liquid or solid to the material under study.

<sup>23</sup> P. A. Rebinder, V. I. Likhtman, and V. M. Maslennikov, *Compt. rend. acad. sci. U.R.S.S.*, **32**, 125-29 (1941); through *Chem. Abs.*, **37**, 812-13 (1943).

<sup>24</sup> E. P. Zakoschikova, *J. Tech. Phys. (U.S.S.R.)*, **8**, 1973-85 (1938); through *Chem. Abs.*, **33**, 6676 (1939).

<sup>25</sup> R. W. Wood and A. L. Loomis, *Phil. Mag. (Series 7)*, **4**, 417-36 (1927).

<sup>26</sup> L. Bergmann, *Ultrasonics and Their Scientific and Technical Applications*, translated by H. S. Hatfield from the German edition (1938), John Wiley & Sons, Inc., New York, 1948.

<sup>27</sup> K. Sollner, "Sonic and Ultrasonic Waves in Colloid Chemistry," Chapter 15, pp. 337-73 in *Colloid Chemistry*, Vol. V, J. Alexander, Editor, Reinhold Publishing Corp., New York, 1944.

<sup>28</sup> Also termed supersonic or supersonic. Current nomenclature, however, reserves *supersonic* for a speed in excess of that of sound and *ultrasonic* for frequencies greater than those of audible sound waves.

Cavitation is the mechanism by which ultrasonic waves produce dispersion. When a liquid is subjected to rapid expansion, dissolved gases form nuclei for the disruption of the liquid, and a two-phase system of gas (and vapor) and liquid results. These cavities collapse when the force causing expansion is removed. Pressures of large magnitude (estimated as thousands of atmospheres) develop momentarily, and the resulting stresses are distributed over a very small region. It would be expected, therefore, that mechanical dispersion of suspended particles would result. Both high pressure and high vacuum, which eliminate or greatly reduce cavitation, prevent dispersion. The evidence<sup>29</sup> that cavitation is the cause of the dispersion effects was noted by the first workers and appears now to be well substantiated.

The most frequently cited examples of ultrasonic dispersion are emulsions of oil and water and mercury and water. In addition, various low-melting metals (e.g., sodium, mercury, tin), fusible alloys, sulfur, and other substances have been dispersed by this means. The procedure is to heat the oil to a temperature at which the substance is melted and then subject the system to ultrasonic radiation. Particle sizes of the dispersed material are around 0.5 micron, and, with very high intensity fields, finer particles are obtainable.

Application of ultrasonic waves for the dispersion of pigments is sometimes attempted. In the experience of the writer, the disintegrating effect of this radiation on pigments such as iron blue, carbon black, and barium lithol, suspended in oils, is negligible. Since the energy input is high, heating of the suspension is marked, but the changes produced by ultrasonic radiation cannot be distinguished from those caused simply by heating and stirring. In all dispersions studied the extent to which aggregates were broken down was inappreciable. Sollner,<sup>30</sup> in discussing the dispersion of solids, points out that fracture and splitting are observed if the solids are of moderate cohesion and that colloidal dispersions may result. With other materials of high cohesion (e.g., glass, quartz, marble) colloidal suspensions are never produced.

Although the actual disintegration of aggregates by ultrasonic radiation is negligible, structure within colloidal systems is easily broken down. Thus, on irradiation, thixotropic suspensions of iron oxide become fluid and gum solutions exhibit lower apparent viscosity. Of special interest in this connection is the preparation of photographic "emulsions" (dispersions of silver halides in gelatin) by means of ultrasonic radiation. Experiments by B. Claus<sup>31</sup> demonstrated that the homo-

<sup>29</sup> An analysis of the mechanism of emulsification by ultrasonic radiation has been given by C. Bondy and K. Sollner, *Trans. Faraday Soc.*, **31**, 835-43 (1935).

<sup>30</sup> K. Sollner, *Trans. Faraday Soc.*, **34**, 1170-4 (1938); see also reference 27.

<sup>31</sup> Described by Bergmann, reference 26, pp. 206-8.

geneity and stability of the emulsions were considerably improved by radiation. Clumping (termed agglomeration in this connection) of the grains is considerably reduced. It is stated that a higher content of silver halide is possible and the temperature of the ripening stage may be increased because the ripening points are less localized.

### Basic Factors in Mechanical Dispersion

From the direct experimental evidence at hand and from supplementary information, it appears certain that the particles in a dispersion are partly in the form of primary particles and to some extent in the form of aggregates. The size of the aggregates varies with the nature of the solid and the suspending medium and is established chiefly by the magnitude of the shearing forces to which the composition was subjected. The residual aggregates may be in the form of "ultimate working units," but this designation is not entirely adequate, for it may imply that all the particles are of this dimension.

Three factors need consideration in a comparison of mills of different construction and operation: (1) the clearance between the grinding surfaces; (2) the relative velocity with which the surfaces are moving in relation to each other; and (3) the plastic viscosity of the composition. These define the limits in which a mill acts as a crusher and indicate the magnitude of the shearing forces within the mixture. Estimated clearances and approximate viscosity limits for mixers and mills of widely different types are given in Table I.

The practical aspects of pigment dispersion may be summarized in the following way. The large aggregations of primary particles are broken down first by crushing. The conditions under which a given mill are operated establish the limit for aggregate size reduction: in a roll mill the clearance between the rolls establishes the upper limit for the aggregates. Further reduction in aggregate size is accomplished largely by shearing within the viscous mixture of pigment and vehicle, and to some extent by actual contact of the aggregates with each other during shearing. The persistence of a few aggregates, which may be more resistant to breakdown than the average, often demands repeated passes of the material over the mill or lengthens the milling period excessively. The efficiency of mill operation is lowered by these few resistant particles. There are three ways in which this situation can be remedied: (1) use of the highest viscosity grinding media and the highest concentration of solids in the dispersion that can be processed on a given mill; (2) selection of pigments that are free from hard aggregates and avoidance of excessive compaction; and (3) centrifuging the finished dispersion (usually

after dilution with appropriate vehicle components) to remove the over-size aggregates.

These points will be considered in greater detail in the following chapters in which the important types of dispersion equipment are described.

TABLE I. ESTIMATED CLEARANCE AND APPROXIMATE VISCOSITY LIMITS FOR VARIOUS MILLS

Mill	Clearance		Plastic-Viscosity Range (poises)
	Mils (0.001 inch)	Microns (0.001 mm)	
Roller (3, 4, 5 roll) *	0.2-1.0	5-25	10-10,000
Rubber (2-roll)	50-250	1,250-6,200	100,000-50,000,000
Dough Mixer	∞	∞	100-1,000,000
Banbury	∞	∞	100-50,000,000
Colloid	1-10	25-250	1-100
Uni-roll *	Variable	Variable	1-1,000
Ball (steel) †	....	....	1-200
Pebble (flint) †	....	....	1-100
Buhrstone	1-10(?)	25-250	1-100
Iron ("pot")	1-10(?)	25-250	1-100

\* Where settings are maintained by hydraulic pressure, operating clearance depends primarily on viscosity.

† For large-size production mills.

## 8. Mixing

The purpose of a mixing operation, prior to more intensive dispersion on a mill, is essentially threefold: (1) to cause the liquid vehicle to wet the powdered solid with concomitant displacement of air; (2) to effect a blend of different components; and (3) to produce an initial breakdown of the largest aggregates, thus reducing the time required in a more costly milling process. The mixing step in a pigment-dispersion sequence is usually given scant attention. It is possible, nevertheless, to reduce the burden on other dispersion equipment by more effective preliminary mixing. There are few published studies on mixing of pastes, although mixing of fluid compositions has been extensively studied.

Alternative terms are often used to describe the mixing process: *malaxation*, meaning to soften by kneading, is frequently used in patent specifications; *mastication*, meaning to crush and knead, is found in the literature on rubber technology. For pigment dispersion, *plastic mixing* is now commonly used. Ordinarily the extent to which aggregates are reduced in this step is limited, for the viscosity of the mixture is low and the function of mixing therefore becomes chiefly a matter of blending and wetting of the solid. By application of high shearing forces, however, it is possible to make the mixing operation serve as a primary comminution process. Subsequent milling can then be reduced to that necessary for finishing or, for some dispersions, can be completely eliminated.

Mixers of many types are on the market, and new designs are continually appearing. A description of standard types will be found in the monograph by Riegel<sup>1</sup> and in references on chemical engineering. The following discussion will be limited to the mixers that are used extensively for pigment dispersion, along with a brief description of mixers for low-viscosity suspensions.

<sup>1</sup> E. R. Riegel, *Chemical Machinery*, Reinhold Publishing Corp., New York, 1944; Chapters 10 and 11, pp. 221-52.

### Low-Viscosity Mixing

As a unit operation in chemical engineering, mixing of low-viscosity suspensions has been studied in great detail.<sup>2</sup> The most common arrangement is an impeller agitator, operating at high speed, introduced into a vertical cylindrical tank. The criterion for good mixing is that all portions of the liquid come under the influence of the agitator, so that a continuous streaming takes place. Several simple rules should be observed for efficient mixing.<sup>3</sup> (Figure 1.)

1. The impeller should be immersed sufficiently to prevent vortexing which introduces air into the liquid and, with some materials, may cause excess foaming and frothing. The depth of immersion should be greater than 1.5 times the propeller diameter. This depth holds for different types of agitators. Ordinarily the proper position can be determined by observation.

2. The height of liquid in the mixing tank is an important variable. The usual arrangement is to have the height of liquid equal to the diameter of the tank, and, with the impeller placed one-third of the distance from the bottom of the tank, effective agitation results. Where lower levels of liquid occur, as during draining of a tank with continued agitation, special arrangements become necessary.

3. Streaming of the liquid should be sufficiently vigorous to keep all particles in suspension. If the viscosity is too high or the size and power of the mixer are too low for the volume in the tank, then efficiency drops very rapidly. Fillets placed at the edge of the bottom and the cylindrical wall assist in keeping larger particles from collecting out of reach of the full action of the streaming liquid.

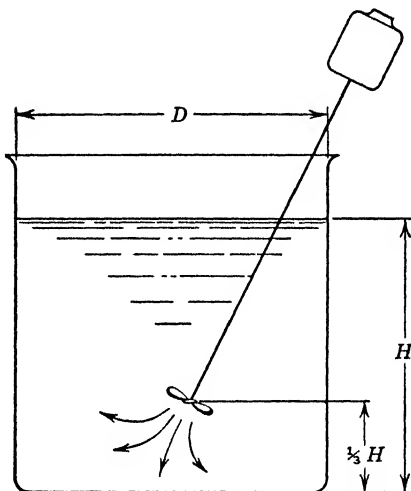


FIGURE 1. Mixing with high-speed impeller agitator. (For efficient mixing,  $H = D$ , and the impeller is placed approximately  $1/3 H$  with the thrust directed downward at an angle.)

<sup>2</sup> See, for example, the "Symposium on Agitation and Mixing," *Ind. Eng. Chem.*, **36**, 487-531 (1944).

<sup>3</sup> Cf. E. S. Bissell, H. J. Everett, and J. H. Rushton, *Chem. & Met. Eng.*, **53**, 118-119 (1946). See also, E. J. Lyons, *Chem. Eng. Progress*, **44**, 341-46 (1948).



4. The impeller should be rotated to direct the flow downward and placed slightly off-center to ensure complete mixing from top to bottom.

The propeller-type mixer is probably the most widely used. Other designs with special types of rotors are available; these have special uses.

Mixing of this type is frequently used for aqueous dispersions. Pigments treated to confer dispersing properties in water can be processed quite effectively. Carbon-black dispersions are also made in this way where the maximum fineness is not required. Settling or centrifuging the dispersion will remove the larger aggregates.

### Change-Can Mixer

The change-can mixer is also termed a pony mixer. It has the advantage that ingredients can be weighed into the container (can) and then brought to the unit, mixed, and without transferring to another vessel can be delivered to the next operation. This economy in handling of materials has led to wide use of the mixer, and it is available commercially in models that range in capacity from laboratory quantities to several hundred gallons.

The mixer is constructed with a set of blades arranged to rotate from an overhead drive. The agitator and drive assembly can be raised to receive a charge and lowered into the container for mixing. The container also rotates. The blades, placed off-center in relation to the center of rotation of the container, sweep through the mix and wipe the sides of the container. (Figure 2.)

The mixer may be charged in several ways. Most commonly the vehicle is weighed into the mixer with part of the pigment; mixing is then started and, as the powdered solid is incorporated, additional pigment is added to the quantity required for the formulation. This procedure is followed to obtain full mixing capacity and to reduce dusting of the powder.

Several variants on the agitator design are available. In one type, a pair of U-shaped blades intermesh, as in an egg-beater, and produce somewhat more effective interchange of the mix. A loose-fitting cover is sometimes used to reduce dusting. Most of the change-can mixers in use are designed for charges of moderate consistency, but heavy-duty mixers capable of handling extremely viscous pastes have been constructed. Because of complications in design and high relative cost, they have not found favor, and dough mixers (described in the next section) are preferred for high-viscosity pastes.

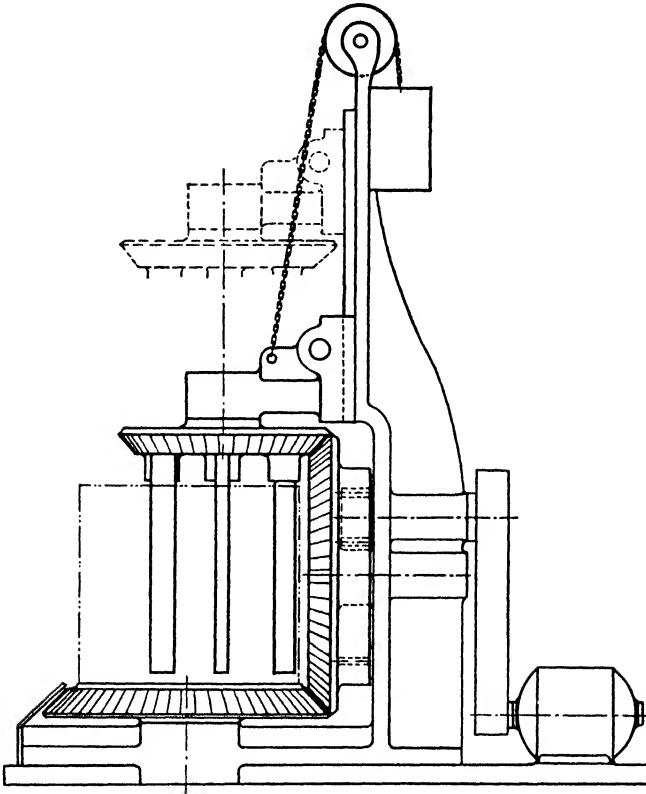


FIGURE 2. Mechanism of a typical change-can mixer. (After an illustration courtesy Charles Ross & Son Co.)

### Dough Mixers

Dough mixers are made in a range of sizes, from small laboratory models to production machines capable of processing several hundred gallons. (Figure 3.) As the name suggests, these mixers are designed for the processing of dough-like compositions; they are sometimes referred to as kneaders, and the mixing process is frequently described as malaxation. More recently, the term plastic mixing has been adopted. The construction of commercial models is adapted to accommodate a rather wide range of plastic viscosities. The machines with the lightest construction are suitable for preliminary mixing of paint and printing-ink stock or base dispersions; the mixers of the heaviest constructions permit the completion of a dispersion process without further grinding.

There are, in general, two types: one in which the blades rotate at differential speeds in depressions in the mixing tank without overlap, and a second type in which the paths of the blades overlap. A variety of blade shapes is available, but those most generally used are of the S or Z or sigmoid shape. The mixers are equipped with jackets to permit either cooling with circulating water or heating with steam under pressure, and many models are adapted for the attachment of a

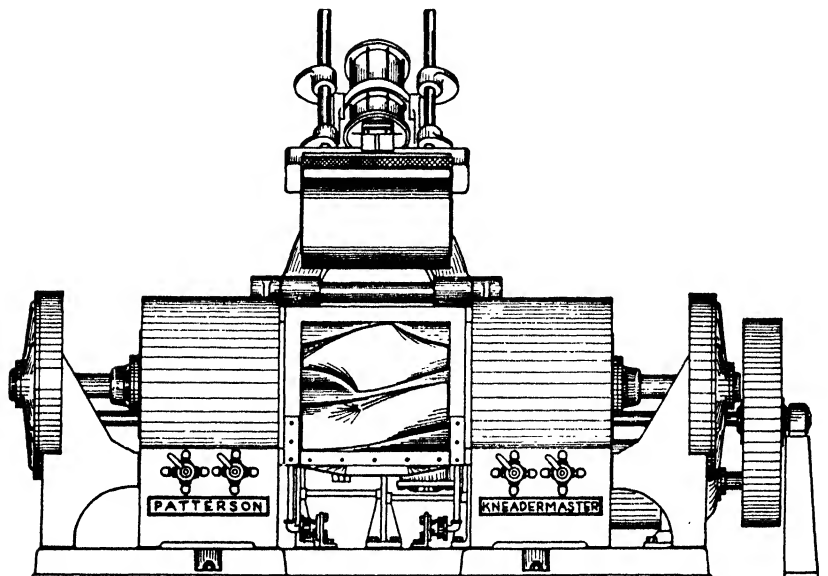


FIGURE 3. Over-all view of a heavy-duty dough mixer shown in discharge position. (Courtesy Patterson Foundry and Machine Co.)

vacuum-tight cover which extends the utility of the instrument considerably. On the whole, the dough mixer in its present commercial models is a highly versatile instrument. It is, however, an instrument that demands considerable skill for satisfactory operation and necessitates, moreover, vigilance in observing certain safety measures.

The dough mixer is used chiefly for the mixing of pigment dispersions before they are finished on other equipment such as the roll mill; other uses include the flushing of aqueous pigment pulps, described in Chapter 12, preparation of certain types of finished pigment dispersions, and blending.

The dough mixer and its application has been described by Schmiel<sup>4</sup> with examples of the dispersion of titanium dioxide in synthetic resin

<sup>4</sup> E. M. Schmiel, *Paint, Oil, Chem. Rev.*, **109** (No. 9), 6-8 (1946).

vehicles. The mixer is charged with the full quantity of resin solution and about three-fourths of the total pigment. A suitable starting ratio for a 100 gallon mixer is 750 pounds of titanium dioxide and 28 to 30 gallons of an alkyd resin solution containing 50 percent solid resin. The mixer is operated slowly for several minutes to form a paste, and the remainder of the pigment, 250 pounds, is then added gradually. Heating with steam aids in forming a paste. As soon as a viscous, plastic mass is obtained, heating is stopped and cooling water is circulated into the jacket. The temperature should not exceed 140° F. for this type of product. Mixing is continued for the time required to obtain the necessary dispersion quality, and the remainder of the resin solution together with thinners is then added. Thinning requires care, for, if too large a quantity of solvent is added initially to the viscous mixer paste, lumps are formed which are difficult to break down and distribute. The product is finally discharged from the mixer into storage or blending tanks. The time for this cycle, adapted from typical production runs of titanium dioxide in alkyd and urea-formaldehyde resin solutions, is given by Schmiel as follows:

Operation	Time (minutes)
Preparing charge	30
Forming plastic paste	5
Dispersing	30
Dilution (with resin solution)	30
Thinning	30-240
Discharging	5

The entire operation can thus be concluded in less than two hours, but it is likely to extend to 5 or 6 hours. The longest time, it will be noted, is for dilution or "let down." The importance of this step in the operation cannot be overemphasized, for if the diluents are added too rapidly at first, the let-down time may extend to several hours before a paste uniformly free of lumps is obtained. Some mixers are now equipped with a two-speed drive: the higher speed of agitation is used for the thinning operation. Cleaning is not included in this time schedule, for successive batches can be made without scraping the mixer blades and tank.

Processes for dispersing pigments in nitrocellulose vehicles by means of the dough mixer are described in several patents. Hemingway and Weidlich<sup>5</sup> mix pigment, nitrocellulose, and a small amount of solvent for the binder until a highly viscous paste is formed. Similar processes are described by de Stubner.<sup>6</sup> For the manufacture of a carbon-black

<sup>5</sup> H. J. Hemingway and W. A. Weidlich, U. S. Patent 1,798,840 (March 31, 1931).

<sup>6</sup> E. C. de Stubner, U. S. Patents 2,034,861 (March 24, 1936) and 2,125,103 (July 26, 1938).

lacquer, 250 parts of a high-color carbon black are mixed with 600 parts of alcohol until the pigment is wetted; at this point 400 parts of alcohol-wet nitrocellulose are added in small quantities during continued agitation. A stiff, plastic mass is formed in two to three hours which is then added to a clear lacquer for the preparation of a finished product. Alternatively, a solvent for the nitrocellulose is added during the dispersion operation. Hucks,<sup>7</sup> using a similar procedure, starts with an aqueous pigment pulp, and the transfer or flushing of the pigment to the colloidal nitrocellulose mass takes place during mixing.

Another variation is to mix water-wet nitrocellulose with a plasticizer and dry pigment; after a period of mixing, water separates and is removed; on continued mixing (20 to 40 minutes at temperatures below 35° C.) a viscous paste is formed and dispersion of the pigment is then completed.<sup>8</sup>

Hazards associated with the use of nitrocellulose in plastic mixes should not be overlooked. The possibility of fire and explosion can be minimized by (1) mixing at low temperatures, (2) using plasticizers (e.g., tricresyl phosphate), (3) maintaining minimum viscosity consistent with the required dispersion quality, and (4) avoiding reactive pigments (e.g., lead chromate). The mixer should be open. Despite all feasible precaution, however, fires and explosions can occur without warning, and Schmiel, representing one of the equipment manufacturers, states that the use of the dough mixer for nitrocellulose dispersions should be discouraged.

The versatility of the dough mixer fits it for numerous products. Bodied linseed oils, mineral oils, all types of synthetic resin solutions can be successfully used as dispersion media. With non-reactive pigments and vehicles (e.g., carbon black in mineral oil) the temperature of the mix can be raised to effect dehydration of the system.

The extent to which aggregate breakdown is accomplished depends largely on the plastic viscosity of the mixture. Generally the highest plastic viscosity within the mechanical limits of the machine and the properties of the pigment-vehicle system should be employed. At high plastic viscosities, exchange of the mix from one blade to the other is facilitated and the maximum amount of work is done on the charge. The actual quantities loaded into the mixer are sometimes critical: with too small a charge the mix packs on the agitator blades without interchange; too large a charge will cause some of the material to ride above the rotating agitators. After thinning, some of the composition adheres

<sup>7</sup> R. T. Hucks, U. S. Patent 2,140,745 (December 20, 1938). Cf. also references to the flushing process in Chapter 12.

<sup>8</sup> Anon., *Verfkroniek*, **21**, 189 (1948).

to the side walls and the blades. When the mixer is discharged, only the freely flowing portion should be taken, the residue, which ranges approximately from 5 to 20 percent of the total charge depending on the viscosity, being allowed to remain in the mixer for blending with the next batch.

The sequence in charging a dough mixer can be given in general terms as follows: (1) A portion of the vehicle is introduced into the mixer, and the agitators are started; (2) pigment is added in small portions, care being taken to avoid compacting between the agitator edge and the saddle of the tank, until a highly viscous mixture is obtained; (3) the mixer is operated until the dispersion, as judged by ratings on samples taken at intervals, is considered satisfactory; (4) additional vehicle or thinner is then added, in very small portions at first, each addition being allowed to distribute throughout the mass before another quantity is introduced; (5) the product is discharged by allowing it to flow from the mixer, any material compacted on the sides or agitator blades being rejected. If the product is to receive a finish grind on another mill, the last precaution is not essential.

### Edge-Runner Mill

The edge-runner mill consists of one or two circular stones or steel runners attached to a vertical shaft and set to rotate around the center of a flat grinding surface (Figure 4). The flat surfaces of the stones or

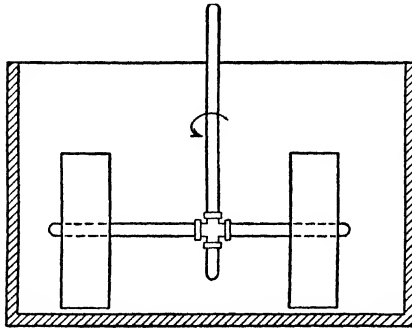


FIGURE 4. Diagram of an edge-runner or putty-chaser mill.

mullers mash and knead the mixture. Scrapers and plows control the movement of the mix, returning it to the pan for further mulling. This mill has various other names, of which putty-chaser mill is the most commonly used. It is actually one of the oldest designs: early versions, still extant, were used for crushing grains, mashing grapes for wine, etc. Variations on the design are used in mineral dressing.

The edge-runner mill is suitable for pulverizing dry powders as well as dispersing pastes. The heavy runners are pivoted and ride on the material. For this reason, the charge of the mill is not critical. It cannot be used, of course, with very fluid compositions; instead, its greatest utility is found with pastes that have a high yield value and relatively low viscosity. Aggregates present in such a mixture are reduced in size by mechanical action between the muller and the grinding plate. In this respect the edge-runner mill is unique, for no other mixer is engineered to process such pastes with any measure of efficiency. Coating compositions, putties, cements, and similar materials are examples of the products made with the edge-runner mill.<sup>9</sup>

### General Aspects of Mixing

Because of the variety of products and the many variables that need consideration, mixing processes for high-viscosity compositions cannot be generalized. A thorough study of process variables for paste mixing is still to be reported. Articles on the subject are chiefly descriptive.<sup>10</sup> There are, of course, many patents on mixing machines, only a few of which find their way into actual use. Wornum and Read-Baker<sup>11</sup> mention some of the imponderables in specifying requirements and in designing dispersion equipment. The trade journals carry occasional general articles on the subject.<sup>12</sup> Some aspects of the processing of viscous materials are noted by Levey.<sup>13</sup>

### Oil Absorption

The amount of vehicle taken up by a dry pigment to form a paste is of considerable interest in manufacturing operations, particularly as it affects preliminary mixing procedures. The oil-absorption value of a pigment is the weight of oil absorbed by 100 parts by weight of pigment, but relative volumes of pigment and vehicle may be used in place of the

<sup>9</sup> Cf. E. M. Rupp, *Paper Trade J.*, **111**, 10-11 (1940).

<sup>10</sup> For helpful discussions see C. M. Frey, Chapter 23, pp. 727-50, *Protective and Decorative Coatings*, Vol. III, J. J. Mattiello, Editor, John Wiley & Sons, Inc., New York, 1943, and E. R. Riegel, *Chemical Machinery*, Reinhold Publishing Corp., New York, 1944.

<sup>11</sup> W. E. Wornum and G. W. Read-Baker, *J. Oil & Colour Chemists' Assoc.*, **25**, 166-92 (1942).

<sup>12</sup> A series of papers which covers various aspects of the subject appeared in *Farben-Chem.*, **10**, 1939. Page citations follow: 5-18, 25; 26-32; 44-46; 111-12; 126-29; 142-43.

<sup>13</sup> H. A. Levey, *Chem. & Met. Eng.*, **46**, 371 (1939).

weight relationship. This property is usually determined by the Gardner-Coleman method.<sup>14</sup> Twenty grams of the pigment are placed in a round-bottom jelly glass, and oil is added dropwise from a burette. At the first stages, the pigment-oil mixture forms soft lumps; these are distributed by mixing with a spatula until, with further additions of the vehicle, the whole mass becomes uniform and easily smears the side of the glass. Considerable variations in the behavior of different pigments are to be observed, and the test requires experience on the part of the operator in judging comparable end points.

Another procedure, designated the rub-out or spatula test,<sup>15</sup> is to mix the pigment with oil by means of a steel spatula on a slab. The oil is added dropwise from a pipette, or burette, and mixing is continued until a stiff paste, similar to putty, is formed. The rub-out method is described also by Azam,<sup>16</sup> who takes as the end point a consistency at which the paste does not flow off the spatula. As an additional check on the saturation of the pigment with oil, a lump of the dispersion is placed in a graduate containing the vehicle: if no change in volume occurs, the paste is considered saturated. The rub-out method gives lower oil-absorption values than those obtained with the Gardner-Coleman method.

One variation of the test, intended for an evaluation of surface-active agents, is described by Daniel and Goldman<sup>17</sup> and depends on agitating the paste on the spatula blade by tapping.

Inasmuch as the amount of oil absorbed depends on the particle size and extent of aggregation of the pigment, the extent of dry pulverizing to which the pigment has been subjected, the presence of adsorbed substances (especially moisture), and the technique used for the test, it could hardly be expected that an oil-absorption value would represent a characteristic property of a given pigment. Bartell and Greager<sup>18</sup> attempted a correlation between oil-absorption data and adhesion tension of the liquids. They concluded that the highest oil absorption would be represented by a zero contact angle and low adhesion tension. Sherrington<sup>19</sup> states that oil-absorption values increase with higher temperatures. The small amount of moisture present in some pigments causes the oil absorption to decrease; the amount appears to be critical. This decrease

<sup>14</sup> H. A. Gardner and G. G. Sward, *Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors*, Eleventh edition, Henry A. Gardner Laboratory, Bethesda, Md., 1950; pp. 290-1.

<sup>15</sup> American Society for Testing Materials, Standard Test D 281-31.

<sup>16</sup> M. A. Azam, *Ind. Eng. Chem., Anal. Ed.*, **14**, 545-46 (1942).

<sup>17</sup> F. K. Daniel and P. Goldman, *Ind. Eng. Chem., Anal. Ed.*, **18**, 26-31 (1946).

<sup>18</sup> F. E. Bartell and O. H. Greager, *Ind. Eng. Chem.*, **21**, 1248-51 (1929). Cf. also, J. T. Baldwin, *ibid.*, **21**, 326-29 (1929).

<sup>19</sup> A. Sherrington, *J. Oil & Colour Chemists' Assoc.*, **31**, 72-78 (1948).



in oil absorption can be partly explained by the extent of flocculation of the pigment: fatty acids present in the oil have a deflocculating action and hence would increase the apparent oil demand; moisture, by causing flocculation, would perhaps decrease the oil demand. Marsden<sup>20</sup> in a critical review and analysis of the test concludes that the oil-absorption values obtained depend on the following: (1) an oil-coating factor which is dependent on the specific volume of the pigment, the specific gravity of the oil, and, most important, on the technique of the operator; (2) an oil-absorption factor which is related to the nature of the pigment and its subdivision but is independent of the operator.<sup>21</sup>

Some of the properties of pigments connected with oil-absorption data are reviewed by Thynne.<sup>22</sup> In general, pigment particles that approach spherical shapes have the lowest oil requirement. Pigment mixtures in which the relative sizes of the components are markedly different have generally low oil requirements. Carr,<sup>23</sup> however, considers oil-absorption data to have no theoretical significance.

Data obtained by these procedures are useful chiefly for comparison of different lots of a given pigment. An oil-absorption value cannot be considered a significant physical property, and the data reported, chiefly in manufacturers' literature, are of extremely limited value. Nevertheless, oil-absorption values are often used in an attempt to predict the consistency of mill-ground pigment pastes. Thus a pigment with a low oil-absorption value would be expected to produce a dispersion of comparable low plastic viscosity. Such an inference is certainly not valid, and numerous workers have pointed out the fallacy in this practice. The oil-absorption value is helpful, however, in estimating the performance of a preliminary mixer operation with various pigment-vehicle combinations.

<sup>20</sup> E. Marsden, *Official Digest Federation Paint & Varnish Production Clubs*, No. 287, 962-74 (1948).

<sup>21</sup> In this connection see the paper on critical pigment-volume relationships by W. K. Asbeck and M. Van Loo, *Ind. Eng. Chem.*, **41**, 1470-75 (1949).

<sup>22</sup> A. W. F. Thynne, *Paint Technol.*, **11**, 423-27 (1946).

<sup>23</sup> W. Carr, *Paint Manuf.*, **25**, 99-100 (1945).

## 9. Roll Mills

Roll mills of several types are of primary importance in the manufacture of colloidal dispersions. The principle of operation is shearing at the nip between two rolls driven at different speeds. Dispersion of the solid is accomplished by two related processes: particles larger than the roll separation are crushed mechanically by the co-acting roll surfaces; at the same time the differential speed of the rolls imparts high shearing stresses to the dispersion. Roll mills in several basic designs commercially available are suitable for compositions of a wide range of plastic viscosities.

Although antecedents of the roll mill can be found in primitive version in the relics of ancient Egypt, the modern mill evolved from prototypes that were introduced about the middle of the nineteenth century. At that time notable changes were made in several industrial processes. Grinding of grains for flour, crushing and comminution of ores, and mastication of rubber were greatly improved in efficiency when rolls were introduced. Developments in these industries appear to have been isolated, and the lack of collaboration can be ascribed, in part at least, to the secrecy maintained by manufacturers, and, in part, to the mechanical difficulties that beset early machinery. A satisfactory mill required hardened rolls, and the art of their manufacture was well advanced first in Europe where other industrial processes utilized rolls. Among these were calendering, rolling of metals, drying, etc. In the United States rolls became available in the second half of the nineteenth century, although imported rolls were used up to the outbreak of World War II.

The adoption of roll mills for pigment dispersion, both in the United States and abroad, apparently dates from the first days such units became available. For the printing ink manufacturer, in particular, the roll mill held an obvious advantage: the viscous pastes necessary for printing ink could be ground economically and rapidly. Several designs were introduced. The Neal mill, invented in 1860, was a two-roll mill

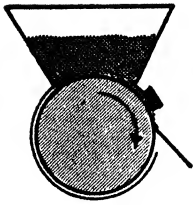
with a driven lower roll and a fixed top roll. The Kindon mill, introduced in 1873, also had two rolls; the upper roll was smaller than the lower roll and was driven in an opposing direction. An outgrowth of this design was the Dodge mill with a 4-inch top roll and a 12-inch lower roll. The paste for grinding was fed onto the top roll from a brass hopper and after passing between the rolls was removed by a scraper blade on the lower roll. The Dodge mill was made for many years.

These mills are now obsolete, but mills equipped with two rolls are important instruments today. One is designed chiefly for rubber compounding but it is suitable also for the milling of plastic molding compositions and other high-viscosity products. A second form is the paste two-roll mill which is equipped with a hopper for grinding of paint. The Banbury mixer or mill resembles in some respects the two-roll mill. Two rotors, encased in a mixing chamber, turn at different speeds and are shaped so that the plastic mixture is pressed against the walls of the chamber, forming a wedge during the kneading operation.

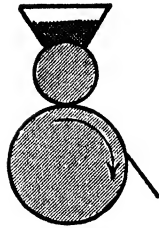
Of the roll mills, the three-roll mill is the most versatile, and its wide use attests the success of this design. Although this mill was doubtless available some decades earlier, the period between 1870 and 1900 saw the greatest activity in design and production. Water-cooled rolls were introduced in the 1890's. Some mills were fitted with solid granite or diorite rolls, but hollow-bore, chilled-iron rolls were preferred. One mill, known as the Plymouth triple-roll mill, had rolls 4, 8, and 12 inches in diameter. At this time every conceivable arrangement of rolls and combinations of rolls of different diameters were tried in an empirical effort to obtain superior performance. One German mill had a total of nine rolls and was actually a combination of three-roll mills. Such combinations, however, present mechanical difficulties, both in construction and maintenance, and preferred practice is to run separate mills in tandem.

The first five-roll mill was patented in 1888, but it was rarely employed until the 1920's, when a number of essential mechanical refinements were introduced into all grinding machinery of this type. These improvements included superior rolls, the installation of roller bearings in place of bronze bearings, more uniform boring of the rolls to equalize expansion when the rolls heated during operation, and, finally, more precise finishing of the roll surfaces.<sup>1</sup> (Figure 1.)

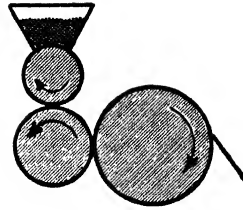
<sup>1</sup> The gradual development of the roll mill in various industries can be traced in the following references: Anon., *Am. Ink Maker*, 13, No. 9, pp. 15-18 (September, 1935); *ibid.*, 16, pp. 22-23, 39 (May, 1939); Anon., *The Story of Flour*, Pillsbury Flour Mills, Minneapolis, 1935; H. A. Bellows, "A Short History of Flour Milling," Reprint from the *Northwestern Miller*, The Miller Publishing Co., Minneapolis, 1924; B. W. Dedrick, "Practical Milling," *Nat. Miller*, Chicago, Ill., 1924; E. K. Fischer,



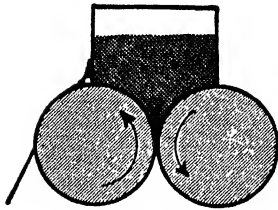
Uni-roll mill



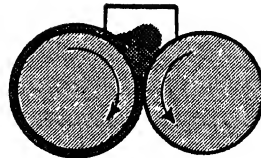
Dodge mill



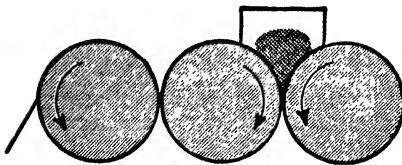
Plymouth mill



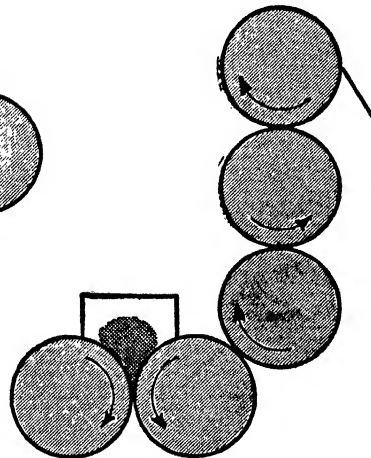
Two-roll paste mill



Two-roll rubber mill



Three-roll ink and paint mill



Five-roll ink and paint mill

FIGURE 1. Cross-sectional diagrams of various types of roll mills.

*Interchem. Rev.*, **3**, 91-104 (1944); H. C. Pearson, *Rubber Machinery*, India Rubber World, New York, 1920; S. C. Stillwagon, *India Rubber World*, **101**, No. 1, 50-4, 62 (October 1, 1939); G. F. Zimmer, "Flour and Flour Manufacture," *Encyclopedia Britannica*, Eleventh edition, Vol. **10**, p. 548; P. Zipper, *The Manufacture of Chocolate*, Second edition, E. Spon, Ltd., London, 1902.

Despite the importance of the several classes of roll mills, designed specifically for the dispersion of pigments, comparatively few data have been published on the related engineering factors and the theoretical basis of operation. Successful operation depends on the skill of trained operators and the empirical adjustment of formulations to suit the equipment.<sup>2</sup>

### The Single-Roll Mill

In the single-roll mill<sup>3</sup> the mixture for grinding is introduced into a hopper placed above the roll, and the paste adhering to the roll is passed between the roll surface and a stationary bar pressed against the roll by a spring or hydraulic mechanism. A scraper blade is fitted to the mill below the pressure bar. The single-roll mill is analogous to a colloid mill in which a rotor operates against a stator.

A single-roll mill is limited to compositions of low or intermediate viscosity, and the shearing action of the mill is consequently on the low side. For this reason the mill is sometimes considered a finishing or blending mill, but it is capable of satisfactory production of many compositions in which relatively soft-grinding pigments are incorporated. For this purpose the mill has several advantages: the operation is relatively simple, solvent loss can be minimized by enclosures that are easily constructed, maintenance is generally rated as inexpensive, and the production rate is high for certain products.

The single-roll design noted above has been modified in several ways to improve performance. A second pressure bar which can be adjusted to a closer setting than the first bar has been added; in this way, a two-step reduction in aggregate size is obtained, since the first bar, with a loose setting, accepts coarser particles than the second bar with a close setting. This arrangement is analogous to the three-roll mill in which the clearances at the two sets of rolls are adjusted for an initial coarse grind followed by a fine grind. Another improvement introduced into the single-roll mill is in the design of the pressure bar. In the Keenok Uni-Mill<sup>4</sup> this "vane bar" is designed with a wedge-shaped pressure chamber which serves to lead the composition under the nip of the vane bar. (Figure 2.) The bar itself is U-shaped, providing two grinding

<sup>2</sup> The need for a systematic study of the engineering aspects of mill operation has been frequently noted by writers. See, for example: W. E. Wornum, and G. W. Read-Baker, *J. Oil & Colour Chemists' Assoc.*, **25**, 166-92 (1942); R. D. Bonney, *Official Digest, Federation Paint & Varnish Production Clubs*, No. 237, 345-58 (1944); G. A. Vasel, *Am. Ink Maker*, **14**, No. 10, 18-22, 39 (1936); *ibid.*, **24**, No. 4, 29-30 (April, 1946).

<sup>3</sup> C. R. Draper, *Paint Manuf.*, **13**, No. 4, 67-72 (April, 1942).

<sup>4</sup> Product of Vickers-Armstrongs, Ltd. (Keenok Sales Dept.), London.

surfaces which interrupt the passage of the paste. The angle of the vane bars supplied with the mill range from  $5^{\circ}$  to  $25^{\circ}$  with the  $20^{\circ}$  bar considered suitable for typical paint products.

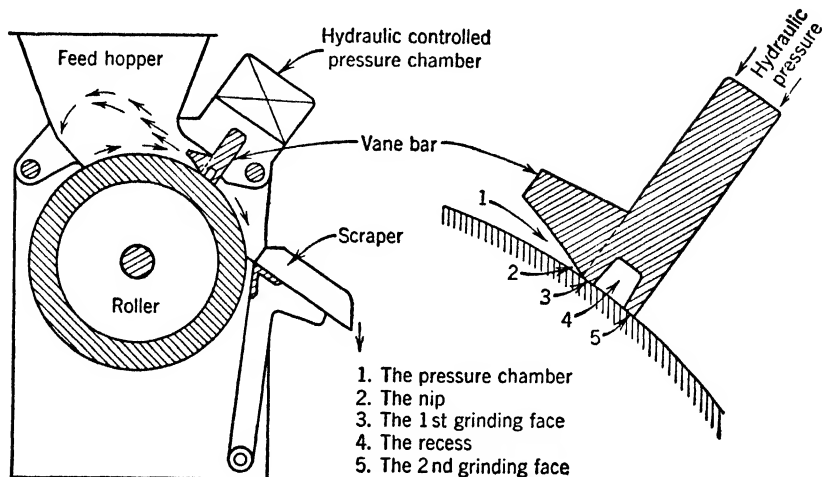


FIGURE 2. Cross-sectional diagrams of a single-roll mill showing feed arrangement and pressure vane bar. (Courtesy Keenok Co., Ltd.)

The single-roll mill has found favor in Europe but is used only to a limited extent in the United States. Farr<sup>5</sup> reports that in Germany the single-roll mill was widely used as a refining mill, but Voet<sup>6</sup> states that they were unsatisfactory for printing ink.

### Multi-Roll Mills

For the processing of pigment dispersions of intermediate viscosity, the three- and five-roll mills have proved highly successful and their field of utility extends to other products including the milling of soap, cosmetic and pharmaceutical products, and chocolate.

In the three-roll type, which is the most commonly employed, chilled-iron rolls are set rigidly in bearings and driven at different speeds. The center roll is fixed, and the outer rolls are adjustable. The first two rolls act as feed rolls, and the mixture introduced into the nip of these rolls is subjected to an initial shearing and crushing at the roll interface. End plates prevent the bank of dispersion from spreading laterally and

<sup>5</sup> H. O. Farr, *Paint, Oil, Chem. Rev.*, **109**, No. 11, 5-7, 42 (May 30, 1946), from Field Information Agency, Technical, Office of U. S. Military Government for Germany, Office of the Director of Intelligence, Report 681.

<sup>6</sup> A. Voet, *Am. Ink Maker*, **25**, No. 9, pp. 64, 67, 69, 71 (September, 1947).

falling off the rolls. The dispersion transfers to the second roll and is carried into contact with the more rapidly moving third roll to which it adheres. It is then removed by the scraper blade attached to the apron of the mill. Although the dispersion is subjected to shearing at only two places where the rolls meet, virtually all the power is applied at these

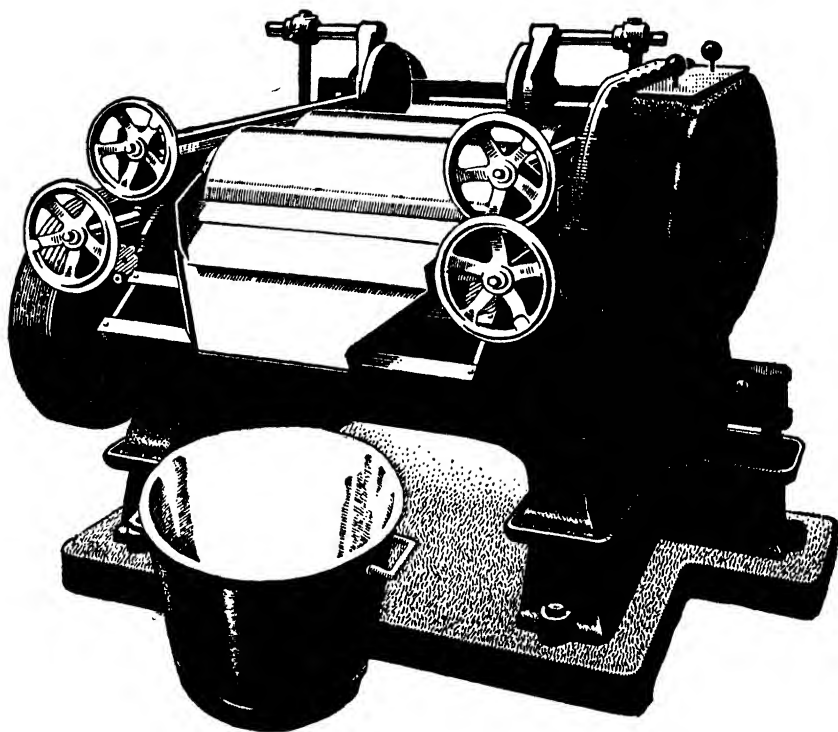


FIGURE 3. Typical three-roll mill. (Courtesy Keenok Co., Ltd.)

areas, and consequently mixtures of fairly high plastic viscosity can be processed. The five-roll mill subjects the dispersion to two additional grinding interfaces and in principle is identical with the three-roll mill. (Figures 3 and 4.)

The multi-roll mill has become one of the standard instruments in pigment dispersion. The mills currently being manufactured are equipped with rolls finished to tolerances of the order of 0.0002 inch, and the drive mechanism has been stabilized so that high roll speeds can be obtained. A variety of sizes is available. Mills with rolls 4 inches in diameter by 8 inches long and 5 inches in diameter by 12 inches long are widely used laboratory models. Production-size mills are commonly

equipped with rolls of the following dimensions: 9 by 24 inches; 12 by 32 inches; 16 by 36 or 40 inches. Mills with larger rolls have been constructed, but these have not found general favor.

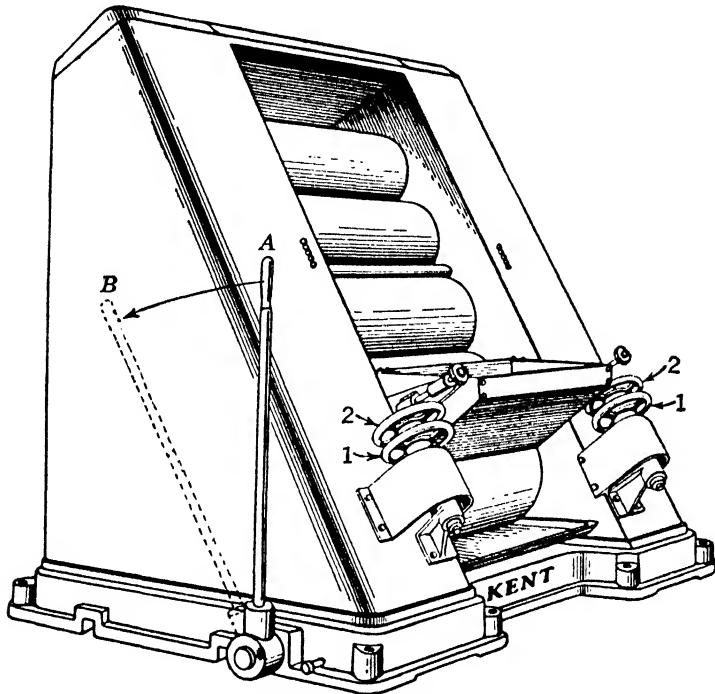


FIGURE 4. One type of five-roll mill. (Courtesy Kent Machine Works, Inc.)

### Action of roll mill

The manner in which a roll mill functions may be visualized as follows. Pigment and vehicle, in imperfect mixture, are introduced onto the first two rolls. The oil wets the roll surfaces and adheres tenaciously, pulling aggregates of the pigment into the nip of the rolls. Particles larger than the roll separation are mechanically crushed while smaller particles are subjected to the turbulent shearing forces at the tangent of the two rolls. Very large particles and lumps of material are not drawn into the rolls until the volume above the rolls is very small; at that time, however, the oversize particles enter the nip and, if excessively large, are crushed or compacted into a dry mass which may carry through the rolls.

The second roll picks up the viscous dispersion and carries it to the nip of the third roll. The clearance at this point is smaller than that of



the feed rolls, and, since the rate of shear is higher, additional work is performed in reducing aggregate sizes of the suspended pigment. When the material reaches the take-off blade, it has been subjected to two actual shearing surfaces in the three-roll mill.

The amount of material transported is determined by the roll clearance, the speed of the rolls, and the plastic viscosity of the composition. It is evident that the quantity carried by each roll is proportional to the film thickness and the rate of removal. It can, indeed, be considered a ribbon of a thickness proportional to the roll clearance and feeding from the mill at the peripheral speed of the third roll. In charging a mill with a mixture containing large aggregates, the roll clearance must be large; consequently, the work done on the mixture is comparatively small. As the oversize is reduced, however, and the dispersion is subjected to repeated passes through the roll system, the internal shearing forces become greater and the aggregates are reduced to the dimensions of the component primary particles.

In this analysis, emphasis has been placed on the part that plastic shearing plays in the process. A further examination will indicate the magnitude of the dimensions and the forces involved.

It has been shown <sup>7</sup> that the apparent separation of a tightly set laboratory mill operating with a viscous mixture is of the order of 5 to 10 microns. Two experimental procedures were employed for this measurement. In one procedure a pigment containing excessively hard aggregates, which could be reduced only by direct mechanical comminution, was ground in a viscous oil, and the dimensions of the largest particles measured microscopically. In one mill, no aggregates larger than 6 microns were observed; in another mill, none larger than 10 microns was noted. A second method was based on the output as affected by viscosity and clearance as described in the next section. Confirmation of these figures was obtained. Another estimate has been given by Craig,<sup>8</sup> who states that the average setting of a 12 by 30 inch mill is about 40 microns. Lacking more extensive data it may be tentatively assumed that the operating clearances for roll mills is in the range of 10 to 40 microns. (Figure 5.)

These clearances represent, of course, approximations. Actually, any attempt to measure the clearance is beset with difficulties, for the mill

<sup>7</sup> E. K. Fischer and D. M. Gans, Chapter 14, pp. 286-327, in *Colloid Chemistry*, Vol. VI, J. Alexander, Editor, Reinhold Publishing Corp., New York, 1946.

<sup>8</sup> T. J. Craig, *Am. Ink Maker*, **16**, No. 10, 27, 29, 31 (October, 1938). Estimates by R. F. Bowles for the front rolls on a high-speed three-roll mill are as follows: clearance, 15 microns; rate of shear,  $10^5$  to  $10^6$  sec<sup>-1</sup>. See *J. Oil & Colour Chemists' Assoc.*, **25**, 179 (1942).

frame, as well as the rolls, is subject to elastic deformation. The magnitude of this deformation is established by the stresses on the mill during operation. Accordingly, it is futile to make a mill setting by means of shim gauges placed between stationary rolls and to expect the

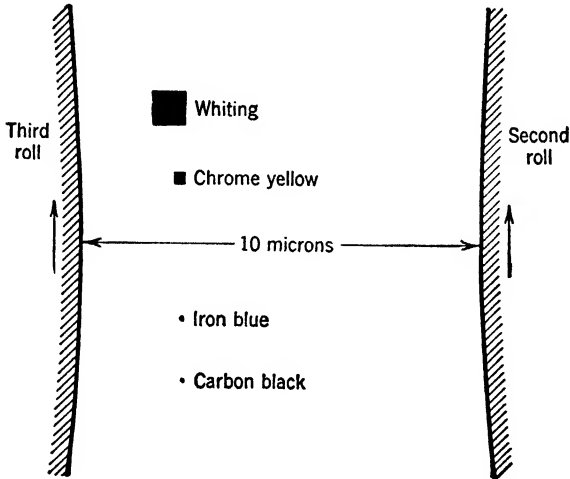


FIGURE 5. Diagram comparing clearance between rolls and size of primary pigment particles as approximated for three-roll mill during operation.

clearance to remain at the set value when the mill is operating under load.

The output of a roll mill is directly proportional to the plastic viscosity of the dispersion. This factor is well known qualitatively, as shown by the data in Table I, classified from the data reported in a

TABLE I. RELATION OF OUTPUT TO PASTE CONSISTENCY FOR ROLL MILL

(Five-roll mill, high speed, 13" × 32".)

Consistency Rating	Output (pounds per hour)
Very thin	30-130
Thin	80-230
Medium stiff	120-180
Stiff	550-1,400

series of studies on roll-mill grinding with production-size mills.<sup>9</sup> Although only qualitative consistency ratings are given, it will be noted that the same mill varied in production from a low output of 30 pounds

<sup>9</sup> New York Club, *Nat. Paint, Varnish Lacquer Assoc., Sci. Sect., Circ. 629*, 351-72 (1941).

per hour to a high output of 1,400 pounds per hour as the consistency ratings ranged from "very thin" to "stiff."

A more quantitative study of the relation of viscosity to output of a roll mill has been described.<sup>7</sup> (Experiments performed in cooperation with C. W. Jerome.) In these tests a series of pigment dispersions and viscous oils of known viscosity were passed over a 5 by 11 inch three-roll laboratory mill, and the time for a given volume of composition to trav-

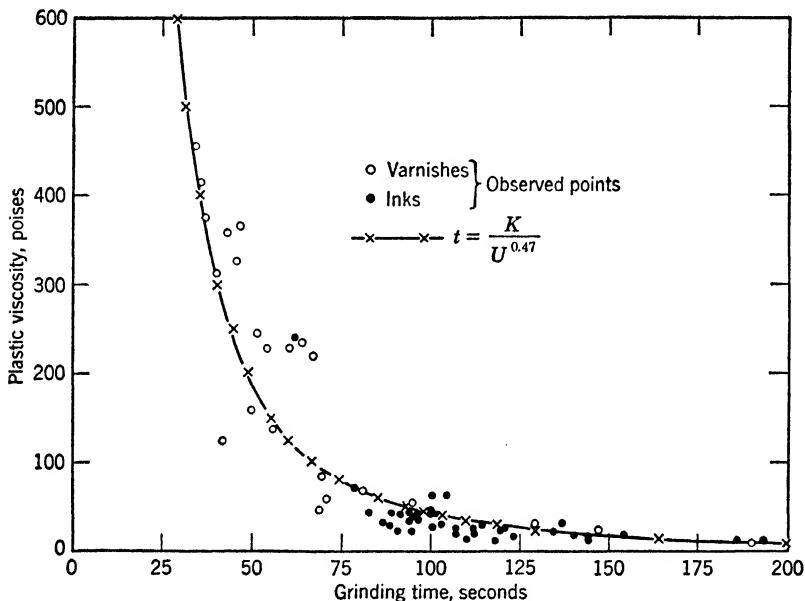


FIGURE 6. Relation between output on a three-roll laboratory mill and viscosity of the dispersion.

erse the roll system was measured. Initial roll settings were made by calibration marks on the hand-wheels used for setting the rolls. These data are plotted in Figure 6.

It will be observed that the output is extremely low for materials having a viscosity of 25 poises or lower and that the volume discharged from the mill increases greatly as the viscosity exceeds 200 poises. An empirical equation connecting these variables was found to be of the following form:

$$t = \frac{A}{dwsU^k} \quad (1)$$

where  $t$  is the grinding time for unit volume of material;  $A$  is a parameter based on roll dimensions and the driving gear ratios;  $d$  is the clearance

between the rolls during operation;  $w$  is the width of the rolls;  $s$  is the peripheral speed of the rear roll;  $U$  is the plastic viscosity in poises; and  $k$  is an empirical constant.

The quantity  $dws$  may be considered the volume of material extruded through an orifice of  $w$  width,  $d$  thickness, at  $s$  velocity.

It should be recognized that many compositions exhibit anomalous viscosity characteristics and that by measurement of the flow properties on a rotational viscometer it is possible merely to approximate the conditions obtaining in the roll mill. There are, in effect, two rates of shear, different in magnitude, to be considered for the three-roll mill: at the first pair of rolls, the clearance is larger and the differential speed lower than at the second pair. Consequently, the higher rate of shear obtains at the second pair of rolls. For a pseudoplastic composition the apparent viscosity is lower at these rolls. A dilatant composition, however, will exhibit greatly increased apparent (or momentary) viscosity at this point, and, if a critical rate of shear is exceeded by the mill, the apparent viscosity becomes very large with a correspondingly large rate of delivery from the mill. It has been observed that dilatant compositions track uniformly and that they frequently leave the rolls free of any adhering composition.

Increased production on roll mills by addition of small quantities of a material that presumably modifies the flow characteristics in the direction of increased viscosity has been described.<sup>10</sup>

Thixotropic structure and the existence of a measurable yield value have a negligible effect on roll-mill operation. A high yield value, however, may keep the composition from entering the nip of the feed rolls at a steady rate and, for this secondary reason, may result in a lowered output.

The mode of action of the roll mill has already been noted. The first two rolls act primarily as crushing rolls for oversize particles and aggregates. At the succeeding roll interfaces the comminuted particles are subjected to viscous shear within the suspending vehicle and, in highly loaded compositions, to friction of particles against each other.

In an extended series of tests on roll-mill dispersion performed by the technical committee of the New York Paint and Varnish Production Club,<sup>11</sup> an effort was made to correlate the chemical and physical properties of oils used as grinding media with the character of the

<sup>10</sup> L. Roon and A. Minich, U. S. Patents 2,180,721 (November 21, 1939); 2,301,142 and 2,301,143 (November 3, 1942).

<sup>11</sup> *Nat. Paint, Varnish Lacquer Assoc., Sci. Sect. Circ. 523*, 409-37, plus supplement 100 pages (November, 1936).

finished pigment dispersions. Although the data are not complete and quantitative correlation of all the factors cannot be made from these tests, the findings are of considerable interest. Photomicrographs of titanium dioxide dispersions made with oils of increasing viscosities show progressively fewer aggregates as the viscosity of the oil was increased from a low of 0.23 poise to 48 poises. The grinding time also decreased when oils of higher viscosity were used as vehicles.

The speed at which the rolls run determines, along with the clearance, the effective rate of shear and consequently the work done on the system. Early three-roll mills had relatively low differentials between rolls: 2 to 1 was common. Draper<sup>12</sup> in a discussion of roll-mill construction refers to some experiments on different roll speeds. At high differentials (20 to 1) the quality of the dispersion was found to be greatly improved as judged by the "finish" of typical paint and enamel formulations. A 3 to 1 ratio was noted by Lynch<sup>13</sup> as preferable to lower ratios. (See Table II.)

TABLE II. APPROXIMATE ROLL SPEEDS OF TYPICAL 12 BY 30 INCH MILLS

Mill Type	Roll				
	1	2	3	4	5
5-Roll	25	50	100	200	300
3-Roll	30	90	270	...	...
3-Roll, high speed	35	115	345	...	...

It could be expected that increasing the drive speed of a mill would result in a linear increase in output. This relationship has been observed over a limited range, but other factors, some of which have already been noted, make it improbable that a simple function would describe the connection between mill speed and output. At excessive speeds, low-viscosity materials fly off of the high-speed roll. For high pigment loadings, there is the possibility for dilatant flow in the composition with a consequently high output; pseudoplastic compositions would give an opposite result. Several mechanical factors also complicate the relationships; for example, there is difficulty in maintaining constant roll settings as the mill speed is increased. Data are lacking on this point, but it is of interest to compare the results reported by Hopkins<sup>14</sup> for lacquer pastes on two 12 by 30 inch mills (Table III).

<sup>12</sup> C. R. Draper, *Paint Manuf.*, **13**, No. 3, 42-47 (March, 1943).

<sup>13</sup> W. Lynch, *Official Digest Federation Paint & Varnish Production Clubs*, No. 176, pp. 244-49 (May, 1938).

<sup>14</sup> F. W. Hopkins, *ibid.*, No. 73, p. 9 (December, 1927).

TABLE III. PRODUCTION RATE OF ZINC OXIDE LACQUER PASTE ON 12 BY 30 INCH ROLL MILLS

	Speed of Rolls			Output (pounds per hour)
	1	2	3	
High-speed	26	78	234	186
Regular	18	54	162	140

### Contamination

The contamination introduced by roll-mill grinding, as a result of wear on the moving surfaces, is inconsequential for most products. Where trace quantities of iron deleteriously affect the optical properties of the dispersion, as is true with infrared reflecting paints, roll-mill grinding introduces an objectionable amount of iron, particularly when abrasive pigments or extenders, such as barytes, are employed in the formulation. The abraded steel comes from three chief sources: (1) the take-off knife; (2) the end plates; and (3) the rolls. The extent of contamination can be minimized by operating the mill with the take-off knife set at the lowest possible pressure which will remove the dispersion from the mill and by adjusting the end plates to allow a small but uniform clearance between the plate and roll surface. End plates made of hardwood, rather than bronze, may be advantageous. Formulation with a relatively high viscosity vehicle and operation of the mill with "loose" roll settings will also assist in keeping the contamination with iron at the minimum.

### Comparison of three- and five-roll mills

There has been considerable discussion on the relative merits of three- and five-roll mills. Comparison is sometimes based on the number of roll interfaces, and, with this criterion, the five-roll mill should be the equivalent of two three-roll mills. There are conditions where this relationship may hold, but for most manufacturing operations the comparison needs to include other factors, chief of which are the standards of fineness required and the aggregate size of the material fed to the mill. Suppose, for example, that a comparatively crude preliminary mixing of the pigment and vehicle has been made before subjecting the composition to grinding on a five-roll mill. The feed rolls will then require a relatively loose setting to accept the coarse material, and the clearances of the succeeding rolls will be adjusted empirically to transfer the composition at various stages of comminution, in accordance with the sizes of the suspended aggregates. The last pair of rolls will evidently establish the fineness, but the setting on these rolls can be made only in relation to feed rate determined by the settings on the preceding rolls. On

the other hand, if the same material is introduced onto the feed rolls of a three-roll mill, the first passage will serve to reduce the aggregate oversize; at the second pass both sets of rolls will be given a closer setting and will then discharge an acceptable product. Additional passes of the composition will be made at the closest settings possible.

That the oversize aggregates present in the preliminary mix establish the permissible clearances between rolls has been emphasized by Beakes,<sup>15</sup> who points out, further, that roll settings closer than those that accept the oversize merely strain out the aggregates which remain at the feed. At the end of the run the compacted material is forced through the roll system, and the dispersion, which appeared satisfactory at the start of the grinding, then is contaminated throughout with oversize particles.

If the preliminary mixing of pigment and vehicle results in reduction of aggregate sizes to the point at which fairly close roll settings can be made on a three-roll mill, it is possible to obtain satisfactory dispersion quality by a single pass on the three-roll mill. The comparison of the two types of mills thus resolves into a matter of the economics of the complete dispersion process. If an efficient preliminary mixing operation can be accomplished, by means, preferably, of an instrument capable of imparting high shearing forces to the dispersion, the three-roll mill will probably be the more satisfactory mill; if the mixture fed to the mill contains larger aggregates, as the consequence of a less severe shearing action during preliminary mixing, the five-roll mill may prove to be the more satisfactory instrument, for then the dispersion can be completed in a single pass on the mill. Production experience seems to be in accord with this view.<sup>16</sup>

Suggested pigment-vehicle ratios suitable for processing on the roll mill are given in Table IV essentially as listed in the standard color-testing methods recommended by the New York Printing Ink Production Club.<sup>17</sup> The pigment contents of the compositions given were de-

<sup>15</sup> H. L. Beakes, Chapter 2, pp. 80-90, *Protective and Decorative Coatings*, Vol. II, J. Mattiello, Editor, John Wiley & Sons, Inc., New York, 1944; *Paint, Oil, Chem. Rev.*, **98**, pp. 16, 18, 66 (April 16, 1936).

<sup>16</sup> *Official Digest, Federation Paint & Varnish Production Clubs*, No. 181, pp. 553-54 (December, 1938); C. R. Draper, *Paint Manuf.*, **13**, No. 4, p. 68 (April, 1943); A. F. Sterbenz, *Nat. Paint, Varnish Lacquer Assoc., Sci. Sect., Circ. 588*, pp. 101-103 (1939). Printing ink manufacturers in Germany were reported as favoring the three-roll mill: A. Voet, *Am. Ink Maker*, **25**, No. 9, pp. 64, 67, 69, 71 (September, 1947).

<sup>17</sup> H. J. Wolfe, E. K. Fischer, N. Rosen, P. Duffey, P. W. Greubel, H. Ochs, *Am. Ink Maker*, **22** (No. 11), 29-31, 33, 34, 51 (November, 1944).

TABLE IV. PIGMENT-VEHICLE GRINDING RATIOS FOR MULTI-ROLL MILLS

Pigment	Pigment Content (weight %)
Aluminum hydrate	50
Benzidine yellow	40
Blanc fixe	80
Cadmium red *	75
Cadmium orange *	75
Cadmium yellow *	75
Carbon black ("short flow")	25
Carbon black ("long flow")	25
Chrome yellow	75
Chrome orange	80
Chrome green	65
Chlorinated para red toner	40
Guignet green	75
Gloss white	65
Green toner †	40
Hansa yellow	40
Iron blue (all shades)	50
Lithol toner	40
Lithol rubine	40
Magnesium carbonate	50
Molybdate orange	75
Orange mineral	85
Orange toners	40
Para red toner	40
Persian orange	50
Peacock blue (fugitive type)	50
Peacock blue †	40
Purple toner †	40
Red lake C	40
Toluidine toner	40
Titanium dioxide	75
White lead	80
Zinc oxide	65
Zinc yellow	65

\* Full strength and lithopone types.

† Phosphotungstate acid lakes or similar types.

signed primarily for a bodied linseed oil with a viscosity of 12 poises. Some variation will, of course, be desirable for vehicles of either higher or lower viscosities. For many dispersions, however, these ratios will prove quite satisfactory and adjustment can be made for special dispersions.



### Operation of the roll mill

A few observations on the proper operation of the roll mill may be useful, for it has been observed that sometimes even presumably experienced technicians subject the mill to unnecessary wear and expose themselves to needless hazards.

The mill should be installed so that it is accessible from at least three sides by placing the side of the mill designed for connection to the cooling water supply against the wall. If an arrangement for piping through the floor is possible, the mill can stand free and be accessible from all sides. The electrical connections should be arranged so that starting and stopping is possible from any position: in a small mill this can be accomplished by placing the starting button at the top and at one side; in a large mill, in which two buttons are used, it is imperative that each stop button be equipped with a lock to prevent accidental starting from the second position. Various safety devices have been installed.<sup>18</sup> To prevent the operator's hand from entering the feed rolls, a round bar is held in holes in the end plates and at a slight distance above the nip. This expedient is considered generally unsatisfactory, for it impedes proper feeding of viscous pastes and, moreover, is removed during cleaning when the hazards are far greater. Consequently, most operators prefer quick stopping devices such as a cable or pivoted-bar arrangement spanning the space across the top of the mill and connected to the control switch. For individually driven mills this arrangement is satisfactory.

Accidents during operation are far less likely than during cleaning. The cloth used to wipe the rolls should be folded into a small pad and care should be taken to avoid loose ends which may pull into the nip. The hand should be held at least 180° from the nip on the first roll, and a steady pressure applied against the rotation of the roll. The take-off knife and the pointed end plates should be handled with considerable care and, if placed on a work bench, should be pointed toward a wall or protecting cover to prevent chance cutting.

Operation of a three-roll mill can be generalized in the following steps:<sup>19</sup> (1) the rolls are backed off and the take-off knife is released; (2) the pigment-vehicle mixture is introduced onto the feed rolls; (3) the mill is started and the feed rolls tightened slightly; (4) the third roll is then set to pick up the ink from the second roll, and the take-off knife is tightened; (5) the material discharged while these adjustments are

<sup>18</sup> Anon., *Am. Ink Maker*, 15, No. 3, pp. 16, 17, 18, 19 (March, 1937).

<sup>19</sup> Instructions as supplied by the manufacturers of mills should be consulted for more explicit directions.

being made is scraped off the delivery apron and returned to the feed rolls. If the composition feeds properly, the setting sequence is repeated, this time with adjustment for uniform feed rate and pressure.

Some compositions present difficulties. When materials are being dispersed in oleoresinous vehicles that contain volatile solvents, some of the solvent may evaporate and the mixture then becomes progressively more viscous. It may be necessary to add solvent to the paste on the mill. An enclosure for the mill, intended to reduce such solvent loss, has been described by Bernstein.<sup>20</sup>

The take-off knife of a modern mill is made of a thin steel strip inserted in a slot in the apron. These blades flex, and the tension on the setting spring should be the lowest that will remove the material from the roll. If higher pressures are used, the blade may grind to a bevel so that subsequent adjustments will have to be made to the same or greater pressures. This results in excessive power consumption and burring of the blade. Sonsthagen<sup>21</sup> states that the blade should repose at an angle of about 45° (to the tangent at the point of contact) and estimates that the area of contact of a blade  $\frac{1}{16}$  inch thick is about 0.06 square inch per inch of roll. For a 40-inch roll this amounts to 2.4 square inches. Sonsthagen also states that the blade pressure required to remove the film increases with higher viscosity of the composition, higher roll speeds, and with a smaller scraping angle.<sup>22</sup> A burred blade may introduce air into the composition, and this condition can be mistaken for poor comminution of the pigment. Usually the air will be removed by re-milling with the take-off knife in proper condition.

The grinding of small batches of a pigment dispersion, particularly on laboratory mills, is frequently performed with the end plates set to allow the composition to spread over only the central portion of the rolls, leaving part of the rolls dry. This practice is highly injurious, for the areas of the rolls and the take-off knife that are unlubricated are apt to score and wear unevenly. Contamination is also greatly increased. Instead, the end plates should be placed near the ends of the rolls and

<sup>20</sup> I. M. Bernstein, U. S. Patent 2,325,171 (July 27, 1943).

<sup>21</sup> L. A. Sonsthagen, *Verfkroniek*, **12**, 172-75 (1939); abstracted in *Paint Technol.*, **11**, 188 (1946).

<sup>22</sup> The author has observed conditions in which the blade appears to "float" at the roll junction. A bright blue luminescence (visible in a darkened room) has been noted at the leading edge of the knife during mill operation. This effect was most striking in a composition containing a dark chrome green dispersed in an alkyd-resin solution. The fact that the delivery roll usually carries a thin, residual film past the blade is further evidence for the possibility that the blade is not in direct metal-to-metal contact with the roll surface.

set at a slight uniform clearance from the roll surface. Operating in this way, the contact of unlubricated metal surfaces is avoided and the composition during grinding extends over all moving surfaces, thus ensuring uniform wear.

A simple test for the condition of the roll surfaces is made by placing a light bulb under the rolls of the mill and observing the variation in the width of the line of light when observed from a position directly above the mill. It is helpful if the room is darkened somewhat for this test. The rolls should be clean and free of any excess oil which may have been applied. If the roll surfaces and bearings are in good condition, an unwavering line of light will be observed. Varying degrees of eccentricity in the rolls will show as a line of light varying in width.

The rules for proper operation of a roll mill have been summarized by Ferrise,<sup>23</sup> as follows: (1) pre-mix pigment and vehicle thoroughly; (2) start the mill with the rolls backed off slightly and tighten to a final setting when the mill is running with the composition on the rolls; (3) adjust the end plates to a slight clearance between the rolls and plates; (4) adjust the take-off knife to bear against the discharge roll at the lightest pressure which removes the composition; (5) keep the full width of the rolls covered with the fluid composition at all times when the mill is operating, and avoid the transfer of dry pigment at the end of a run by adding fluid composition from the apron or additional vehicle to the nip rolls; (6) formulate the composition at the highest viscosity that is practicable for the drive capacity of the mill and efficient handling and packaging of the product.

### The Two-Roll Mill

The two-roll mill, or rubber mill as it is sometimes designated, is a batch mill. The rolls operate at clearances from about  $\frac{1}{16}$  inch to the maximum of approximately  $\frac{1}{2}$  inch, and the viscosity of the material during grinding is of the order  $10^7$  poises. Dispersion is evidently achieved only by internal shearing, and the mill is thus comparable in its action to the heavy-duty dough mixer in which the extent of dispersion is established partly by the time of operation.

In construction the two-roll mill is far more rugged than the multi-roll mills described above.<sup>24</sup> Several sizes are available. Production mills are usually equipped with rolls 22 or 24 inches in diameter and 4 to 7 feet in length. A laboratory size that is widely favored has rolls 6 inches in diameter and 12 inches in length, but a smaller mill is also

<sup>23</sup> L. J. Ferrise, *Am. Ink Maker*, **21**, 25-26 (January, 1943).

<sup>24</sup> E. R. Riegel, *Chemical Machinery*, Reinhold Publishing Corp., New York, 1944.

used. The rolls are of chilled iron and are hollow to allow the circulation of cooling water or the injection of steam under pressure. Roll speeds are low (15–25 r.p.m.). Usually the rolls are driven at a slight differential, 1.2 to 1, but the ratio may be as high as 3 to 1.<sup>25</sup> One roll is adjustable, and setting of the roll clearance is facilitated by means of calibrated dials affixed to the frame at the adjusting screws. When used for rubber compounding, the batch is removed by a hand-held knife, but, for other materials, knives running the full length of the rolls are attached to lever arms so that they may be quickly pressed against the roll to strip the sheet. Most installations include a safety switch on a bar arrangement directly over the rolls; if the operator inadvertently gets into a hazardous position over the nip of the rolls, the power to the motor is cut and a magnetic brake brings the rolls to an instant stop.

It may be pertinent at this point to note that the Banbury mixer is designed to operate on the same class of materials as the two-roll mill and, for many purposes, may be used for pigment dispersions with minor modifications in the formulations adapted for this mill. The dispersion after discharge from the mixer is usually given a "sheeting" pass over the two-roll mill.

Thorough analysis of the forces effective during dispersion on a roll mill remains to be made. The calculations of Eley<sup>26</sup> are of considerable interest in this connection. Eley calculated the roll pressures  $q$  in milling a plastic mass on the two-roll mill. When the plastic enters the rolls, it is compressed, and the pressure on the rolls is established by the feed rate, the viscosity of the plastic, and certain mechanical features of the mill. Eley made the following assumptions: (1) no slip occurs at the roll surfaces, and frictional forces can, therefore, be neglected; (2) the deformation is a homogeneous compression and is entirely viscous without an elastic component; and (3) the plastic mass itself is incompressible. It is evident that the simplification makes the calculation a limiting or an ideal case, for shearing as the result of differential roll speeds is eliminated by the first assumption. Moreover, many plastic masses show elastic properties. The equation given is

$$q = \eta \frac{8V \tan \theta}{h^2} \quad (2)$$

where  $q$  is the vertical roll pressure at any point on the arc of contact,  $V$  is the volume rate of flow of the plastic mass per unit width of roll,

<sup>25</sup> A multi-roll mill with high roll speeds for rubber and plastic materials has been patented by V. Conrad, U. S. Patent 2,326,927 (August 17, 1943).

<sup>26</sup> D. D. Eley, *J. Polymer Sci.*, **1**, 529–34 (1946).

$\eta$  is the viscosity,  $\theta$  is the angular coordinate of the arc of contact, and  $h$  is the height of the plastic at the point of contact corresponding to  $\theta$ . (Figure 7.) Calculations of roll pressures  $q$  at different points on the axis led to values from 1,400 to 10,000 pounds per square inch (rounded figures). This case was for a material with  $\eta = 3.2 \times 10^7$  poises. An average value  $q$  was computed as 5,200 pounds per square inch and an experimentally determined pressure for this system was 4,300 pounds per square inch, thus affording a rough check of the computation.

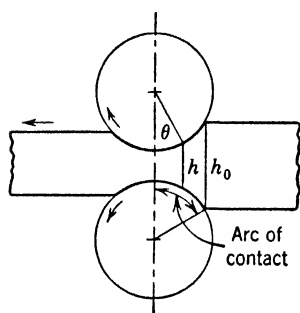


FIGURE 7. Diagram of rolling of plastic mass. (After Eley.)

An extension of Eley's reasoning leads to formulas for the "work of rolling" and to temperature effects.<sup>27</sup>

*Rubber compounding.* Since the two-roll mill has been employed largely for rubber-compounding processes, most of the information on its operation derives from this source. Gallay<sup>28</sup> has summarized the mechanical factors in the milling of rubber. In general it has been found that a greater effective mastication is obtained in a given time for small batches and with increased differentials in the speeds of the rolls. The power consumed decreases as the rolls are

loosened, and a corresponding decrease in the effectiveness of mastication results. The milling of rubber is complicated by oxidation reactions and thermal decomposition as well as by the shearing stresses imposed. All these factors combine to produce a degradation in the structure as evidenced by the decreased viscosity of solutions of masticated rubber in hydrocarbon solvents.

The mechanism of breakdown of rubber has been studied by Busse. During milling, the rate of oxidation is increased by activation of oxygen by the electric charge that develops. Peroxides are formed. On a cold mill no electric discharge occurs under the bite of the rolls, but there is a steady glow over the surface of the rubber just before it enters the nip. The crackling and frying noises associated with milling are attributed to the electric discharges, rather than to the bursting of air bells trapped in the rubber mix.<sup>29</sup>

Rubber testing and processing on the two-roll mill have become fairly

<sup>27</sup> D. D. Eley, *ibid.*, **1**, 535-39 (1946).

<sup>28</sup> W. Gallay, Chapter IV, pp. 150-80, in *The Chemistry and Technology of Rubber*, C. C. Davis and J. T. Blake, Editors, Reinhold Publishing Corp., New York, 1937.

<sup>29</sup> Cf. W. F. Busse, *Ind. Eng. Chem.*, **24**, 140 (1932) and W. F. Busse and E. N. Cunningham, *Proc. Rubber Technology Conf.*, London, May 1938; pp. 288-301.

well standardized. Carpenter<sup>30</sup> lists the recommendations of the Physical Testing Committee of the Rubber Division, American Chemical Society, for standard-testing procedures:

Mill: Rolls 6 inches diameter, 12 inches long, working distance 10.5 inches.

Roll speed: Slow roll 24 r.p.m.; gear ratio 1/1.4.

Cooling: Water controlled at 70° C.

Roll openings: Vary with batch size; e.g., 0.055 inch for 300 cc. batch, 0.170 inch for 7200 cc. batch.

Roll setting for sheeting: 0.085 inch.

The sequence in which the compounding ingredients are added is preferably: (1) accelerators and antioxidants, (2) carbon black, (3) fillers, (4) softeners, (5) sulfur. Variations in this sequence are frequent.<sup>31</sup> In the testing procedure described by Drogin,<sup>32</sup> the "break-down" mastication of rubber with tight rolls was continued for 10 minutes. Ingredients of the formula were then added in the following order: fatty acid and softeners, carbon black, zinc oxide, accelerator, sulfur. The total batch weighed 600–700 grams, and the mixing time was 25 minutes.

Several of the precautions to be taken in milling rubber are described in various handbooks.<sup>33</sup> Thus, vulcanization can start during milling, and consequently it is advised that temperatures be kept low during milling and that fast-curing stocks be chilled immediately after removal from the mill by dipping in cold water. Master batches, in which the ingredients are incorporated separately, permit greater flexibility in arranging the grinding cycle.

Milling of rubber with cobalt linoleate produces an oxidation product sometimes called rubbone. This material in the form of a solvent cut has some advantages in producing flat paints with good flowout and in compounding with oleoresinous varnishes with improved water and acid resistance together with good flexibility.<sup>34</sup>

*Dispersion in nitrocellulose and resins.* Although the two-roll mill finds its greatest use in processing elastomers, it is used as well for the dispersion of pigments in any medium of sufficiently high viscosity.

<sup>30</sup> A. W. Carpenter, Chapter 24, pp. 777–84, in Davis and Blake, *Chemistry and Technology of Rubber*, Reinhold Publishing Corp., New York, 1937.

<sup>31</sup> Columbian Carbon Co., "The Carbon Reinforcement of Buna S (GR-S)," and "The Carbon Reinforcement of Neoprene GN," *Columbian Colloidal Carbons*, Vol. IV (1943) and Vol. VI, No. 1 (1945).

<sup>32</sup> I. Drogin, *India Rubber World*, **106**, 561–69 (September, 1942); **107**, 42–49 (October, 1942).

<sup>33</sup> Cf. S. R. Rogers, Editor, *The Vanderbilt Rubber Handbook*, R. T. Vanderbilt Co., New York, 1948.

<sup>34</sup> H. W. Chatfield, *Varnish Constituents*, Leonard Hill, Ltd., London, 1944, pp. 452–54; S. C. Stokes, *Paint Manuf.*, **17**, 261–63 (1947).

Grenquist<sup>35</sup> and Sweitzer<sup>36</sup> describe procedures for dispersions in nitrocellulose. When plasticizers and resins are added to nitrocellulose, a plastic, colloidal mass is obtained which forms an effective dispersion medium. In combination with copper soaps, carbon black is finely dispersed and deflocculated in the nitrocellulose, and the product, being friable, may be pulverized and stored as a stock dispersion. Dispersions of this type have been successful commercial products, not only because their formulation is convenient but also because the dispersions make finished lacquers of high gloss and excellent jetness.

In an extension of this procedure, Wiegand<sup>37</sup> describes a two-step process. The pigment is mixed with resinous materials, such as phenol-formaldehyde resin and ester gum, by means of a dough mixer to obtain a preliminary "massing" or agglomeration; the mixture is then placed on a two-roll mill and subjected to the higher shearing action of closely set rolls, cooled by circulating water if necessary, until the consistency is comparable to a rubber mixture, or, as described by Wiegand, "leather-like." Using the same technique, Vogel<sup>38</sup> mentions a variety of resins that are suitable for high-viscosity shearing: oil-modified alkyd, phenol-formaldehyde, urea-aldehyde, coumarone-indene resins, and the natural resins. Wiegand and Vogel do not limit their processing to carbon black, but mention, in addition, various other colored pigments as adaptable for the processing in which the two-roll mill is also the main instrument. In a variation of this process, described by Barrett,<sup>39</sup> in which a preliminary mixing of the pigment and resin composition is accomplished by tumbling, grinding is done on the two-roll mill, and the resulting dispersion is reduced with additional vehicles in a special plastic mixer. Barrett maintains a relatively high pigment-resin ratio, and the solvent, present with the resin component, is partly lost during grinding, resulting in a mill sheet that is readily crushed.

A large variety of resinous materials may be employed for the two-roll mill dispersion of pigments. The primary requirement is that sufficiently high plastic viscosity develop during operation in order to obtain adequate shearing forces within the mixture. It is necessary, further, that the pigment and resin combination be non-reactive; otherwise the equivalent of livering will occur and the product will, in consequence, exhibit poor solubility. Some changes in the polymeric structure of the

<sup>35</sup> E. A. Grenquist, U. S. Patents 2,085,512 (October 20, 1934) and 2,085,528 (November 9, 1934).

<sup>36</sup> C. W. Sweitzer, U. S. Patent 1,987,980 (January 15, 1935).

<sup>37</sup> W. B. Wiegand, U. S. Patent 2,045,006 (June 23, 1936).

<sup>38</sup> M. R. Vogel, U. S. Patent 2,173,430 (September 19, 1939).

<sup>39</sup> W. R. Barrett, U. S. Patent 2,232,426 (February 18, 1941).

resin during milling are inevitable, but these cannot be predicted, and are, in a sense, analogous to the complex changes that occur in rubber. Thermosetting resinous materials, such as those used in molding powders, can be run on the mill for only a short time (a minute or two). For molding powders the mill is essentially a blender. One of the most versatile vehicles for two-roll mill dispersion of pigments is ethyl cellulose, since it tracks well on the rolls, provides an efficient dispersing medium for the pigment, and retains solubility after milling. In addition the hazards associated with nitrocellulose are avoided. Typical formulations are given in Table V from the data of Wiggam.<sup>40</sup> The time

TABLE V. TWO-ROLL MILL DISPERSIONS

Ingredient	Carbon	Zinc	Titanium	Chrome	Iron	Cadmium	Chrome
	Black (high color)						
Ethyl cellulose, %	56	32	20	17.5	40	24	24
Tricresyl phosphate, %	14	.	5	7.5	12	6	6
Dibutyl phthalate, %	..	8					
Pigment, %	30	60	75	75.0	40	70	70
Back roll temperature, °C.	115	110	135	115	115	125	125
Front roll temperature, °C.	95	100	110	100	100	100	100
Milling time, minutes	26	26	5	26	26	15	15

D. R. Wiggam, U. S. Patent 2,184,539 (December 26, 1939).

for dispersion ranged up to 30 minutes for these tests. Most pigments are dispersed to the optimum state in less time, and some (chrome yellow, titanium dioxide, zinc oxide, as examples) require as short a time as five minutes. It will be noted that the roll temperatures reached 135° C. It is probable that somewhat higher temperatures prevail momentarily at the nip of the rolls. Prolonged milling time is not always advantageous, for the vigorous action of the mill and the high temperatures developed will decompose thermally unstable pigments.

Because the composition becomes heated to rather high temperatures, any moisture present in the pigment is largely volatilized. The dispersion is perhaps more nearly anhydrous than those made by any other method, and, as a consequence, the flocculating effect of water on the system is eliminated.

In general, the pigment-resin ratios suitable for operation on the two-roll mill follow the ratios listed in Table IV for dispersions in viscous oils on multi-roll mills. As examples of the range permissible, the data given by Wiggam are noted in Table VI. When maximum pigment loadings are used, the composition heats up rapidly and a "short" or friable sheet may form which will not adhere to the rolls. Excess pigmentation re-

<sup>40</sup> D. R. Wiggam, U. S. Patent 2,184,539 (December 26, 1939).



TABLE VI. PIGMENT-RESIN RATIO LIMITS FOR TWO-ROLL MILL DISPERSIONS

Pigment	Maximum	Maximum
	(%)	Practical (%)
Carbon black (high color)	55	40-45
Iron blue	65	55-60
Chrome yellow	85	75-80
Zinc oxide	85	75-80

D. R. Wiggam, U. S. Patent 2,184,539 (December 26, 1939).

sults also in decreased solubility of the resulting chip for carbon blacks and many organic pigments. It is probably for this reason that Sweitzer<sup>36</sup> used a rather low carbon-black content (about 10 percent) for nitrocellulose-resin dispersions. The procedure for dispersing pigments in heat-convertible resins has been described by Engle, Sheridan, and Fischer.<sup>41</sup>

Surface-active agents are of considerable assistance in forming a sheet on the mill. If the composition during milling appears granular and breaks into fragments, the addition of a deflocculant causes it to assume a more coherent structure with a consequent improvement in over-all working properties. For carbon black, copper<sup>36</sup> and nickel<sup>42</sup> soaps have been specified; Vogel<sup>38</sup> mentions polyamines, such as triethylenetetramine, metaphenylene diamine, and benzidine. For other pigments, alkaline-earth metal soaps,<sup>43</sup> heavy metal soaps, lecithin, or various oil-soluble surface-active reagents are used.

*Operation.* The procedure in operating a two-roll mill differs markedly from that of the three-roll mill described above. Successful and safe operation of a two-roll mill requires skill and dexterity of a high order. Such proficiency can be gained only by experience. Initially the rolls are usually heated, either by water or steam, or, lacking these means, by operating with a charge of rubber until the rolls are warmed sufficiently by friction to enable the resin to adhere. The resin is then introduced onto the rolls, preferably in the form of a coarse powder, with a portion of the plasticizer or a small amount of a solvent. After the resin has formed a coherent mass, adhering preferably to one roll, the pigment is added slowly. The batch is run until the pigment is incor-

<sup>41</sup> L. S. Engle, E. Sheridan, and E. K. Fischer, U. S. Patent 2,454,785 (November 30, 1948).

<sup>42</sup> R. L. Zapp, U. S. Patent 2,173,444 (September 19, 1939).

<sup>43</sup> R. L. Zapp, U. S. Patent 2,173,445 (September 19, 1939); cf. also Brit. Patent 517,640.

porated, and, at intervals thereafter, the mixture is sheeted, reversed, and returned to the rolls to ensure even distribution and uniformity. The temperature of the rolls is controlled by circulating water. For some products it is feasible to mix the pulverized resin, pigment, and plasticizer in the correct proportions and to add this mixture to the hot rolls. To reduce dusting and facilitate mixing, the pigment is dampened with solvents, plasticizer, or water. The temperatures developed during milling are ordinarily sufficient to cause evaporation of solvents and water, and, occasionally, of plasticizers such as dibutyl phthalate and tricresyl phosphate. Adjustment of the formulation should be made for this loss.

When dispersion is complete, the composition is removed from the rolls in the form of a sheet. While still hot it is flexible; on cooling it becomes brittle and friable. For ease in handling later it is desirable to spread the sheet on a flat surface to cool and later to break it into chips.

The quality of the dispersion may be rated by dissolving the chip and examining under a microscope for the presence of aggregates. Care should be exercised in preparing the solution, however, for, if the solvent merely swells the dispersion, fragments of the swollen pigment-resin combination will be incorrectly viewed as aggregates. Further processing will, of course, reduce such particles. While the dispersion is on the mill, it is possible to remove a small strip, allow it to cool, and, after breaking, note the appearance of the edges of the fracture. Imperfect comminution in some, but not all, dispersions will show as a rough, dull surface; when the pigment is finely divided and free of oversize aggregates, the fracture will show high gloss. These tests are relatively crude, but they serve as a guide during operation.

After the dispersion on the mill is completed, the chips may be dissolved or cut in additional solvent and vehicle components by means of a mixer. If the pigment-resin chips are broken into small pieces or pulverized to a coarse powder before solution, the subsequent steps are shortened. The manufacture of dispersions in this manner is described by Verbyla.<sup>44</sup> If the resins used in making the two-roll mill dispersion are of the non-oxidizing type, it is possible to store the product either in the form of pigment chips or as a powder. Oxidizing resins, however, require that the product be processed to a paste form shortly after processing on the mill.

<sup>44</sup> A. E. Verbyla, U. S. Patent 2,000,003 (April 30, 1935).

## 10. Ball and Pebble Mills

Ball and pebble mills have been widely adopted for preparation of colloidal dispersions. In the most common design, a cylindrical chamber, mounted horizontally, is partially filled with pebbles or porcelain or steel balls together with the components of the mixture for grinding. Rotation of the cylinder causes the balls to be lifted to the point where they cascade, rolling over each other, crushing any particles caught between contacting balls, and subjecting the mixture to a highly turbulent mixing action in the spaces between the balls.

Mills that embodied the principle of the modern instruments were long employed for the grinding of ores, Portland cement, and ceramic products before any extensive adoption for pigment dispersion. The early mills were not suitable for this purpose because of mechanical and structural defects. In particular, excessive wear both of the shell of the mill and the balls, together with a high incidence of broken balls, where cast iron or steel formed the material of the grinding medium, were serious obstacles. When, shortly after the close of World War I, essential mechanical refinements were gradually introduced, the ball mill found wider acceptance.<sup>1</sup>

The design of the ball mill holds several advantages over other mills: volatile solvents are retained by the closed drum; preliminary mixing of the components is usually unnecessary; operation may be continued without attention for extended periods until the desired dispersion quality is obtained; and maintenance and operating costs are comparatively low. The general utility of the mill is lessened to some extent, however, by the contamination introduced into the product by the abrasion of the pebbles or balls, but this deficiency can be minimized by careful control of the operating conditions.

<sup>1</sup> Notes on the development of the ball mill will be found in the following references: P. O. Abbé, *Am. Enameler*, **8**, No. 10, p. 6 (1936); W. H. Coghill and F. D. DeVaney, *Bulletin*, Missouri School of Mines and Metallurgy, **13**, No. 1, September, 1938; E. K. Fischer, *Interchem. Rev.*, **3**, 91-104 (1944).

The efficient use of ball and pebble mills requires the balance of a number of variables. Although the analysis of performance of any given mill operation is difficult, requiring in some cases careful and systematic observation over an extended series of trial runs, there are, nevertheless, data from standard practice and experimental work pertinent to many special applications. It can be readily seen that the construction of the mill and its driving mechanism establish permissible loads and speeds, but other conditions well within the control of the operator determine actual grinding efficiency.

### Mill Construction

Nomenclature for ball and pebble mills has become fairly well standardized. Sometimes called tumbling mills, especially in mineral-dressing practice,<sup>2</sup> they are, however, more generally referred to in terms of the grinding medium and constructional features of the mills.<sup>3,4,5</sup> A pebble mill usually has a non-ferrous lining of buhrstone, siliceous, or porcelain, and the grinding medium consists of selected flint pebbles. A ball mill is made with a shell of steel or steel alloy, which may be lined with special alloy steel plates, and the balls used as the grinding medium are made of cast iron or, now more frequently, of alloy steel. (Figure 1.) Where porcelain balls are used the mills are variously designated as pebble or porcelain-ball mills, sometimes without distinction: the latter term is preferable, however, as more precisely descriptive. Rod mills, rarely used for pigment dispersion, employ steel rods for the grinding medium.

The shape of the mill provides another classification. Cylindrical mills are the most common, and this design is characterized by flat ends attached to a cylindrical section. When the length of the mill is greater than twice the diameter, it is usually designated as a tube mill. Conical mills have, as the name implies, either the whole mill or a section in the form of a truncated cone. Several unusual designs have been advanced. One is a cylindrical ball mill with hemispherical ends so arranged that the bearings are placed off-axis to the horizontal axis; in operation, the ends of the mill body rise and fall, and the charge is subjected to a rapid surge from one end of the mill to the other. Other designs have been described, but the trend in design and construction of ball and pebble mills appears to be toward simplicity with ruggedness and long operating life as objectives.

<sup>2</sup> A. F. Taggart, *Handbook of Mineral Dressing*, John Wiley & Sons, Inc., New York, 1945.

<sup>3</sup> E. M. Underwood, *Ind. Eng. Chem.*, **30**, 905-8 (1938).

<sup>4</sup> W. H. Withington, *ibid.*, **30**, 897-904 (1938).

<sup>5</sup> G. F. Metz, *Bull. Am. Ceram. Soc.*, **16**, 461-67 (1937).

Continuous operation methods, in which a ball mill is a unit operation in a sequence of processing steps, have been extensively adopted in some industries, but, for pigment dispersion, batch methods are the rule. Nevertheless, for volume production of a single item, such as certain

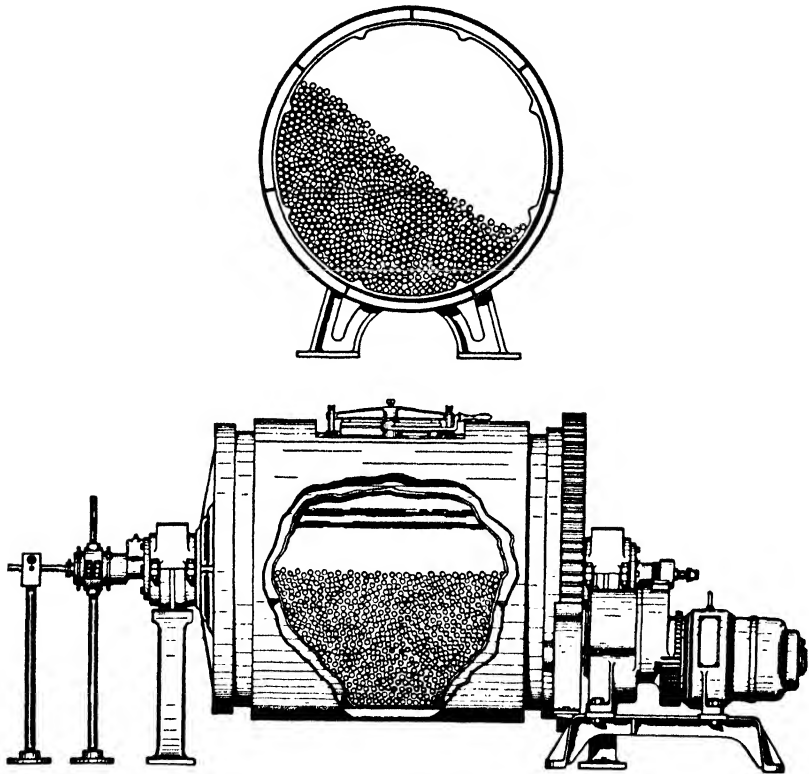


FIGURE 1. Cross-sectional and longitudinal views of a pebble mill. (Courtesy Patterson Foundry and Machine Co.)

types of white paint or news ink, integration of a ball mill with other processing equipment to provide a continuous flow from raw materials to finished product should be advantageous.

The mills intended for operation with pebbles or porcelain balls are lined with blocks of Belgian silex, buhrstone, quartzite, porcelain, or for special purposes with rubber. The blocks are cemented in such a fashion that the thickness of the joints is kept to the minimum. Linings for steel-ball mills are of alloy-steel plates, bolted into place, and fitted with bars to assist in lifting the ball charge to a point at which cascading of the balls is facilitated and slipping is minimized. The actual design of

the lifter bars varies: some manufacturers use a steel bar, rectangular in cross section, bolted to the lining; others use a wave form, integral with the lining; and a third group of designers space the bars at a distance from the lining.

Mill dimensions range from sizes suitable for laboratory development work, six inches in diameter, to production mills with diameters up to nine feet. The small mills, usually designated jar mills, are arranged to operate in clamps or saddles, and some designs allow as many as twelve jars to run in a single unit. Larger mills, scaled to suit production requirements, permit allocation of separate mills for individual colors in order to eliminate waste and cleaning incidental to frequent changes in the product. Since heat is generated during operation, most modern mills designed for pigment dispersion are jacketed for the circulation of cooling water; old mills are sometimes cooled by spraying water directly onto the shell of the mill, collecting the run-off in drains below the mills. The jacketed mill is adaptable also for heating with steam under low pressure, and this arrangement allows the grinding of products that are solid at room temperature, such as carbon-paper coatings.

The drives on large mills are equipped with brakes to ensure rapid stopping and to prevent coasting from the unbalanced, static load. An "inching" button is also provided to enable the operator to locate the mill port directly under a charging hole or over a container for discharge of the finished product.

### Grinding Media

Beach pebbles, rounded and free of pits, have long been employed as grinding media. Generally considered the most satisfactory, from the standpoint of uniformity and hardness, are flint pebbles of Danish origin. French pebbles from Normandy and Picardy are somewhat less regular and flatter than the Danish pebbles.<sup>6</sup> Other sources have been located in Newfoundland, North Carolina, and Texas.<sup>7</sup> There is no conclusive evidence for the comparative merits of pebbles from different sources, but it is stated that the Texas pebbles have the same amorphous, nodular flint structure as the French pebbles.<sup>8</sup> Pebble sizes used in production mills range approximately from 1 to 5 inches in diameter, but smaller pebbles are available and are particularly advantageous for laboratory jar-mill charges.

The dispersion of white pigments necessitates a grinding medium that would not deleteriously affect the whiteness of the product. Since mi-

<sup>6</sup> S. W. Kendall, *J. Oil & Colour Chemists' Assoc.*, **15**, 66-96 (1932).

<sup>7</sup> G. F. Metz, *Bull. Am. Ceram. Soc.*, **24**, 357-60 (1945).

<sup>8</sup> E. M. Underwood, *Chem. and Met. Eng.*, **49**, No. 7, p. 134 (July, 1942).

nute quantities of abraded material are an inevitable consequence of the rubbing of the balls, the contamination should be finely divided and should not contribute color. Porcelain meets these requirements and the manufacture of balls, suitable for grinding media, has been made largely automatic. The extruded plastic ceramic is spun to a spherical shape, then dried and fired. Although porcelain balls have been widely adopted, several disadvantages are inherent in their use: comparatively high rate of wear, low specific gravity, and high cost. Zirconium oxide has been introduced as a material for linings and balls. Since balls made from this oxide have a specific gravity of 3.7, approximately fifty percent greater than that of porcelain, higher efficiency may be expected. The rate of wear is also reported to be considerably less than that of porcelain.<sup>7</sup>

Steel balls provide the greatest efficiency in ball-mill pigment dispersion. Before alloy steels were available, cast iron and cast steel balls were employed, but since excessive contamination was introduced, they were useful only with dark colors. The alloys now in use contain chromium, manganese, nickel, and molybdenum. With a specific gravity of 7.8, these balls allow high viscosity charges, and when properly used they acquire a satin-smooth polish. Sizes range from  $\frac{1}{16}$  inch up to several inches in diameter.

Occasional use is made of other materials for grinding media. Granite was once favored. Quartz balls are stated to be more durable and economical than porcelain or flint. Glass beads are used in grinding biological preparations and have been patented for milling calcined pigments.<sup>9</sup> "Carbide balls" are composed of a combination of cobalt and the carbides of tungsten, tantalum, columbium, and titanium. The shape is that of a cylinder  $\frac{5}{8}$  inch in diameter with rounded ends, and this spheroid-cylindrical form is considered superior to balls for some purposes. Since the specific gravity is high, approximately twice that of steel, and the rate of wear low, the carbide balls, despite their high cost, are finding a place where other grinding media are unsuitable.

## Operating Variables

### Ball paths

The course of the ball charge in a rotating mill has occupied the attention of investigators of mill operation for many decades. To observe the ball paths, special mills were constructed with a screen or plate glass for one side. This arrangement permitted direct visual observation or photography. Four general types of ball path were noted: *cascading*,

<sup>9</sup> C. Robertson, U. S. Patent 2,361,059 (October 24, 1944).

in which the balls roll over each other in a coherent, mobile mass (as suggested by analogy with a waterfall); *cataracting* in which individual balls are thrown clear of the ball mass and move independently until they are forced to rejoin the charge at the bottom of the mill; <sup>10</sup> *slipping* (slip-page), in which the ball mass moves as a static unit in relation to the walls of the rotating mill; and *centrifuging*, in which the balls are held by centrifugal force at the interior periphery without motion relative to the drum.

Cascading is the desired form for the movement of the charge for pigment dispersion, since it represents the conditions for optimum efficiency. During rotation of the mill, the balls are lifted to a point at which the top balls are no longer held near the mill lining and at this "angle of break" begin to cascade or roll downward. At the bottom of their path the balls are pulled into the mass and again start the upward movement. The motion of the balls is transferred from one to another, and a surge is set up which slowly shifts the material from one end of the cylinder to the other. For maximum efficiency it is desirable that the balls be lifted to the highest possible point so that their paths of travel will be at the maximum.

The other types of ball motion are undesirable for pigment dispersion. Slipping results in greatly lowered efficiency and abnormal wear. Cataracting is equally undesirable since work is wasted in impelling the balls to move independently. Centrifuging represents an extreme condition in which it is apparent that no useful work is accomplished. The path is determined largely by the speed of rotation, the ball load, and the flow properties of the composition being processed. These factors will be discussed in turn. For a more detailed analysis of the dynamics of the ball charge the reader is referred to the monograph on mineral dressing by Gaudin,<sup>13</sup> and the paper by Gow and collaborators.<sup>10</sup>

## Mill speed

The speed of a mill, one of the important operating factors, has received much attention from investigators. One of the earliest studies by H. Fischer provided the basis for subsequent work.<sup>11</sup> Fischer offered the following equation to express the relation between mill diameter and the speed at which balls would be held by centrifugal force to the interior of the mill cylinder:

$$S = \frac{K}{\sqrt{D}} \quad (1)$$

<sup>10</sup> A. M. Gow, A. B. Campbell, and W. H. Coghill, *Am. Inst. Mining Met. Engrs., Tech. Pub.* 326 (1930).

<sup>11</sup> H. Fischer, *Z. Ver. deut. Ing.*, **48**, 437-41 (1904).



where  $S$  is the mill speed,  $K$  a constant, and  $D$  the diameter of the mill.

This speed has since been designated as the critical speed and has been quite generally adopted as the reference point in describing ball-mill operation. Theoretically, the critical speed is reached when the centrifugal forces acting on an infinitely small particle are equaled by the centripetal forces as expressed by the equation <sup>12</sup>

$$S = \frac{54.18}{\sqrt{r}} \quad (2)$$

where  $r$  is the mill radius in feet.

This relationship is invaluable in comparing mills of different diameters, but some discretion should be exercised in extending the interpretation to actual production results. Coghill and DeVaney <sup>12</sup> point out that the balls are not infinitesimally small nor do they achieve the speed of the drum of the mill because of slipping. For these reasons the theoretical centrifuging speed does not correspond with any actual set of operating conditions.

As an optimum for pigment dispersion, the speed equation is sometimes written with the square root of the mill diameter in place of the radius. This relationship, also designated as Davidson's rule, is implicit in the earlier work of H. Fischer. Mellor's equation includes ball size and is given as

$$S = 43.3 \sqrt{\frac{1}{D - d}} \quad (3)$$

where  $D$  is the diameter of the mill in feet and  $d$  is the diameter of the balls in feet.<sup>13</sup>

Several other variations on the speed equation have been given in an effort to include, in addition, the effects of the mill lining material, ball type and size, consistency of the grind, and the shape of lifter bars. Such equations, however well they may apply as approximations, suffer from the difficulty of including appropriate empirical correction factors, and, since these cannot be determined with sufficient precision, it is perhaps better to rely on an evaluation based on a knowledge of the separate properties of the mixture being ground and the characteristics of the grinding media.

Commercial mills for pigment dispersion are designed to operate at 50 to 65 percent of critical speed, as shown by the curves in Figure 2

<sup>12</sup> W. H. Coghill and F. D. DeVaney, *Bulletin*, Missouri School of Mines and Metallurgy, **13**, No. 1, September, 1938; U. S. Bur. Mines, *Tech. Paper* 581 (1937).

<sup>13</sup> See Kendall, reference 6, and D. E. Star, *Paint Manuf.*, **17**, 108-13 (1947).

where the speeds of mills of various manufacturers are shown by the shaded area in comparison with the theoretical critical speed.

An example of one method for calibrating the performance of a mill in terms of the noise level of operation is given in the "electric ear" described by Hardinge.<sup>14</sup> Skilled mill operators depend on their hearing in judging whether or not a mill is operating efficiently; the method described by Hardinge utilizes a microphone, in place of the ear, which

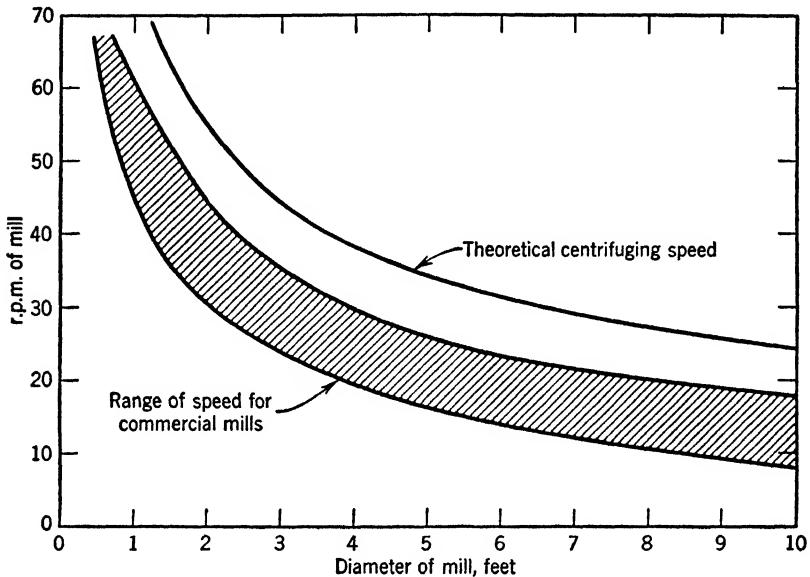


FIGURE 2. Operating speeds of commercial ball and pebble mills in relation to the theoretical centrifuging speeds.

offers a more nearly quantitative correlation. When a mill is running without a charge to cushion the balls, there is a maximum sound intensity; on the other hand, when the balls are cushioned by a highly viscous charge, the noise level is at the minimum. Best operating conditions fall between these extremes, and the curve reproduced in Figure 3 represents such a calibration.

Some slipping of the ball charge occurs in ball-mill operation, and the function of the lifter bars is to reduce slipping by lifting the ball mass to a high "angle of break." Laboratory experiments in a mill 12 inches in diameter and 16 inches long, loaded to varying amounts with 1.5-inch

<sup>14</sup> H. Hardinge, *Ind. Eng. Chem., News Ed.*, **17**, 408-9 (1939); U. S. Patents 2,235,928 (March 25, 1941), and 2,308,917 (January 19, 1943); *Am. Inst. Mining Met. Engrs., Tech. Pub.* 1076 (1939).

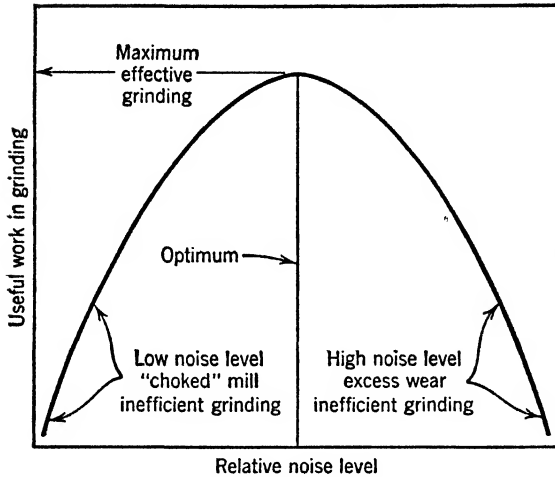


FIGURE 3. Generalized chart showing the relation between efficiency of grinding and noise level in ball mills. (Courtesy Hardinge Co., Inc.)

balls, have been reported by Gross.<sup>15</sup> In these experiments, the mill speed was gradually increased until centrifuging of the balls took place, and slip (or slippage) was computed as a percentage of the theoretical critical speed as expressed by the following relationship

$$\text{Slip} = \frac{S_2 - S_1}{S_2} \quad (4)$$

where  $S_1$  is the theoretical centrifuging speed and  $S_2$  is the empirically observed centrifuging speed. It was observed that ball load materially affected slippage and that a charge of 46 percent of mill volume established, in effect, a non-slip relation and that, with small charges, slip became excessive. The consistency of the material being ground also affected the conditions for slippage; low consistency favored, whereas higher consistency appreciably reduced, the magnitude of the computed value for slip.

Power consumption may also be used as an indication of optimum speed. This point has been studied in detail by Gow and co-workers,<sup>16</sup> Fahrenwald and Lee,<sup>17</sup> and others.<sup>18</sup> Generally, the power consumption

<sup>15</sup> J. Gross, "Crushing and Grinding," U. S. Bureau of Mines, *Bulletin* 402, 1938, 148 pages. (This bulletin contains an annotated bibliography of 142 items.)

<sup>16</sup> A. M. Gow, M. Guggenheim, A. B. Campbell, and W. H. Coghill, *Am. Inst. Mining Met. Engrs., Tech. Pub.* 517 (1934).

<sup>17</sup> A. W. Fahrenwald and H. E. Lee, *ibid.*, *Tech. Pub.* 375 (1931).

<sup>18</sup> A. M. Gaudin, *Principles of Mineral Dressing*, McGraw-Hill Book Co., Inc., New York, 1939.

rises in a nearly linear relationship with speed, until, near 90 percent of the critical speed, there is a rapid decrease in power consumed. These results hold for ball charges that are in a region of commercial practice—40 to 55 percent of total mill volume. In one experiment reported by Gross,<sup>16</sup> work input reached the maximum at 73 percent of critical speed with a ball charge of 42 percent. It has been pointed out, however, that the power consumption cannot by itself be taken as a valid criterion for efficient output without consideration of associated variables, such as ball load.

### Ball load

Recommended ball loads vary. For steel-ball charges, manufacturers commonly recommend 33 percent of the mill capacity. Pebble and porcelain-ball charges are frequently given as 50 percent of mill volume. These figures are determined in part by the ruggedness of the mill construction and the capacity of the driving mechanism. Considerable work on efficiency of operation in mineral dressing has shown that the optimum loading is between 45 and 55 percent of mill volume. At low loadings, particularly where the mix is considerably in excess of the voids in the ball mass, the efficiency is greatly lowered; at higher loadings, the mill is "choked," and the motion of the balls is impeded.

Experiments on the path of the ball charge in an operating mill have been performed by numerous investigators of whom H. Fischer<sup>11</sup> was one of the first. More recently, Gow, Campbell, and Coghill,<sup>10</sup> employing a photographic technique on a three-foot squirrel-cage mill, were able to correlate the effect of different ball loadings with mill speed. When a ball charge of 10 percent was introduced, slipping predominated, and none of the balls could be made to cataract, nor was there any evidence of centrifuging at the critical speed. At a 30 percent load, the toe of the ball mass was evident, and, although it was evidently cascading, slipping was noticeable. Above a 40 percent loading, however, no slipping was observed.

The optimum loading may be deduced from power consumption, since the maximum work input is related to optimum ball mobility. It has been found that the work input increases to a 55 percent loading and drops sharply as the loading is further increased.<sup>17</sup>

Power consumption is decreased by both slipping and centrifuging. This result can be visualized readily. As the ball charge is increased, the work necessary to lift the ball mass increases until, as the gross ball volume becomes about equal to that of the mill cylinder, the center of gravity is located at the axis of rotation. At intermediate ball loading,

slipping at the mill liner decreases the work demand; similarly, balls immobilized by centrifuging establish, in effect, a balanced load.

### Volume of charge

The optimum grinding conditions in a ball mill are obtained when the pigment aggregates are exposed to the maximum number of contacting ball surfaces. Any portion of the mixture that overlays the cascading

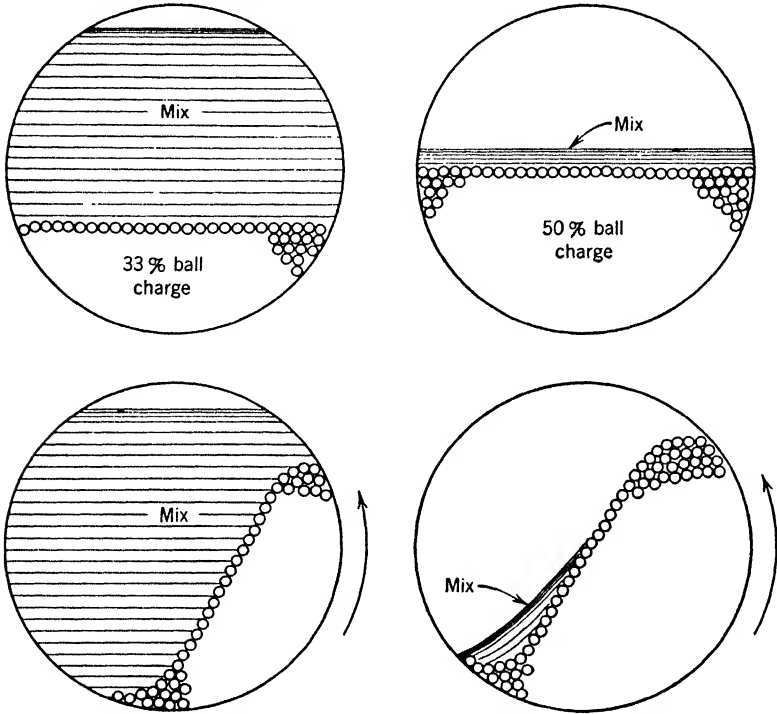


FIGURE 4. Diagrams showing ball and mix loads in commercial mills.

balls is subjected merely to a tumbling action (Figure 4). The actual loading, however, is not necessarily determined by the most rapid dispersion, for other factors in plant operation may require adjustment of the cycle to permit, for example, an overnight run and scheduling of discharge with other processing steps.

The manner in which the balls pack during operation determines the volume of interstices available. In rhombohedral or close packing of spheres of equal size, the voids represent approximately 26 percent of the gross volume. This relationship holds for spheres of any given, uniform diameter, but not for mixed sizes or for shapes that depart from spherical. Actually, however, the volume of the interstices is consider-

ably greater although it never appears to reach the limit for cubical packing, 47.6 percent. Evidence is available that the void volume resulting from random packing, as would be expected in a mill, is in the range of 38 to 42 percent. In mills in which the balls wear to various sizes or to deformed shapes, the actual working volume is considerably decreased.

Charging a mill to fill only the voids in the grinding media provides, in comparison to the gross volume of the mill, only a small portion of the potential capacity, and commercial practice is to carry a considerably greater volume. Several explanations have been given for adherence to this practice. It is stated, for example, that the highest point of the cascading balls should remain in the mix; consequently, a relatively large volume of fluid would lie over the balls. This criterion may be valid for low-viscosity grinds in which the material drains rapidly from the ball voids. In general, however, with more viscous charges, drainage is relatively slow, and the material within the ball voids cannot drain clear of the balls during rotation. There is, moreover, a natural desire to load the mill to maximum volume in order to grind in one charging as large a quantity of a product as possible, although by so doing over-all efficiency may be greatly reduced.

Some experimental evidence is available from pigment-dispersion practice to support the view that ball loadings near the 50 percent point, with mix charges only slightly in excess of the ball voids, contribute to efficient operation. In Table I, data for the dispersion of a hard-grinding

TABLE I. RELATIVE MIX VOLUME AND GRINDING RATE

(Iron blue, 30% by weight in linseed oil; laboratory ball mill, ball size 0.6 inch, gross ball volume 50% of mill volume.)

Relative Mix Volume	Filling Ball Voids	Excess over Ball Volume; Mill Filled 80%
Charge of mix, grams	510	1,200
Strength, %, at		
7.8 hours	81	65
24 hours	99 *	83
48 hours	100	89
102 hours	100	99 *
Output for equivalent product, grams/hours	21.2	11.8

\* Basis for calculation of output.

iron blue in linseed oil are given. The output was approximately doubled for equivalent dispersion for a given milling time.<sup>19</sup> After 24 hours, the

<sup>19</sup> E. K. Fischer, *Ind. Eng. Chem.*, **33**, 1465-71 (1941).

pigment exhibited 99 percent of maximum strength with a charge equal in volume to the ball voids, whereas with the maximum loading of the dispersion, the strength was of the order of 92 percent. A milling time in excess of 100 hours was required with the maximum loading to equal 99 percent strength. Data from a series of experiments are shown in Figure 5 to supply similar evidence.

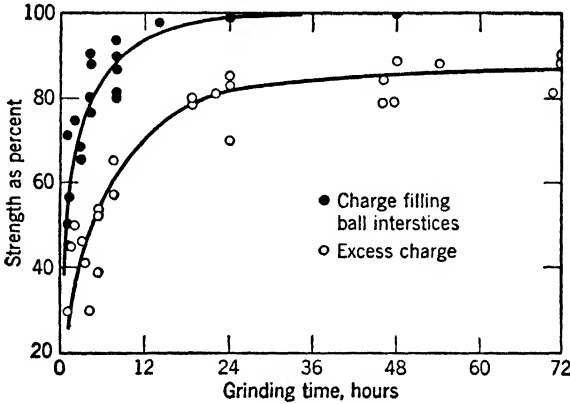


FIGURE 5. Relation of dispersion rate and relative volumes of charge. (Iron blue in linseed oil.)

### Ball size and dispersion rate

The attrition produced by the balls becomes greater as the number of contacts between balls increases. A calculation of the number of contacts of balls of different sizes, assuming close packing as shown in Table II, will make this relationship clear. For small balls, 0.13 inch in diameter, the number of points of contact in a given volume is 56 times

TABLE II. CALCULATED NUMBER OF CONTACTS OF STEEL BALLS

Average Size (inch)	Number (per pound)	Calculated Number Contacts (per pound)
0.131	2,840	17,040
0.250	435	2,610
0.375	130	780
0.50	53	318
0.65	24	144
0.75	16	96
1.0	6.4	38
2.0	0.8	4.8

that of balls 0.5 inch in diameter. In close packing, each ball touches a total of twelve adjacent balls, and, since each contact is formed by two balls, the theoretical number of grinding interfaces is half the number of contacts, or six times the number of balls. It may be inferred also that, with equal ball mobility, the rate of shear within the interstices of the ball mass is proportionately greater with small balls.

When used for the size reduction of minerals, ball diameters are graded to suit the size of the feed material. Gross<sup>15</sup> noted that when the ball diameter was less than three times the diameter of the largest portion of the feed, efficiency was greatly decreased. These ratios are ordinarily of little concern in pigment dispersion, for pulverized pigments have dimensions corresponding to sieve sizes and are usually finer than 100 per inch. An exception should be noted, however. Pelletized pigments, which are finding increased favor, have particle diameters up to  $\frac{1}{8}$  inch. With these products, ball diameters less than  $\frac{3}{8}$  inch, on the basis of the criterion furnished by Gross, should not be used if optimum efficiency of the mill operation, particularly in the initial stages of grinding, is to be realized.

Data showing the rate of dispersion obtained with balls of four different sizes are given in Table III. It will be observed that the smallest balls gave the most rapid strength development.<sup>19</sup>

TABLE III. RELATION OF BALL SIZE TO RATE OF STRENGTH DEVELOPMENT

(Iron blue, 30%; No. 0, Litho (linseed) varnish, 70%; viscosity, 2.2 to 3.9 poises; yield value 0.)

Ball Size (inch)	Strength as % of Maximum			
	2 hours	8 hours	24 hours	72 hours
0.131	78	98	98	98
0.250	65	86	95	100
0.375	46	71	87	92
0.50	55	71	85	90

In plant practice, ball sizes are sometimes mixed but there is no conclusive evidence for the value of this procedure. Experiments indicate that a mixture of two or more sizes is largely additive in effect. A mixture of 0.25- and 0.5-inch balls was found to effect a rate of dispersion intermediate between that of the same volume of each size used independently. During grinding the balls classify partially according to size, and any theoretical advantage is thereby lost. If, however, there is a wide distribution in sizes, the smaller balls are ground by the larger, and abnormal contamination results.



Although mixed ball sizes do not appear justified in a cylindrical mill, there are conditions where a few large balls will aid in preventing localized cementing of grinding media by the material being ground. Kendall<sup>6</sup> and Mills<sup>20</sup> tabulate recommended mixtures for this purpose. In a 5-foot mill, for example, 15 percent of balls of 1.5 to 1.75 inches are added to the bulk of balls of size 0.75 inch.

Although the efficiency of milling may be increased by small balls, practical difficulties should not be overlooked, such as, "floating" of balls, cementation, separation of balls accidentally discharged with the product, more rapid rate of wear, and possibly other problems. Hence, present practice is based largely on steel balls 0.5 to 0.75 inch in diameter.

### Mill diameter

The rate at which a pigment reaches the required fineness is generally considered to be directly proportional to mill diameter, and production-size mills are accordingly rated as more efficient than small laboratory mills. This difference in grinding time is a reflection of the influence of the ratio of ball and mix charges, the effect of the different radii of curvature of the large and the small mills on the mobility of the balls, and the result of uncontrolled viscosity differences. It is reasonable to assume that, with low-viscosity charges and with equivalent charging ratios, differences in performance among mills will be lessened. With high-viscosity charges, however, the ball load in a small mill will pack and result in decreased grinding action; the larger mass of balls in a production mill, on the other hand, will retain high mobility with undiminished grinding action on the same mixture. There is some evidence for this view.<sup>19</sup> In the data given in Table IV for the dispersion of car-

TABLE IV. RATE OF DISPERSION AND MILL DIAMETER

(Carbon black beads in mineral oils.)

Mill Diameter (feet)	Strength at 4 Hours (%)	Pigment (%)	Viscosity (poises)	Yield Value (dynes/sq.cm.)
0.49	96	15	3.3	160
0.49	95	15	19	750
1.25	94	15	15	400
2.0	96	15	15	180
5.0	95	20	8.3	340
5.0	93	25	23	360

bon-black beads, four mill sizes were employed. The strength developed after 4 hours' grinding varied from 93 to 96 percent in mills that ranged

<sup>20</sup> W. G. B. Mills, *Nat. Paint Bull.*, **10**, 5, 6, 12 (February, 1946).

from 0.5 foot to 5 feet in diameter. The range in viscosity was from 3.3 to 23 poises. Shown graphically in Figure 6 are the data from a large series of experiments on various carbon blacks in the same mills. The points fall within the solid curves drawn as approximate limits which include various operational differences such as temperature, pigment content, viscosity, yield value. These experiments indicate that mill

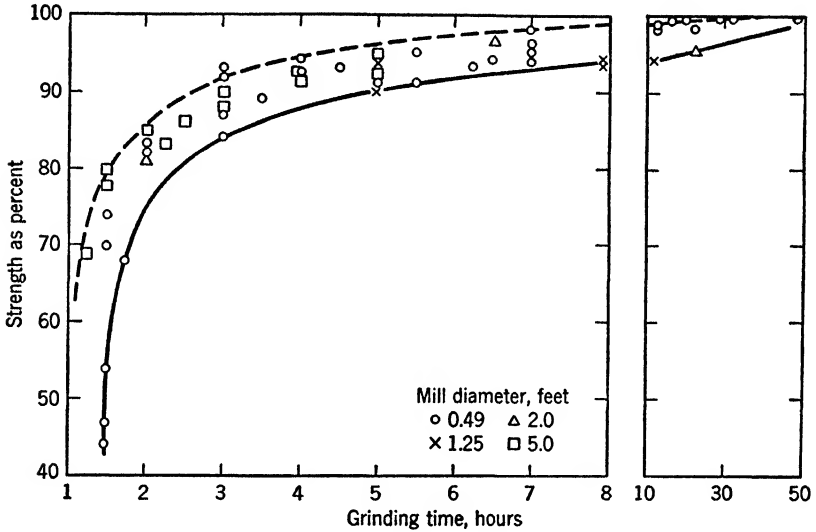


FIGURE 6. Rate of dispersion in ball mills of different diameters. (Carbon black in mineral oil.)

diameter is not the predominant factor in determining the rate of dispersion.

This point is of considerable importance because laboratory experiments, first performed in developing a product, must be translated to the requirements for volume output. A formulation adapted for efficient laboratory dispersion will of necessity be of somewhat lower plastic viscosity than the same product intended for a production mill. The transition from laboratory to factory conditions can be accomplished as follows: the dispersion in each case is formulated with the same ratio of pigment to vehicle solids, but the viscosity is adjusted by variation in solvent additions to provide a relatively low viscosity in the laboratory mill and an appropriately higher viscosity in the production mill.

**Viscosity**

Adjustment of the flow properties of the composition offers the greatest single opportunity for control of grinding. Despite the acknowledged

importance of viscosity as a factor in mill operation, it remains one of the imponderables. In mineral dressing the consistency of the charge is controlled empirically, but the actual viscosity at the comparatively high shearing rates obtaining at the interfaces of contacting balls is virtually that of the water which serves as the suspending medium. When pigments are dispersed in oleoresinous vehicles, on the other hand, the plastic viscosity may reach values of several hundred poises.

Approximate limits may be estimated. Laboratory-size mills, one gallon or less in gross capacity, operate well at viscosity levels of approximately 10 poises. As the mill diameter increases, the viscosity may be increased without loss of ball mobility, and in mills five feet in diameter, a mix measuring 200 poises is practicable. Pebble mills and porcelain-ball mills, because of the smaller mass of the grinding medium, should be charged with mixes of lower viscosity.

A measure of empirical judgment is necessary in adjusting viscosities to other mill factors. The distinction between thixotropic and plastic flow properties should be noted. Pigment-vehicle combinations that exhibit a high degree of thixotropy may be deceiving, for at rest in a container they will be falsely judged as of high viscosity, when actually the same material subjected to the shearing in a ball or pebble mill will break down to an easily milled dispersion. The paste, in other words, should not be thinned with solvents until some measure of performance in an operating mill has been obtained. It has been found convenient in preliminary tests to start a mill with a charge slightly higher in viscosity than is estimated desirable for maximum ball mobility and to examine the charge at regular intervals. Additional vehicle or solvent can then be added in increments until optimum grinding conditions are obtained.

Flow properties of a dispersion change during processing. The plastic viscosity generally increases as comminution progresses, and the measurement may be taken as an indication of the new surface exposed at the pigment-oil interface. Yield-value measurements usually show a rapid change to a value that remains essentially constant for the duration of the grind. In the example shown in Figure 7 in which carbon black was dispersed in mineral oil the yield value increased. It has been observed that with "flow blacks," dispersed in linseed-oil vehicles, the yield value decreases to a constant value, a result that may be attributed to the known interaction of the vehicle and the pigment.

It should be noted that any appreciable rise of temperature lowers the viscosity of a dispersion, although the yield value may not be affected to the same degree. Consequently it is desirable that the viscosity be measured at temperatures corresponding to the equilibrium reached in

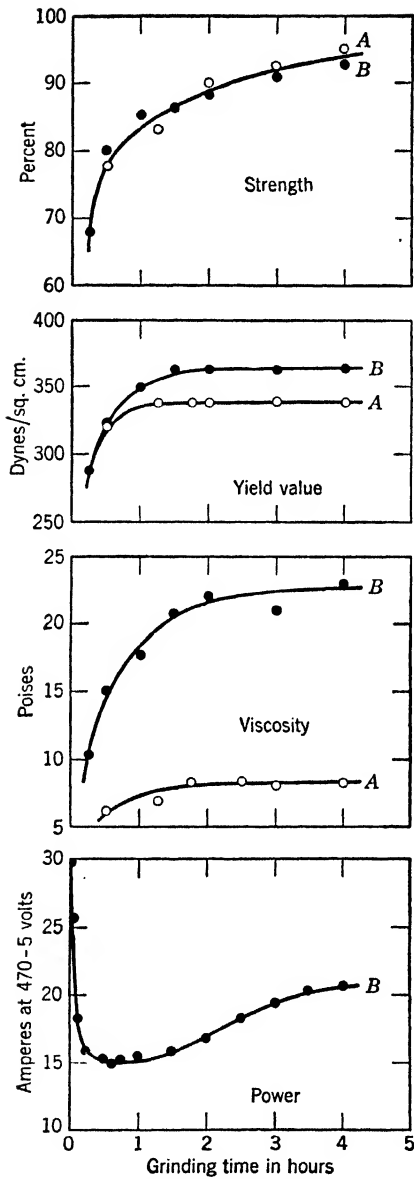


FIGURE 7. Change in color strength, rheological properties, and power consumption during ball-mill dispersion. (Carbon-black beads in mineral oil.)

an operating mill. If this precaution is not observed, the viscosity during grinding will be too low for efficient dispersion. On the other hand, if it is feasible to disperse a composition at elevated temperatures, vehicle components may have higher viscosity or pigment concentrations may be increased, for the viscosity of the mixture will drop as the mill becomes heated.

### Wear of grinding media and contamination

One of the most serious limitations on ball- and pebble-mill operation is the contamination produced by wear of the grinding media. Unusual milling conditions result also in deformed balls as well as chipped and scarred balls. These conditions not only degrade the product but result in decreased efficiency and lead to a shortened life for the grinding media. The actual wear of steel balls depends on the composition and the tempering treatment. A tabulation of rates of wear is given by Taggart for ores which shows approximately a twofold difference when used under comparable conditions.

The mechanism of wear of steel balls was investigated by Webb on bearing surfaces.<sup>21</sup> Mild steel balls develop a tenacious layer of iron oxide which protects the steel surface from abrasion. Hard steel, however, is less susceptible to oxidation and the metal continues to be removed. The action of abrasive materials in a ball mill are conducive to continued removal of steel and contamination of the product.

That the rate of wear of balls comprising the grinding media is proportional to the surface appears to be substantiated by extended experimental work. A summary is given by Taggart.<sup>2</sup> In a cascading charge, the wear has been found to be proportional to  $d^2$  (where  $d$  is the diameter) although other work had shown the wear to be proportional to  $d^{2.3}$ . If the ball charge is cataracting, however, the wear approaches  $d^{3.5}$ . The wear of grinding media has been expressed in terms of (1) weight per unit amount of feed or output, (2) weight per unit of power input, and (3) percent weight loss per unit operating time. For batch operation of mills in pigment dispersion, the last method is the most useful since it enables calculation of quantities of contaminant.

From experiments on the wear of balls used in grinding quartz, Gross<sup>15</sup> concluded that the rate could not be correlated with time of batch operation, probably because of decreased abrasiveness of the particles as the comminution progressed, but that the wear increased with mill speed and ball charge to 44 percent of mill capacity. Increased consistency of the pulp lessened the wear. Andrews<sup>22</sup> in reporting preliminary experi-

<sup>21</sup> W. A. Webb, *Science*, **99**, 369-71 (1944).

<sup>22</sup> L. Andrews, *Paint Technol.*, **7**, 201-4 (1942).

ments on the forces involved in ball wear computed the shearing force of a ball and a liner surface to be approximately 6,000 pounds per square inch.

The wear of grinding media in a 2-gallon porcelain-jar mill used for grinding plant samples has been determined.<sup>23</sup> Porcelain and mullite balls decreased in weight by 0.3 percent in 100 hours of grinding, but flint pebbles showed about half this rate of wear, 0.13 percent for the same period. With both porcelain and flint there was little wear on the lining of the jar, but mullite balls, being appreciably harder, caused considerable wear of the jar.

Reliable data on the rate of wear in grinding pigment-vehicle compositions are lacking. Estimates given by Kendall<sup>6</sup> as the result of a long series of observations may be considered representative. (Table V.)

TABLE V. ESTIMATED WEAR ON GRINDING MEDIA PER 100 HOURS

Porcelain balls	2.0-3.0%
Granite balls	0.5-1.0
High-carbon forged steel	0.3-0.7
French flint pebbles	0.3-0.5
Danish flint pebbles	0.2-0.3
Forged chrome steel	0.2-0.5
Forged chrome manganese steel	0.1-0.3

For many dispersions these figures are high, judged by the isolated data that are occasionally published. Further, the material of the balls varies considerably, and improvements in alloys and porcelain for grinding media are constantly being made. It is stated that zircon balls wear at a considerably slower rate than porcelain, a rate presumably intermediate between pebbles and porcelain. The carbide balls, noted previously, are considered the most resistant to wear of all grinding media and should, therefore, be placed at the bottom of the list.

The effect of contamination from steel balls is striking in infrared reflecting paints. Endres<sup>24</sup> states that finely divided iron has an infrared reflectance of 5.6 percent, and the presence of trace quantities of iron sharply reduces the infrared reflectance of paint. As an example, an olive-drab lustreless finish paint ground in a flint pebble mill had an infrared reflectance of 46.9 percent; when the same material was ground in a steel ball mill the reflectance dropped to 23.8 percent. In both mills the grinding time was four hours. Similar results for a grinding time of 25 hours resulted in a decrease in infrared reflectance from an initial 41

<sup>23</sup> S. L. Hood, R. Q. Parks, and C. Hurwitz, *Ind. Eng. Chem.*, **16**, 202-5 (1944).

<sup>24</sup> H. A. Endres, *Official Digest Federation Paint & Varnish Production Clubs*, No. 227, 202-16 (June, 1943).

percent to 14 percent.<sup>25</sup> With dark-colored products, these changes may not be apparent to the eye, but whites and light colors show a marked degradation.

Deformation of steel balls after a period of use is fairly common. Departure from sphericity is gradual and arises from several conditions, chief of which are initial unevenness or fritting. Eventually the balls show flattened areas, some with concavities in these areas.<sup>19</sup> It is of interest to note that specimens will show 12 flattened areas, indicating that during grinding the balls tend to assume close packing. (Figure 8.) As the condition grows worse, the shape may approach that of a tetrahedron or a cylinder with concave ends.<sup>2</sup>

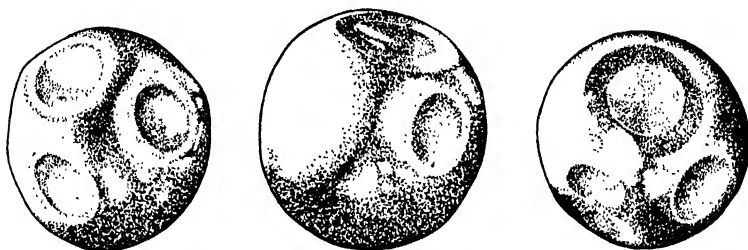


FIGURE 8. Deformation of steel balls resulting from improper operating practice, showing flattened areas and concavities in flattened areas.

Pebbles form oblate or prolate spheroids on abrasion,<sup>26</sup> and porcelain balls used for grinding refractory materials have been observed to assume cubical shapes.<sup>27</sup>

Grinding efficiency is appreciably decreased by a grinding medium so deformed for the following reasons: (1) the flat areas remain in contact during an appreciable part of the grinding cycle; (2) attrition between the ball surfaces is greatly reduced; (3) turbulent flow in the interstices is reduced; (4) the packing volume of the deformed balls is decreased, and a larger volume of the mixture lies above the ball level. Evidence for the decreased efficiency is provided in the work of Coghill and DeVaney<sup>12</sup> who observed that tetrahedral shapes required about 10 percent more power than spheres, although the over-all rating was 15 to 20 percent inferior. Similarly, balls that had assumed polyhedral shapes were rated about 11 percent less efficient than spherical balls.

The cause of this deformation may be theorized as follows. In a large mill, the loading of the balls at the point of tangential contact becomes

<sup>25</sup> Los Angeles Paint and Varnish Production Club, *Paint, Oil, Chem. Rev.*, **104**, (December 17, 1942).

<sup>26</sup> Lord Rayleigh, *Nature*, **154**, 169-71 (August 5, 1944).

<sup>27</sup> J. H. Chesters, *ibid.*, **155**, 486 (April 21, 1945).

very large, possibly several hundred tons per square inch. Some elastic deformation of the ball occurs, and, if the ball interfaces are not lubricated, welding with seizure occurs when the mill is started and the balls begin to slide or rotate against each other. Seizure followed by displacement results in a scarred or fritted surface which can then serve as the locus for the orientation of another ball. Continued operation, particularly with an abrasive material, leads to growth of the flattened areas, and concavities in the flattened areas are formed by the apposition of the spherical surface of a normal ball.

Ball mobility is, of course, related to the formation of flattened areas. If the ball surfaces are covered with oils or vehicles of relatively high viscosity, the surfaces are lubricated, preventing or at least reducing the likelihood of seizure, and the traction exerted on the ball by the vehicle aids in turning it, presenting new areas of contact continuously. In this way the wear on the ball surface is more nearly uniform and the original spherical shape is maintained. On the other hand, when a mill is cleaned by being run with solvents that have virtually no lubricating properties, seizure is far more likely. In addition, slipping of the ball charge presents an opportunity for the balls adjacent to the liner to wear to flat areas; excessive speed, resulting in cataracting, contributes to chipping.

Restoration of spherical shape of steel balls badly deformed during operation is difficult and to be successful requires extended grinding with abrasives, a process that leads to mill-time loss, additional wear on the mill linings, power waste, and eventually a great reduction in ball size. Prevention of deformation through proper mill-operation practice, rather than an expedient cure, is essential. Generally, wear may be reduced by operating the mill with the highest dispersion viscosity practicable, maintaining ball charges above 40 percent, and controlling the mill speed to avoid cataracting or slipping.

### Commercial Practice

The application of ball and pebble mills in pigment dispersion has been the subject of occasional reports and discussions in the trade literature.<sup>28-40</sup> Although these reports are in essential agreement as to

<sup>28</sup> R. G. Baines, *J. Oil & Colour Chemists' Assoc.*, **29**, 182-94 (1946).

<sup>29</sup> H. M. Brown, *Official Digest Federation Paint & Varnish Production Clubs*, No. 284, pp. 668-76 (1948).

<sup>30</sup> E. K. Fischer, C. J. Rolle, and L. W. Ryan, *ibid.*, No. 287, pp. 1050-65 (1948).

<sup>31</sup> O. H. Garlick, *ibid.*, No. 156, pp. 200-6 (1936); No. 246, pp. 251-54 (1945).

<sup>32</sup> W. H. Henszey, *ibid.*, No. 148, pp. 350-54 (1935).

<sup>33</sup> V. R. Olsen, *ibid.*, No. 237, pp. 340-44 (1944).

<sup>34</sup> G. B. Wheeler, *Paint, Oil, Chem. Rev.*, **111**, No. 25, pp. 12, 14, 26 (1948).



procedure, the numerous variables encountered in industrial practice appear to make a uniform practice infeasible.

In this connection experiments reported by Venuto<sup>40</sup> are of special interest. The objective was determination of the best mill-operation conditions for carbon black in an alkyd-resin vehicle with reference to color (jetness), rate of dispersion, and stability of the finished composition. For this purpose a high-color black in both bead and powder form

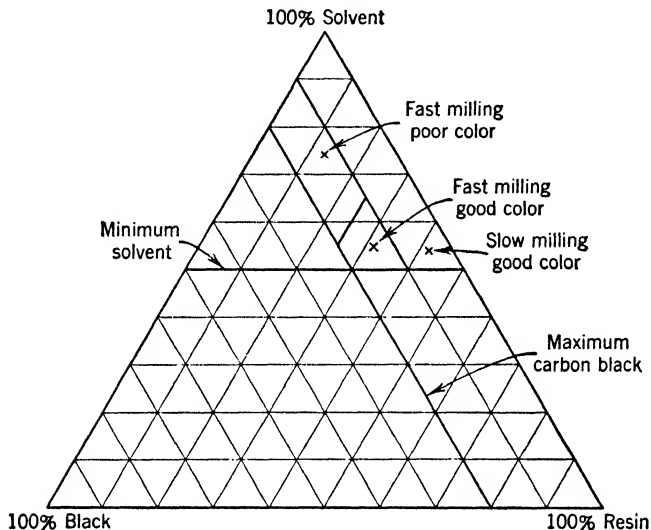


FIGURE 9. Dispersion of high-color carbon-black beads in alkyd resin showing regions of optimum formulation. (After L. J. Venuto; courtesy Binney and Smith Co.)

was used. The results, shown in triangular coordinate graph, are reproduced in Figure 9. The optimum ratio for bead black to resin was found to be as follows: 50 parts of pigment to 100 parts of dry resin. With large solvent volumes, low resin and high pigment content, the milling time was excessively prolonged, and the dispersion quality as well as color were rated as poor. With a high resin and low pigment

<sup>35</sup> O. Promnitz, *ibid.*, **99**, No. 6, 22 (1937).

<sup>36</sup> C. R. Draper, *Am. Ink Maker*, **22**, No. 3, pp. 26-29 (March, 1944); *Paint Manuf.*, **14**, pp. 7-8, 11 (January, 1944).

<sup>37</sup> W. G. B. Mills, *Nat. Paint Bull.*, **10**, pp. 5, 6, 12 (February, 1946); *Oil Colour Trades J.*, **108**, No. 2458, pp. 873-75; No. 2459, pp. 920-22 (1945).

<sup>38</sup> O. F. Redd, *Bull. Am. Ceram. Soc.*, **19**, 253-55 (1940).

<sup>39</sup> H. W. Rudd, *Paint Manuf.*, **9**, p. 107 (April, 1939).

<sup>40</sup> L. J. Venuto, *Official Digest Federation Paint & Varnish Production Clubs*, No. 194, pp. 159-73 (1940).

content, the dispersion rate was slow but the color was rated as good. The formulation for optimum conditions for bead black was found to be as follows: pigment 15 percent, resin 30 percent, and solvent 55 percent. In comparison with carbon black in powder form, bead black allowed incorporation of a higher pigment and resin content with lower solvent volume for equivalent quality.

It is apparent that the results reported by Venuto cannot be directly translated to production, for other factors such as viscosity control, noted above, need consideration. The experimental procedure, however, was systematically planned and can be readily adapted for other products; in combination with plant trials such experiments can simplify the perplexing transition from laboratory-scale to large-volume plant production.

Examples of typical dispersions are given by Mills,<sup>37</sup> who emphasizes that increase in production may be accomplished most efficiently by grinding concentrated base dispersions, rather than by larger mix volumes in the mill, and that the mill charge should not exceed 18 to 20 percent of the total mill volume with a ball or pebble charge of 45 to 50 percent. The extent to which the concentrated base may be extended depends on the pigment and the type of product; carbon-black enamels, for example, will require considerable dilution with vehicles and solvents, but white undercoat finishes will require only a small dilution. A variation in the usual procedure of grinding pigment with vehicle is described by Ryan.<sup>41</sup> In this method the dry pigment is partially dispersed and pre-wetted by a petroleum hydrocarbon solvent by grinding in a ball or pebble mill; an alkyd dissolved in xylene is then added and dispersion completed. Voet<sup>42</sup> describes the dispersion of compacted carbon black in a ball mill by grinding at temperatures between 140° and 200° F. with "high-boiling" vehicle components. These examples could be considerably extended, for the ball mill is a flexible instrument and many variations in dispersion procedures are possible.

### Summary

Although the variables in ball and pebble-mill operation may appear too complex to justify generalizations, it is possible to list the conditions that have been found by a large number of investigators in different fields to contribute to efficient operation. These may be distinguished from other factors that are peculiar to a particular pigment or vehicle and cannot therefore be generalized.

<sup>41</sup> P. J. Ryan, U. S. Patent 2,211,912 (August 20, 1940).

<sup>42</sup> A. Voet, U. S. Patent 2,453,557 (November 9, 1948).

1. *Mill speed*: 50 to 65 percent of the critical centrifuging speed. The actual speed for any given condition of mill operation should be adjusted to obtain cascading of the ball charge.

2. *Ball load*: 40 to 55 percent of total mill volume. Higher loads reduce the cascading, giving in effect a choked mill. Lower loads may contribute to slipping of the ball charge with excessive wear and deformation of the grinding media.

3. *Dispersion volume*: 18 to 20 percent of mill volume. A charge that is slightly in excess of that which fills the ball voids is most rapidly dispersed. For plant operation this may not be the most economical overall charge, however, since power rates, labor costs, production cycles, and other factors need to be considered.

4. *Ball size*: smallest practicable in view of feed size, viscosity of the dispersion, and mechanical arrangements for straining at the discharge port. Mixed ball sizes in cylindrical mills have little or no advantage. A few large balls, however, sometimes assist in maintaining maximum ball mobility.

5. *Viscosity*: highest consistent with maximum ball mobility and free cascading of the ball charge. Particular attention should be given to the different viscosity levels for laboratory- and production-size mills. Optimum dispersion rates in a small mill will be obtained with lower viscosity compositions than those used in a large mill. Consequently, formulas developed in the laboratory require adjustment before they can be used in plant operation. Usually it is possible to withhold some of the thinner from the plant-size batch, thus providing a more viscous grind.

6. *Yield value*: at the minimum. In many cases it is possible to reduce yield value by withholding those components of the vehicle that induce flocculation or, alternatively, by adding appropriate surface-active agents.

7. *Ball condition*: spherical. Slipping and cataracting of the ball charge produce deformed balls and excessive contamination.

## //. Disc, Cone, and Colloid Mills

The mills in this classification, although diverse in design and construction, have the common feature of a disc or a cone, which serves as the rotor, acting against a similarly shaped surface which is stationary.

Stone mills represent the oldest historic types, descending directly from the old grist and flour mills which have been used for centuries. In the United States some of the earliest stone mills for the manufacture of paint were made over a century ago. These early mills were constructed with a hardwood frame, supporting a stationary upper or top stone; the lower stone was connected to a drive mechanism through bevel gears. The first mills developed considerable heat, and in the 1870's cooling by means of circulating water was introduced. For this purpose the stones were set into hollow metal castings. The water-cooled mills were built in several sizes, the largest being three feet in diameter. Additional refinements, such as iron frames and improved driving mechanisms, were introduced in the 1890's. These improvements allowed higher running speeds with appreciably increased output. The iron or pot mill paralleled the development of the stone mill. Instead of stone, the grinding surfaces are of cast iron, steel, or bronze. In other respects this mill is quite like the stone mill. Metal grinding surfaces, however, allowed for either cooling or heating during operation, so that this mill found a place that could not be filled by the stone mill. The colloid mill is a relative newcomer, having been introduced in the 1920's. It is distinguished from its forebears by very precise machining and high operating speeds.

### Stone Mills

The design of modern stone mills has changed little since the early 1900's. (Figure 1.) The stones are flat discs, and the lower running stone is held against the upper stationary stone by a pressure device.

The material for grinding, introduced into a hopper set above the top stone, feeds into a hole or eye in the top stone and is gradually transported across the stones to the periphery where it is removed by a scraper blade. The lower stone rotates at a relatively low speed (30 to 70 r.p.m.), depending on the size of the mill.

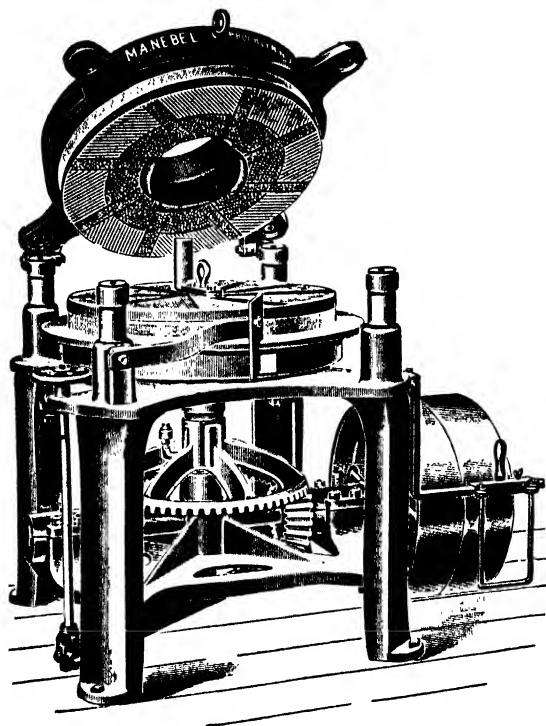


FIGURE 1. Over-all view of a typical stone mill used for pigment dispersion. (Courtesy M. A. Nebel Sons.)

### Construction

For many years the preferred stone used in the construction of the mills was buhrstone quarried in the Marne River region of France. This stone, an aggregation of flint-like material with fossil inclusions, combines the desired qualities of hardness and porosity. Many of the pigments available in the early part of the century were prepared from earth colors and the siliceous particles present required a hard stone for grinding. French buhrstone met the requirements satisfactorily. Other stones of domestic origin were also used.<sup>1</sup> A stone quarried in New

<sup>1</sup> J. W. Kent, *Paint, Oil, Chem. Rev.*, **97**, No. 21, pp. 26-27 (October 17, 1935); Anon., *ibid.*, **75**, No. 22, pp. 8-9 (May 30, 1923).

York state, inland from the town of Esopus on the Hudson River, and "pebble grit" stones quarried in Virginia were used in mills made by some manufacturers. An extremely hard stone known as rock emery, obtained from quarries in Turkey and Greece, is also used. As a result of improvements in the processing of pigments and the widespread use

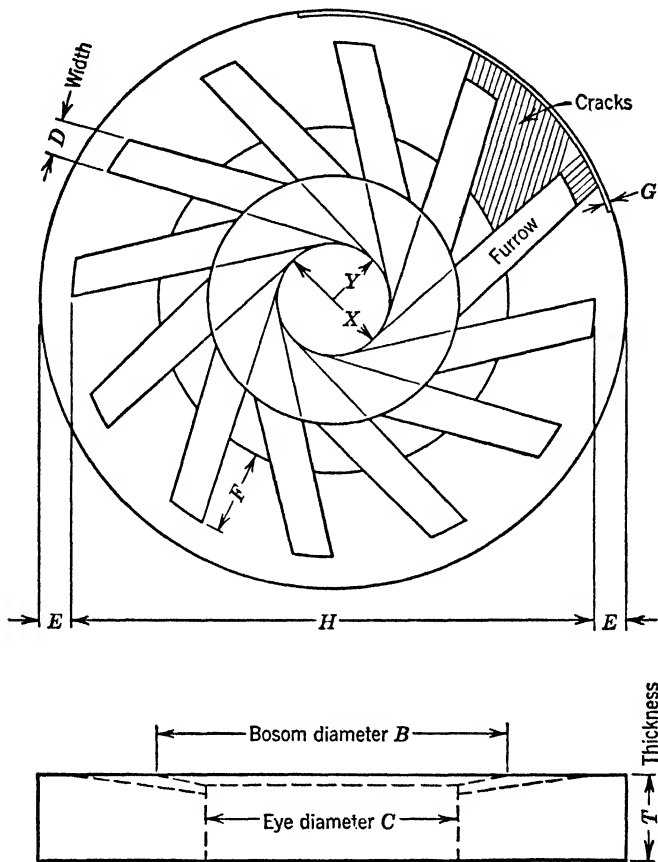


FIGURE 2. Dressing of stones. (Courtesy Charles Ross & Son Co.)

of synthetic pigmenting substances, the need for maximum hardness and "tooth" in the millstones decreased and other stones replaced the French buhrstone to some extent. Some designers now prefer softer stones, claiming superior performance, although re-surfacing may be required more frequently.

The stones are finished by hand cutting, but various mechanical devices have been adopted to reduce the labor in the process and at the same time improve the precision of cutting. Perfectly smooth stones

will perform no grinding, and the transport of the material from the center of the stone to the periphery requires furrows and grooves to guide the flow. In the ancient stones used for grinding grain for flour, grooves running from the center to the edge of the stones may be seen, and these represent a primitive but necessary feature of the stone mill. Eventually the dressing of stones for this purpose became an advanced art. In the mills for pigment dispersion, the dressing of the surface has become fairly well standardized. Details and dimensions of the stones used in representative commercial mills are given in Figure 2 and Tables I and II.<sup>2</sup>

TABLE I. DIMENSIONS OF DRESSED STONES

(All dimensions in inches.)

	Stone Diameter ( <i>A</i> ) (inches)				
	10	16	20	26	30
Thickness of stone ( <i>T</i> )	2.25	3.00	3.25	4.25	4.75
Bosom diameter ( <i>B</i> )	6	10	12	16	18
Eye diameter, top stone ( <i>C</i> )	4.25	8	10.1	13.1	13.1
Eye diameter, runner stone ( <i>C</i> )	3.5	6.75	8.1	10.1	10.1
Number of furrows	6	8	9	10	12
Width of furrow ( <i>D</i> )	1	1.5	2	2	2
Land outside of furrows ( <i>E</i> )	1	1.25	1.25	1.5	1.75
Width of cracks ( <i>F</i> )	1	1.75	2.75	3.5	4.25
Width of skirt ( <i>G</i> )	0.125	0.125	0.125	0.125	0.125
Furrow circle ( <i>H</i> )	8	13.5	17.5	23	26.5
Number of cracks per inch	6	5	5	4	3
Width of cracks	0.0625	0.0625	0.0625	0.0625	0.0625
Depth of cracks	0.0625	0.0625	0.0625	0.0625	0.0625
Depth of furrows	0.125	0.187	0.250	0.312	0.375
Depth of bosom	0.250	0.312	0.375	0.437	0.500
Draft circle diameter	1	5	5	6	6

Data courtesy of Charles Ross &amp; Son Co.

TABLE II. SPEED RANGE OF RUNNING STONE ON MILLS OF DIFFERENT SIZES

Stone Diameter (inches)	Speed (r.p.m.)
10	50-70
20	45-55
26	40-45
30	35-40
36	30-35

<sup>2</sup> The author is indebted to Mr. C. L. Ross and Mr. L. K. Ross of Charles Ross & Son Co., Brooklyn, N. Y., for the engineering data given in this section.

The contour of the top or stationary stone and the lower or running stone is similar. In the top stone a hole or eye serves as the entry port. Cut radially from the center are the furrows, and the line extending from the edge of the furrows toward the center is tangent to the draft circle. The furrows range in depth from  $\frac{1}{8}$  to  $\frac{3}{8}$  inch, depending on the size of the stone, and provide channels through which the mixture of pigment and vehicle feeds onto the stone surfaces. The draft is analogous to the pitch diameter of a screw: the greater the diameter of the draft circle the greater is the travel of material for each rotation of the stone. Little actual comminution is accomplished in the furrows, since they serve mainly to distribute the material. The furrows extend only partly into the "land" and are feather-edged, so that the feed cannot be discharged without attrition at the more closely set areas (islands) adjacent to the furrows. Grinding is accomplished on the land of the stones. The drifts or cracks cut into the land are usually shallow,  $\frac{1}{16}$  of an inch, and of equal width. The drifts are spaced  $\frac{1}{6}$  to  $\frac{1}{2}$  inch apart and are cut tangentially to the draft circle. At the outer edge of the stones the surface is smooth and this area is called the skirt.

### Action of the stone mill

The manner in which the stone mill functions may be visualized as follows. The mixture of pigment and oil, introduced into the hopper, feeds into the eye of the top stone. The material enters the feeding furrows or sectors and is distributed over the stone surfaces, and as it moves toward the periphery it is subjected to a mulling action at the plane surfaces of the stones. The rate of travel is comparatively slow, and the pigment becomes well mixed with the vehicle. Aggregates are sheared by crushing between the stones and at the edges of the drifts and the islands between the drifts which cross each other like the blades of a pair of scissors. When the material reaches the outer edge of the skirt it is scraped off and falls into a container.

The output of a stone mill is a complex function of the speed of the running stone, the number of feeding furrows, the number and lengths of the drifts, the angles at which the drifts intersect, the setting of the clearance of the stones, and the flow characteristics of the paste. Only a partial answer can be given to numerous questions which naturally arise on the relative importance of these factors.

In a series of experiments on the dressing of stones<sup>3</sup> the effect of number of furrows and diameter of the draft circle were connected with fineness of grind and output. A 20-inch stone mill was used. The stones

<sup>3</sup> Baltimore Club, Federation Paint and Varnish Production Clubs, *Nat. Paint, Varnish Lacquer Assoc., Sci. Sect., Circ.* 471, pp. 353-58 (1934).



were faced by means of a mechanical grinder which assured a flat surface, and, after the cutting of the furrows and drifts, the stones were lapped together by running with an abrasive powder (Aloxite 600) mixed with linseed oil. The stones were thus ground into nearly perfect contact, and the places where the shallow drifts had been removed during the surfacing were then re-cut. For the tests on grinding, a hard iron-blue pigment was mixed with raw linseed oil, containing 10 percent heavy-bodied linseed oil, in the ratio of 43 percent pigment to 57 percent vehicle. Strength determinations were made by reduction with a zinc oxide paste and compared with standards containing known amounts of iron blue which had been ground repeatedly through a stone mill. An effort was made to have the tension on the stones equivalent for all the tests.

Several conclusions were drawn from these experiments. The data shown in Table III indicated that the 3-inch draft circle gave somewhat

TABLE III. EFFECT OF DRESSING OF STONE ON COMMINATION OF HARD-GRINDING IRON BLUE

Dressing of Stone	Rate of Output (pounds per hour)		
	3	4	7
	Strength as percent		
10 Sectors; 3-inch draft circle	98.0	97.5	96.0
10 Sectors; 5-inch draft circle	97.0	96.5	92.5
7 Sectors; 3-inch draft circle	99.0	98.5	97.0
7 Sectors; 5-inch draft circle	97.5	97.0	94.5

Baltimore Club, Federation Paint and Varnish Production Clubs, *Nat. Paint, Varnish Lacquer Assoc., Sci. Sect., Circ. 471*, pp. 353-58 (1934).

better results than the 5-inch circle, as judged by strength development for equivalent output. The desired number of feeding furrows or sectors was not so clearly shown, but the stones cut with seven furrows showed somewhat superior performance.

The most important criterion is, apparently, the length of time during which the dispersion is subjected to shearing. It is quite probable that minor differences in dressing of the stones have relatively small bearing on the rate of comminution, and that the primary factor is simply the length of time the composition is subjected to shearing, with the contour of the stones merely establishing the efficacy with which the dispersion is transported. The width of the skirt on the stone affects performance to some extent. Some stones are dressed with the drifts in the shape of a tapered depression and carried to the edge of the stone, leaving a skirt

of very narrow width. These tests showed that a skirt of very narrow width was preferred.

The wear on the stones is appreciable. Sparrow<sup>4</sup> states that the wear is inversely proportional to the space between the drifts and that mills dressed with  $\frac{3}{4}$  inch spacing between drifts required re-surfacing at the end of 350 hours of grinding. Production is increased, however, if the drifts are closely cut. In the same experiments reported by Sparrow, reducing the space to  $\frac{3}{8}$  inch approximately doubled the output. Along with increased output, lower operating temperatures were observed. Wear may be irregular if the drive is improperly aligned. Since the rotation of the stones is concentric, ridging may take place, with the top and running stones wearing together. The concentric ridges so produced act as barriers to the transport of the dispersion. An attempt to minimize such ridging led to the development of a mill in which the running stone was given a planetary motion, throwing it off the axis of rotation.<sup>5</sup>

Because of the difficulty in facing stones, the usual procedure is to have the stones perfectly flat and in perfect contact with each other. Theoretically at least it would be desirable to have one of the stones tapered with the smallest clearance at the periphery of the stones.<sup>6</sup> The logic of this view is that the clearance of flat stones is adjusted to the size of the aggregates present in the feed, and there is then no progressive decrease in clearance appropriate for finer grinding, as comminution proceeds across the face of the stones. Consequently, the actual operating clearance is too large for fine grinding. Tapered stones, on the other hand, cause a progressive decrease in the aggregate size from the eye where the clearance would be largest, to the skirt where clearance would be at the minimum. Some experimental evidence is available in support of this view. Wehrle and Strom<sup>7</sup> compared the performance of a mill equipped with flat stones with that of a mill with tapered stones. A pigment was selected with aggregates measuring 0.005 inch in diameter; this was mixed with vehicle and introduced first onto the mill with flat stones. It was found that a thickness gauge measuring 0.005 inch, corresponding to the dimensions of the pigment aggregates, could be inserted between the stones when the mill was running. The stones were thus operating at a spacing equivalent to that of the pigment-aggregate dimensions. The second pair of stones was dressed with a taper so that the clearance at the eye was 0.006 inch when the edges of

<sup>4</sup> E. E. Sparrow, *Am. Paint, Varnish Mfrs.' Assoc., Sci. Sect., Circ.* 319, pp. 551-60 (November, 1927).

<sup>5</sup> C. R. Draper, *Paint Manuf.*, **12**, 196-99 (1942).

<sup>6</sup> C. R. Draper, *Paint Manuf.*, **13**, 258-63 (1943).

<sup>7</sup> P. W. Wehrle and C. O. Strom, *Am. Paint J.*, **19**, No. 10, pp. 7-9, 44 (1934).

the stones were in contact. When the same pigment paste was run through this mill, a thickness gauge of only 0.001 inch could be inserted at the periphery of the running stone. Examination of the ground pastes showed that many coarse particles were present in the paste ground with the flat stones, but that the tapered stones gave a more complete comminution.

It thus appears that the actual operating clearance of a mill equipped with flat stones is approximately that of the aggregates present in the feed. The stones are spaced by the particles, and comminution to smaller sizes then depends almost entirely on plastic shearing within the mixture.

Little attention has been given to the feed volume of the composition as it spreads across the stones. The rate at which the dispersion is removed from the stones by the scraper blade obviously must equal the feed rate at the bosom of the stones. Because of the progressively greater area for attrition as the composition moves toward the periphery of the stones, the amount of work done on the dispersion becomes correspondingly greater provided that the space between the stones remains filled with the fluid dispersion. If, however, the plastic viscosity is too low and the dispersion leaves the stones only partially filled, then the apparent film thickness at the bosom will be greater than at the skirt and the effective grinding surface is appreciably diminished. The effect of heating and consequent lowering of the viscosity of the dispersion as it feeds through the mill is to decrease the shearing action. For these reasons it appears desirable in this mill, as with other types of dispersion equipment, to formulate the composition with vehicles of the highest viscosity that can be utilized. It is necessary, further, that the yield value of the paste be so low as to establish unimpeded flow between the stones.

The stone mill has been highly regarded by some manufacturers of paint. It is probable that the comparatively slow travel of the pigment-vehicle combination through the mill provides a more nearly adequate time for wetting of the pigment to occur, and the need for storage for the purpose of subsequent "wetting down" is in some measure reduced. Further, the stones leave the pigment uncontaminated with steel, and the color of the product approximates that of the original pigment.

There are, however, several disadvantages to the stone mill. The most important is the relatively low output in comparison with other types of dispersion equipment such as the high-speed roll mill, both in terms of power consumption and factory space required. Comparatively few studies giving reliable production data have been made. The data in Table IV show a comparison of different sizes of stone mills. Comparable figures for roll, pebble, and colloid mills show that the stone mill

TABLE IV. COMPARISON OF OUTPUT OF STONE MILLS

Mill Size (inches)	Drive H.P.	Pounds per Hour	Pounds per H.P. Hour
20 (single)	2	58	29
26 (single)	2.75	80	29
30 (single)	3.5	128	39
26 (tandem)	4.75	156	33
30 (tandem)	6.5	245	38

New York Club, Federation Paint and Varnish Production Clubs, *Nat. Paint, Varnish Lacquer Assoc., Sci. Sect., Circ. 471*, p. 313 (1934).

produces, on the average, less product per H.P. hour than the other mills.<sup>8</sup> In addition, the stone mill can be utilized for the dispersion of pigment pastes of only relatively low plastic viscosity, so that the mill is limited in the range of products that can be adequately processed. Finally, frequent re-surfacing of the stones reduces the effective working time of the mill and contributes to high maintenance cost. For these reasons the stone mills are less popular than the high-speed roll mills and the ball and pebble mills. Plants that have installations of stone mills frequently use them for standby mills when production schedules call for added productive capacity.

### Cone Mills

Cone mills differ from the flat stone mills described above chiefly in the shape of the rotor which is a truncated cone fitted closely into a conical stator. The speed of the rotor in some mills was as high as 1,000 r.p.m. These mills, made with buhrstone grinding surfaces, at one time found wide use for the grinding of paints and certain types of printing inks. Although cone mills are still manufactured, they have been supplanted in large measure by the more efficient colloid mills.

### Iron Mills

The iron or pot mill bears a superficial resemblance to the stone mill. Instead of a flat stone grinding surface, the rotor is usually of cast iron in the shape of a cone, and a comparatively narrow grinding surface is grooved to facilitate, as in the stone mill, the transport of the pigment-vehicle mixture. Discharge of the ground material is accomplished by a scraper blade. The construction of the iron mill allows for heating by

<sup>8</sup> New York Club, *Nat. Paint, Varnish Lacquer Assoc., Sci. Sect., Circ. 471*, p. 313 (1934); *Paint, Oil, Chem. Rev.*, **96**, No. 22, p. 74 (1934).

the injection of steam into jackets around the hopper or pot. Because of the convenience in heating, the iron mill has long been used for the grinding of pigments into waxes, such as those used in carbon-paper coatings. The production rate is low, however, and, as for the stone mill, frequent re-surfacing of the grinding surfaces is required if optimum efficiency is to be maintained.

### Colloid Mills

The colloid mill in its simplest form consists of a rotor in the shape of a truncated cone, turning at comparatively high speed and spaced a small distance from a stator. Material is introduced into a funnel, and the centrifugal action of the rotor sets up a pumping action which forces the composition between the rotor and stator. The force acting on the material is usually designated hydraulic shear in references on the colloid mill. Numerous mechanical modifications of this simple design have been built and patented. Only a few, however, attain the status of practical commercial machines. An excellent review of different types is given by Clayton<sup>9</sup> and descriptions of some of the earlier models will be found in the monograph by Travis.<sup>10</sup>

The colloid mill is generally credited to Plauson who, in 1921, applied for patents on his design.<sup>11</sup> Shortly thereafter a series of papers by various authors appeared in technical and trade journals, and the attendant publicity brought the colloid mill quickly to the attention of users of chemical process equipment. There is ample evidence, however, that the colloid mill as then conceived had been anticipated by others. Travis states that a number of papers published in Russia in the 1900's related to fine-grinding equipment but that they received very little attention and that von Weimarn deserves credit for publication in 1910 of a conception for a mill of this type.

It seems reasonable that attempts at designing fine-grinding machinery should have approached the mechanical features of the present colloid mill. Indeed, the cone mill described earlier has many of the attributes of the colloid mill, and the differences in design relate chiefly to the speed at which the rotor was driven. There was, however, the matter of designation, for the term colloid mill immediately connoted

<sup>9</sup> W. Clayton, *Theory of Emulsions and Their Technical Treatment*, Fourth Edition, Blakiston, Philadelphia, 1943.

<sup>10</sup> P. M. Travis, *Mechanochemistry and the Colloid Mill*, Reinhold Publishing Corp., New York, 1928.

<sup>11</sup> H. Plauson, U. S. Patent 1,500,845 (July 8, 1924); a description of the performance of this mill is given by Plauson in *Z. angew. Chem.*, **34**, 469-74 (1921).

disintegration of solid particles by mechanical means to dimensions that were in the realm of colloidal particles. It was inevitable, therefore, that unwarranted claims would be forthcoming and that confusion would inevitably ensue. Travis emphasizes that the colloid mill accomplishes deflocculation, rather than comminution of particles, but this criterion is extremely faulty.

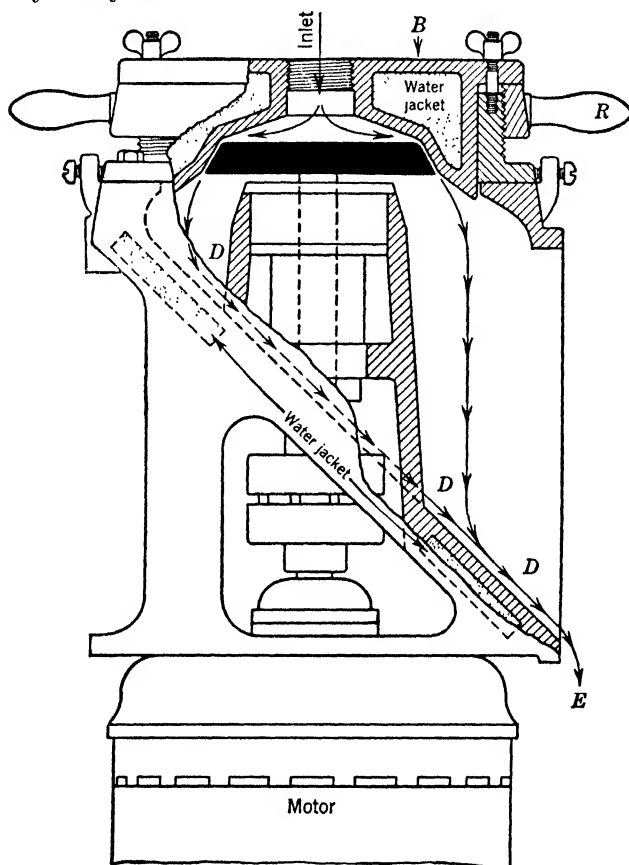


FIGURE 3. Cross-sectional view of paste-type colloid mill. (*B*) Stator; (*D*) spillway; (*E*) discharge; (*R*) handwheel for setting clearance. (Courtesy Premier Mill Corporation.)

Because of the name, the colloid mill is often the only instrument for mechanical dispersion processes mentioned in textbooks on colloid chemistry. As a consequence, this mill acquired a reputation for utility which practice cannot justify; some held the opposite view, that the colloid mill has a very restricted usefulness. Both views are quite un-

sound. Since 1930 the mills made by several manufacturers have demonstrated their ability to perform certain dispersion operations with a record for low maintenance costs and high volume of output. The colloid mill is perhaps most widely used in manufacturing compositions based on emulsions, and for this purpose it is pre-eminent. The mill finds use, also, in a number of pigment dispersion processes, and it is for this class of materials that we shall examine its capabilities.

### Construction

Several types of construction are available in current models. For materials of pasty consistency, the discharge port is constructed so as to

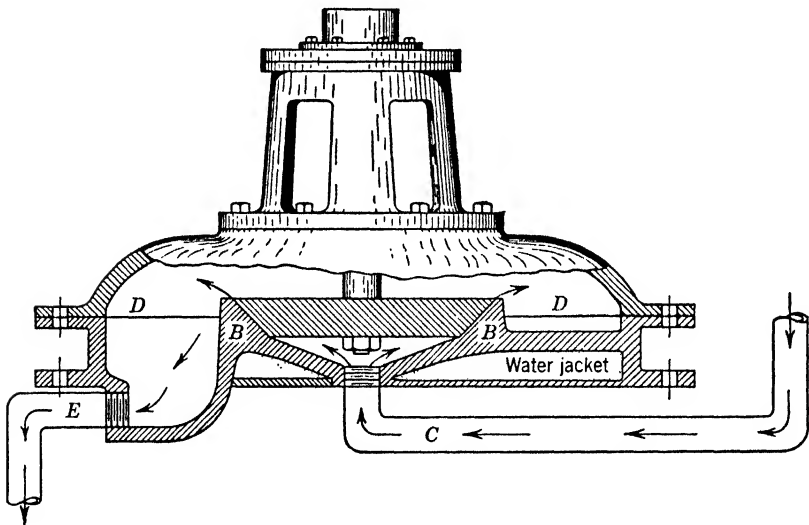


FIGURE 4. Cross-sectional view of liquid-type colloid mill. (B) Stator; (C) inlet; (D) spillway; (E) discharge port. (Courtesy Premier Mill Corporation.)

be easily accessible for cleaning. Fluid compositions, on the other hand, are advantageously processed in a mill with closed housings, and by a suitable arrangement of ports and re-circulation loops, the composition may be subjected to repeated passes through the mill. In some mills the rotor is connected directly to the motor, and in others the power is transmitted through a gear system. Small mills, suitable for laboratory testing, are available in belt-driven models, and, with a combination of pulleys, variable rotor speeds can be obtained. All the commercial mills are built to high standards of precision, and the operator should exercise considerable care in setting the mill. (See Figures 3, 4, 5.)

In dimensions, the rotor ranges from three inches in diameter for the laboratory-size models to 21 inches for large-volume production mills. Several types are used. Some mills have a corrugated or ribbed rotor which presumably subjects the mixture to more violent turbulence during the time it is running through the mill. The ribbed rotor has an advantage in conferring a shredding action, and for this reason is recom-

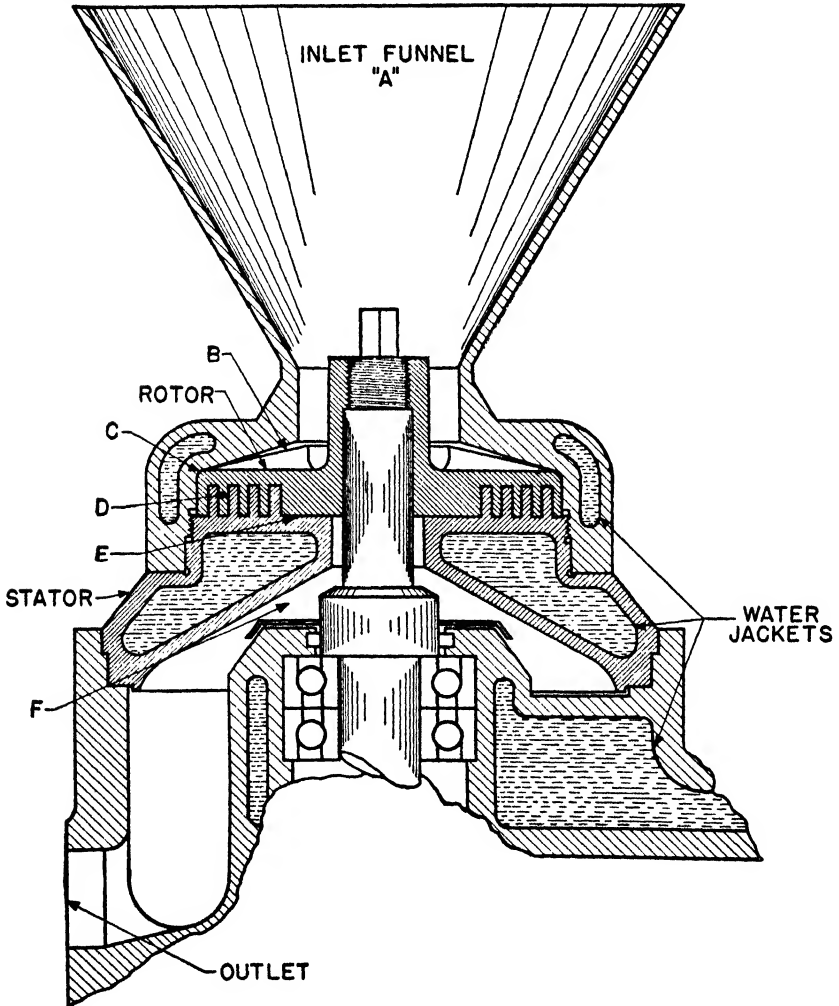


FIGURE 5. Cross-sectional view of colloid mill with special rotor-stator design. (A) Inlet; (B) impellers on rotor; (C) region where initial shearing takes place; (D) interlocking rings on rotor and stator; (E) smooth area between rotor and stator; (F) spillway. (Courtesy C. O. Bartlett & Snow Co.)



mended for the processing of fruit juices, purées, etc. The smooth-surface rotor and stator are easier to clean and, when fabricated with stellite<sup>12</sup> grinding faces, are highly resistant to wear. The slight "tooth" of the alloy aids in the comminution of pigments. Most colloid mills are designed so that the feed enters at a point near the center of rotation of the rotor, and centrifugal force assists in driving the composition between the grinding surfaces. In one type of mill, illustrated in Figure 5, the opposite path is taken. Material entering the feed port is thrown by impellers attached to the top of the rotor to the periphery of the rotor, and the composition is then forced toward the center of the rotor and the discharge port. The path taken by the composition is considerably longer in this type of mill. Rotor-and-stator combinations with interlocking rings are available, and the rings may be slotted to afford a greater shredding action. Most mills are constructed of steel, but stone faces are also available.

### Action of the colloid mill

It may be seen from the geometry of the colloid mill that the intensity of the shearing forces acting on material passing between the rotor and stator is determined by the following factors: (1) peripheral speed of the rotor; (2) clearance between surfaces; and (3) rheological properties of the material. Production-size mills are usually coupled directly to the motor, so that the first factor is constant, but some laboratory mills have adjustable speeds. Where the mill has been equipped with a universal motor, the actual speed of the rotor varies with the load on the motor, and, as a consequence, a very viscous material will cause the mill to slow down excessively and, in some cases, to stall. A mill so constructed is suitable only for low-viscosity compositions, and results obtained with it should not be construed as representative of larger, more adequately powered units.

A listing of mill speeds is given in Table V. The data show the relation between the peripheral speed of the rotor in feet per minute, the rotor size, and the motor speed under load. It will be noted, for example, that a 3-inch laboratory mill turning at 17,130 r.p.m. is equivalent in peripheral speed to a production-size mill with a 15-inch rotor operating at 3,425 r.p.m. With equal clearance, the two mills should give approximately the same performance. Variable speeds in a laboratory mill can thus be turned to advantage in charting development work, and the transition from laboratory-scale to volume production can be made with the minimum of adjustment.

<sup>12</sup> An alloy of cobalt, chromium, tungsten, and carbon.

TABLE V. OPERATING SPEEDS OF COLLOID MILLS

Rotor Diameter (inches)	Mill Speed Full Load (r.p.m.)	Peripheral Speed of Rotor (feet per minute)
3	17,130	13,500
3	10,280	8,070
3	7,340	5,760
5	13,700	17,900
5	12,180	15,940
5	9,510	12,450
5	3,425	4,480
6	3,425	5,370
7	3,425	6,280
8	3,425	7,170
10	3,425	8,970
12	3,425	10,760
15	3,425	13,450
21	1,725	9,480
21	3,425	18,830

Courtesy Premier Mill Corporation.

The clearance is adjustable on all commercial models, and recommendations are usually made that settings be 0.002 inch or larger. Closer settings can sometimes be made on a new mill or one that is in exceptionally good mechanical condition, but this clearance is too small for all compositions except those of the lowest viscosities. The closer settings produce, of course, the higher shearing stresses, and the extent of comminution of aggregates is proportionately greater. Large mills are usually operated at 0.004- to 0.008-inch clearance. Relevant data are shown in Tables VI and VII.<sup>13</sup> For carbon-black dispersions, a maximum of 95.8 percent strength was obtained at the closest practicable setting, 0.001 inch, and larger clearances resulted in lessened comminution. Repeated passes of the same material through the mill at a constant setting produced a slight gain in strength, but the first pass produces very nearly the maximum comminution obtainable with a given setting and mill speed. The effect of vehicles of different kinds and of variations in viscosity are shown in Table VII. The iron blue used in these experiments was of the "hard-grinding" type, and it will

<sup>13</sup> E. K. Fischer and D. M. Gans, Chapter 14, pp. 286-327 in *Colloid Chemistry*, Vol. VI, J. Alexander, Editor, Reinhold Publishing Corp., New York, 1946.

TABLE VI. DISPERSION OF CARBON BLACK ON 3-INCH LABORATORY COLLOID MILL

(Carbon black in mineral oil; viscosity: 1.7 poises; yield value: 20 dynes per sq. cm.; mill speed: 7,200 r.p.m.)

Setting (inch)	Number of Passes	Strength (percent of maximum)
0.001	1	95.8
0.002	1	93.0
0.003	1	92.5
0.002	1	91.0
0.002	2	95.0
0.002	3	95.0
0.004	1	87.0
0.004	4	89.0

TABLE VII. DISPERSION OF PIGMENTS ON 3-INCH LABORATORY COLLOID MILL

(Mill speed: 7,200 r.p.m.)

Pigment	Vehicle	Pigment Content (% weight)	Viscosity (poises)	Yield Value (dynes/sq.cm.)	Strength (%) Clearance (inches)		
					0.002	0.004	0.008
Iron blue *	Mineral oil A	35	5.8	870	65	40	28
	Mineral oil B	30	64.0	330	67	43	38
	Linseed oil	35	3.1	20	83	66	40
	Litho varnish	35	20.0	32	71	57	50
Ultramarine	Mineral oil A	40	2.3	0	92	91	89
	Mineral oil B	25	11.5	60	93	95	
	Linseed oil	50	4.9	0	95	94	94
	Litho varnish	25	9.9	20	96	...	82
Carbon black †	Mineral oil A	7.2	1.0	240	91	87	81
	Mineral oil B	7.2	12.0	290	93	93	93
	Linseed oil	7.2	1.7	20	95	87	86
	Litho varnish	7.2	10.7	40	100	100	100

\* "Hard-grinding" type.

† Flow black.

be noted that strength ranged from 28 to 65 percent as the clearance was changed from 0.008 to 0.002 inch. Better comminution was observed with ultramarine and carbon black dispersed in the same vehicles, and the carbon black reached complete comminution, as judged by strength determinations, in litho varnish at 0.002-inch clearance. These data also show the effect of plastic viscosity on the extent of comminution: generally the higher viscosity resulted in more effective dispersion of the pigment.

Production data on colloid mills are ordinarily of little value, for the output is determined largely by the clearance, mill speed, and viscosity of the material. For rough comparison, however, manufacturers provide relative figures which range from 5 gallons per hour for a 3-inch mill to about 5,000 gallons per hour for a 21-inch mill. When mechanical factors are constant and feed into the mill is by means of flow under gravity, the viscosity of the composition determines the output. Illustrative data are given in Table VIII. As a general principle, higher

TABLE VIII. RELATION OF OUTPUT OF 3-INCH LABORATORY COLLOID MILL TO VISCOSITY AND CLEARANCE

(Mill r.p.m.: 10,000.)

Material	Initial Viscosity (poises)	Clearance (inch)		
		0.002	0.004	0.008
Water	0.01	670	1,800	2,400
Linseed oil	0.33	85	280	....
Litho varnish	4.5	60	160	250
Litho varnish	18.0	52	94	220
Litho varnish	62.0	44	48	108

viscosities lead to lower output. Increasing the clearance results in a greatly augmented output. If force-feed methods are employed, this generalization, of course, is not valid, for then the output is established by the forced rate of flow.

A pasty consistency, evidenced by a measurable yield value, can affect output by impeding flow of the dispersion into the mill. Sometimes this condition can be overcome simply by increasing the height of the hopper or funnel on gravity-feed mills. One alternative is the addition of deflocculating agents to the pigment-vehicle mixture; another is the connection of a positive displacement pump in the feed line.

Ordinarily any anomaly in the flow of a dispersion can be readily observed. Dilatant flow, however, may be quite deceptive. Dilatant compositions are almost invariably deflocculated and will flow into the mill port without difficulty, but when subjected to the high rates of shear obtaining in the mill, the material will acquire an extremely high momentary viscosity, and the load on the mill then becomes too great for the drive. With a belt-driven mill, slipping and burning of the belt takes place; on a mill directly driven the motor slows down or stalls. Compositions of high pigment content are apt to exhibit dilatant flow. The solution for this difficulty is usually quite simple: (1) addition of a larger amount of vehicle or, preferably, solvent for the vehicle; (2) operation

of the mill at larger clearances; or (3) running the mill at a lower speed.

Low-viscosity compositions experience a negligible rise in temperature on passage through the mill. This is not true, however, for materials of the consistency of stiff pastes when, even in a laboratory mill, temperatures near 100° C. may be developed. The actual temperature rise is determined by the volume of cooling water passing through the housings of the mill, the temperature of the composition introduced into the mill, and the length of time the mill has been running.

### Special Laboratory Designs

Two laboratory testing instruments are derived from the disc and cone mills.

#### Laboratory disc mill

A mill intended for the laboratory evaluation of pigments is the automatic muller.<sup>14</sup> In this instrument the dispersion is ground between two glass discs. The lower disc rotates and is connected to a stop mechanism which shuts off the motor after a selected number of revolutions. This instrument has been quite widely adopted for standardized pigment and color testing, since it replaces the variable human effort involved in hand mulling by uniform mechanical action.

#### Laboratory cone mill

A modification of the cone mill which is adapted for the dispersion of small quantities of pigments in laboratory evaluation tests has been described by Pall.<sup>15</sup> In this mill, designated a micro mill, the grinding surfaces are entirely of glass and are made from standard ground-glass joints. The material to be dispersed is fed into the space between the sections by means of a plunger, and attrition between the rotating member and the external cone serves to disperse the pigment. In order to have the composition feed properly, the male part is grooved, as shown in Figure 6. The male part is turned by means of a motor connected to a speed control; 150 r.p.m. is suitable for most materials. The assembly is arranged with hydraulic plungers to provide controlled pressure both on the feed into the cone and on the grinding surfaces. This mill operates successfully over a wide range of plastic viscosities, and it has the advantage that contamination is minimized. By hand mulling, for ex-

<sup>14</sup> C. E. Hoover, Jr., U. S. Patent 2,150,603 (March 14, 1939).

<sup>15</sup> D. B. Pall, *Ind. Eng. Chem., Anal. Ed.*, **14**, 346-48 (1942); U. S. Patent 2,338,198 (January 4, 1944).

ample, on a ground porcelain slab the reflectance of a titanium dioxide dispersion was 83.3 percent whereas the same material dispersed on the micro mill was 94.5 percent. The contamination in the hand-mulled

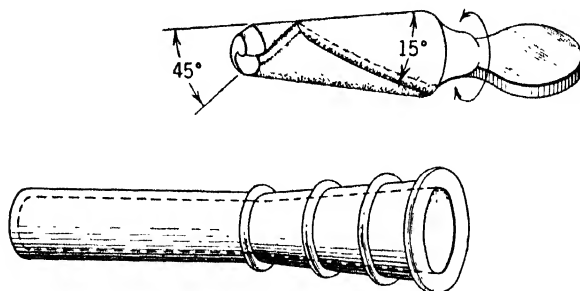


FIGURE 6. Rotor and stator of laboratory cone mill as constructed from standard glass fittings. (After D. Pall.)

sample may be attributed to the steel abraded from the spatula during the pick-up step in the mulling operation. A comparison of different methods of dispersing small quantities of a hard-grinding iron blue, reported by Pall, showed that the micro mill is intermediate between the roll mill and hand mulling in the efficacy with which this pigment was dispersed.

## 12. Dispersion by Phase Transfer— The Flushing Process

The manufacture of pigment-in-oil dispersions directly from aqueous pigment pulps, without the intermediate steps of pigment drying and grinding into oil, is a process that dates back to the last decades of the nineteenth century. The largest initial use was in processing white lead. For this purpose the process was highly advantageous, and it greatly lessened the hazards of lead poisoning.<sup>1</sup> During the intervening years, nearly all commercial colors and pigments have been processed in this way.

In its simplest form, the process consists in agitating filter-press cakes of a pigment with a suitable vehicle by means of a mixer. If the pigment is preferentially wetted by the oil, the particles transfer from the water to oil phase, and the water is spontaneously displaced from the mixture. Numerous modifications of this procedure have been employed, and other variations have been proposed, but all have a common principle: the pigment is processed directly from an aqueous suspension. A chart comparing the steps in manufacturing flushed pigments with a typical procedure for dispersion from the dry pigment is shown in Figure 1.

The sequence of operations has established the nomenclature of the subject. Pigments and colors are said to be transferred from an aqueous to an oil dispersion, or the suspending medium (water) is displaced by the vehicle, whence arises the term, displacement process. The terms, pulping and pulped colors, have been current for a long time. Now, however, flushed colors and flushing process are quite general. We can consider the word flushing as a convenient and picturesque designation of the decanting operation. The patent literature does not record the latter terms until the 1930's, but they were in the vernacular of plant

<sup>1</sup> C. R. Holley, *The Lead and Zinc Pigments*, John Wiley & Sons, Inc., New York, 1909 (out of print).

men in the early 1920's. In scientific literature these terms are infrequently found, but both British and American trade journals have adopted them.

The technical literature on this process is scanty, despite the commercial interest in the products. Descriptions of operations are to be found largely in patent disclosures.<sup>2</sup>

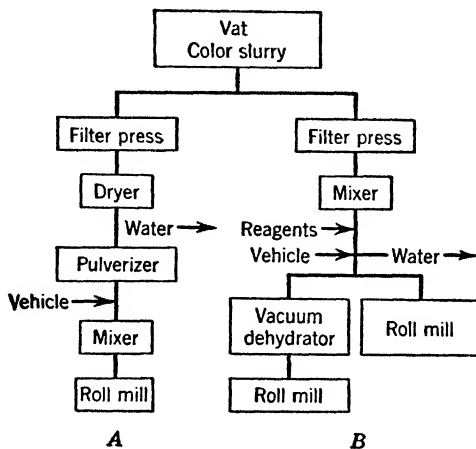


FIGURE 1. Comparison of typical pigment-dispersion processes. (A) From the dried powder by grinding; (B) from aqueous suspension in form of filter-press cakes by phase transfer.

## Theory

The actual transfer of pigment from the aqueous to the oil phase may be pictured in the following manner. Oil added to the dispersion of pigment in water is emulsified, and a large interfacial area is formed. Pigment particles adjacent to the oil-water interface transfer to the oil. As the mixing continues, the transfer is gradually completed, and the water, which served originally as the dispersion medium for the pigment, is depleted from the pigment particles. Because of their higher viscosity and greater tackiness, the oil particles gradually coalesce into a paste, and the water separates. This stage represents a transition from an oil-in-water emulsion formed initially to an unstable water-in-oil emulsion. The release of water is not complete, however, for some remains emulsified as an internal phase in the pigment-oil paste. Complete dehydration requires further processing.

The transfer of a pigment from aqueous to oil dispersion may be analyzed by a consideration of the interfacial energies, represented by

<sup>2</sup> E. K. Fischer, *Am. Ink Maker*, **23**, No. 12, pp. 28-31 (December, 1945).



vectors, which presumably act on the particle.<sup>3</sup> This is based on the classical treatment and is analogous to the theories of mineral flotation. The transfer can be visualized in general terms. Consider a single particle momentarily placed at the oil-water interface (Figure 2). It is possible to postulate that the particle caught in the interface encounters a resolution of forces such that it is held immobile. If the interfacial-tension relations are changed by the addition of a surface-active material or by reaction of the pigment with some component of the oil, then the equilibrium is disturbed, and the solid particle is preferentially wetted by the oil, causing the point  $C$  to move toward the water phase

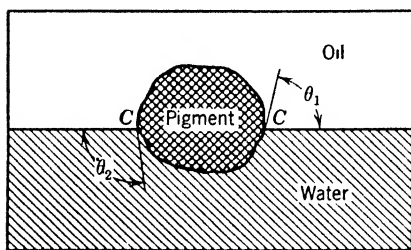


FIGURE 2. Diagram of pigment particle at point of phase transfer.

with the particle moving toward the oil phase. The hypothetical contact angle  $\theta_1$  for the oil-pigment interface then is zero. If flushing takes place, the particle becomes engulfed by the oil. The opposite transfer, from oil to water dispersion, may be described in similar terms. Then the theoretical contact angle  $\theta_2$  for water at the water-pigment interface approaches zero, the

point of contact  $C$  moves toward the oil phase, and the particle enters the water phase.

Although the transfer of pigment from aqueous to oil dispersion is the usual sequence considered, the opposite—transfer from oil to aqueous dispersion—can take place with some pigment-vehicle combinations. One striking example is that of titanium dioxide dispersed in oil and agitated in the presence of water. This is the condition encountered, for example, in printing inks used on an offset press. If the titanium dioxide is “water sensitive,” the first change is an increase in yield value to the point at which a pasty consistency results; further agitation with water displaces some of the pigment from the oil. This may be called a water bleed, but it is in effect a water flush.

### Variables in Processing

A patent by Ismay<sup>4</sup> for the conversion of white lead pulps offers an outline for the flushing process which contains the ideas for numerous

<sup>3</sup> E. K. Fischer and D. M. Gans, Chapter 14, pp. 286–326, in *Colloid Chemistry*, Vol. VI, Jerome Alexander, Editor, Reinhold Publishing Corp., New York, 1946.

<sup>4</sup> C. D. Ismay, U. S. Patent 609,936 (August 30, 1898).

improvements by succeeding inventors. Ismay describes a pug-mill mixing arrangement jacketed for heating and the vacuum evaporation of entrained water. He observes that a final grinding of the product over hot rolls may be desirable. The one claim to this patent reads as follows: "The . . . process of converting white lead into white lead paint consisting in mixing the pulp of white lead with oil, agitating the same to cause the separation of the water, decanting the water and then subjecting the resulting product to heat and vacuum. . . ." The patent was granted in 1895 in England and in 1898 in the United States.

A more elementary form of the process was described ten years earlier by Jessup.<sup>5</sup> The method consists merely in heating a color dispersed in water with oil until the water is evaporated. This procedure was used by Ramage<sup>6</sup> with the addition of a stearate or oleate soap to a concentration of 30 percent calculated on the pigment content, heating the mixture to fusion, and then adding oil. Ramage<sup>7</sup> later reduced the soap content to less than 5 percent and found that with a precipitant for the soap, water separated after agitation of the mixture. Palmer<sup>8</sup> points out the advantage in flushing alkali blue immediately after completion of the chemical reactions forming the color, thus avoiding additional processing operations.

## Mixing

Any mixing method that serves to bring the pigment pulp or slurry into contact with a vehicle can be used to effect transfer of the color. For laboratory tests, spatula mixing on the slab, followed by mulling, is helpful in obtaining a preliminary evaluation. A high-speed drink mixer is a convenient means for laboratory batches, particularly with slurries, and the usual laboratory mixers of the change-can and dough-mixer types are suitable for batches up to several pounds.

For plant production, the most widely used instrument is the dough mixer, partly because it can readily be equipped with a vacuum-tight cover for dehydration. Charges of pulp are placed in the mixer, together with reagents to assist transfer, and the vehicles are added during stirring. It is necessary to adjust the volume in the mixer in order to obtain efficient mixing: too small a load results in packing on the blades with little exchange; too large a charge results in a portion riding above the blades. After the water has been liberated, it is decanted by tilting

<sup>5</sup> J. C. Jessup, U. S. Patent 317,367 (May 5, 1885).

<sup>6</sup> A. S. Ramage, U. S. Patent 1,004,078 (September 26, 1911).

<sup>7</sup> A. S. Ramage, U. S. Patent 1,008,434 (November 14, 1911); 1,084,361 (January 13, 1914).

<sup>8</sup> G. B. Palmer, U. S. Patent 1,339,219 (May 4, 1920).

the tank of the mixer. Further stirring usually causes more water to separate, and several decantations may be feasible. Where the solid content of the press cake is low, as it frequently is with organic pigments, there is a considerable decrease in volume of the mixture after the water separates and is decanted; for such materials, it is advisable to add fresh lots of aqueous pulp with repeated decantation of the water, until the volume of paste in the mixer facilitates exchange from one blade to the other. It can be appreciated that processing is expedited if the filter-press cakes of pigment contain the maximum of solids. Merely increasing the solid content sometimes makes it possible to flush an intractable pigment. There is, of course, the further advantage in increasing the pigment content that less water is transported and handled at all stages.

For processing, Hochstetter<sup>9</sup> obtained a patent on the use of a vacuum-jacketed dough mixer. He noted that 8 to 18 percent residual water was retained by the dispersion after decantation; this was removed by heating to about 140° F. in a vacuum of 28 inches. A similar procedure is described by Cajar<sup>10</sup> who states in an example that the dehydration step requires about four hours.

Several patents deal with special techniques. Acheson<sup>11</sup> adds the oil to the pigment paste at a "rate not substantially exceeding that at which the oil is absorbed" by the mix. This precaution ensures uniform distribution. To facilitate transfer of the pigment, Todd and Silverman<sup>12</sup> add a previously prepared pigment-oil paste to the mixture; this acts as a "seed." Another procedure that is of interest but of uncertain practical importance is described by Dourif<sup>13</sup> who freezes the pigment pulp, shaves the frozen mass to a snow-like condition, mixes with a chilled vehicle in a dough mixer, and gradually raises the temperature of the mixer until the pigment transfers to the vehicle.

When the pigment-vehicle paste is adjusted to a fairly high plastic viscosity, heat is generated merely by mixing. It is necessary to maintain fairly low temperatures for some colors, however, and vacuum dehydration should not be accelerated by excessive heating. Chrome yellow, phosphotungstate acid lakes, and phloxine toner are among the colors that are deleteriously affected if the temperature greatly exceeds 160° F. For this reason, it may be necessary to extend the vacuum-dehydration step in the process for as long as six to eight hours at a rel-

<sup>9</sup> R. Hochstetter, U. S. Patent 1,119,960 (December 8, 1914).

<sup>10</sup> H. Cajar, U. S. Patent 1,576,408 (March 9, 1926).

<sup>11</sup> G. W. Acheson, U. S. Patent 1,590,067 (June 22, 1926).

<sup>12</sup> J. D. Todd and M. Silverman, U. S. Patent 1,986,029 (January 1, 1935).

<sup>13</sup> H. Dourif, U. S. Patent 2,067,906 (January 19, 1937).

atively low temperature, depending on the vacuum, design of the condenser system, viscosity of paste, etc.

With vacuum dough-mixer processing, it is possible to obtain a product that contains no more water than an equivalent dispersion prepared from dry pigment and vehicle. For emulsion paints or inks, however, it is not necessary to subject the dispersion to a dehydration step. Water retained by the dispersion after decantation can be determined by the solvent-extraction method, and the dispersion used with appropriate adjustment in the formulation. In the production of emulsion products flushed colors have their greatest advantage, for the troublesome dehydration stage is avoided.

Dehydration by heating under vacuum is attended with some difficulties. Skinning may occur where the dispersion is lifted above the mixing chamber, undesirable changes in the color may take place, and with reactive pigments livering sometimes occurs. It is usually desirable to give the product a finish or inspection pass on a roll mill.

Some pigments and colors are so hydrophilic that the transfer from aqueous to oil dispersion is difficult. An extreme case is described by Gans.<sup>14</sup> Pigments made by coupling tetrazotized dianisidine with Schaeffer's salt are difficult to filter and on drying form aggregates that cannot be adequately dispersed by grinding with oils. However, by adding the pulp gradually to a mass of resinous vehicle on a two-roll (rubber) mill, the pigment is dispersed into the resin, and the water is removed largely by evaporation, although a small relative quantity of liquid water may separate during milling.

Another mechanical variation is described by Denslow, Erskine, and Horning<sup>15</sup> who pass the pigment slurry and oil through a colloid mill. An intimate admixture of components is effected without emulsifying agents, and the resulting suspension is then filtered in a press to remove the bulk of water. It is then dried at a low temperature.

Repeated passes on a warm roll mill will also remove entrained water. When the plastic viscosity of the dispersion is comparatively high, the water will separate at the nip rolls and drop through, while some will be carried on to the apron. It would seem that exposing the dispersion to air in a thin film, as on a roll mill, would facilitate evaporation of water; actually, however, the water is the internal phase of an emulsion, and evaporation must take place through the oil. As a consequence, repeated passes are necessary to lower the residual moisture content sufficiently.

<sup>14</sup> D. M. Gans, U. S. Patent 2,296,383 (September 22, 1942).

<sup>15</sup> R. R. Denslow, A. M. Erskine, and S. C. Horning, U. S. Patent 2,153,515 (April 4, 1939).

### Emulsification procedures

Emulsification of the vehicle in a color slurry, followed by "breaking" the emulsion, is the variant described in another group of patents. Acheson<sup>16</sup> forms an aqueous color slurry in which the pigment is deflocculated. The slurry is then thinned to the "consistence of thin cream" and added to a vehicle with ammonium hydroxide as a reagent for emulsification. After thorough mixing, the emulsion is broken by the addition of an electrolyte such as alum or hydrochloric acid, and the curd-like mass of the pigment dispersion is separated from the water. Dehydration is accomplished by passing the paste over hot rolls or by heating at low temperatures. A similar procedure is followed by Hailwood, Shepherdson, and Stewart.<sup>17</sup>

In the emulsification procedure described by Grossman,<sup>18</sup> a heat-coagulable protein, which acts as a protective colloid, is used to stabilize the emulsion; on heating, the protein coagulates and the emulsion breaks. Schroeder<sup>19</sup> forms an emulsion with water-soluble soaps (e.g., sodium and potassium soaps) and breaks the emulsion by adding a precipitant to form a water-insoluble soap. For precipitating reagents, salts of the alkaline earth metals, aluminum, and lead are mentioned. Other inventors mention formic acid (Gessler<sup>20</sup>) and citric acid (Hucks and Maher<sup>21</sup>).

The emulsification process described has the advantage that filtering the pigment is avoided. Further, the mixing operations may be completed in a vat or vessel equipped with sweep agitators, impeller stirrers, or other mixing devices normally employed in dry color manufacture.<sup>21a</sup>

Although most of the process variations described in the patent literature and utilized commercially are based on colors and pigments in finished chemical form, it is possible to prepare colors in the presence of the vehicle. Hailwood, Shepherdson, and Stewart<sup>17</sup> prepare insoluble dyes in an aqueous emulsion of the vehicle. The color transfers to the dispersed oil phase, and, after breaking of the emulsion, it is recovered

<sup>16</sup> G. W. Acheson, U. S. Patents 1,431,079 (October 3, 1922); 1,431,080 (October 3, 1922).

<sup>17</sup> A. J. Hailwood, A. Shepherdson, and A. Stewart, U. S. Patents 1,863,331 and 1,863,332 (June 14, 1932).

<sup>18</sup> H. Grossman, U. S. Patent 1,696,034 (December 18, 1928).

<sup>19</sup> A. J. Schroeder, U. S. Patent 2,112,222 (March 22, 1938).

<sup>20</sup> A. E. Gessler, U. S. Patent 1,984,182 (December 11, 1934).

<sup>21</sup> R. T. Hucks and G. R. Maher, U. S. Patent 2,114,713 (April 19, 1938).<sup>1</sup>

<sup>21a</sup> For a study of the process variables see A. F. Schmutzler and D. F. Othmer, *Am. Ink Maker*, **27**, No. 3, pp. 29–31, 59; No. 4, pp. 37, 39, 41; No. 5, pp. 33–35, 59 (March, April, and May, 1949).

as a dispersion. Laking a dye on a substrate which is dispersed in an emulsified vehicle, followed by separation of the combined color and vehicle, is an analogous procedure described by Whatmough.<sup>22</sup>

The inverse procedure—preparation of an oleoresinous vehicle in the presence of a color suspension—is described by Waldie.<sup>23</sup> An aqueous dispersion of a pigment, such as carbon black or zinc oxide, is prepared with the assistance of a saponified fatty oil. The mixture is then acidified, and any water that separates is removed. Finally, glycerine is added and reacted with the fatty components present.

It is evident that any pigment present in the initial stages of resin formation will be subjected to an extended series of mixing and perhaps grinding operations, and the amount of mechanical work done on the pigment particles will assist in obtaining a suitable breakdown of aggregates. In this connection it should be noted that the methods for pigmenting either natural or synthetic rubber latices with aqueous carbon-black suspensions are analogous to the procedure described.

### Vehicles

Any vehicle immiscible with water may be used as the dispersion medium. For convenience in processing, however, vegetable oils that have been bodied to viscosities in the range of 5 to 50 poises and are free of volatile solvents are preferred. The fatty acids present in these oils assist the transfer. The process is by no means limited to these products. Synthetic and natural resin solutions, mineral oils, and waxes can be employed. Solvents can be used also, but removal of residual water is rendered difficult, and such dispersions are more effectively utilized for products in which the entrained water is emulsified as part of the finished composition.

Procedures utilizing nitrocellulose are described by Hucks.<sup>24,25</sup> For this purpose the nitrocellulose may be "colloided" by mixing with plasticizers, alcohols, and solvents before the flushing operation. In an alternative procedure, pigment pulp is mixed with "uncolloided," water-wet nitrocellulose and other ingredients. When added in the proper sequence, "colloidizing" of the nitrocellulose and flushing of the color take place concurrently.

Mixtures of soaps in a vehicle are described by Bernstein.<sup>26</sup> As a first

<sup>22</sup> W. H. Whatmough, U. S. Patent 1,813,371 (July 7, 1931).

<sup>23</sup> W. A. Waldie, U. S. Patents 2,283,518; 2,283,519; 2,283,520 (May 19, 1942).

<sup>24</sup> R. T. Hucks, U. S. Patents 1,875,005 (August 20, 1932) and 2,140,745 (December 20, 1938).

<sup>25</sup> R. T. Hucks and G. R. Maher, U. S. Patent 2,114,713 (April 19, 1938).

<sup>26</sup> I. M. Bernstein, U. S. Patent 2,330,667 (September 28, 1943).

component, soaps of zinc, calcium, magnesium, barium, and strontium are used in the form of "resinates." The second soap component is formed from lead, manganese, cobalt, cerium, or vanadium by reacting with any suitable fatty acid. These are combined in a vehicle containing a petroleum solvent. Since the product is intended as a heat-set ink, the soap should be soluble in the ink solvent.

### Reagents

For transfer to take place, the pigment must be preferentially wetted by the oil. Most organic pigments are in this category, and reagents ordinarily are not necessary to effect transfer. On the other hand, many inorganic pigments are preferentially wetted by water; these materials must react with a component of the oil, or have associated with the surface of the pigment particles some water-insoluble compound, in order to produce a change in wetting properties. Chrome yellow, for example, in water suspension is deflocculated and, in most dispersions, preferentially wetted by water. Addition of a bodied linseed oil, which contains an appreciable fatty acid content, to the suspension results in a marked increase in yield value, and the pigment then can be made to transfer to the oil phase. White lead (basic lead carbonate) reacts readily with fatty acids in aqueous suspension, and transfer to the oil phase occurs quickly. A non-reactive pigment such as titanium dioxide, however, resists transfer, and, in order to make the pigment flush, it is necessary to precipitate a soap of the type, for example, of barium or calcium linoleate in the suspension.

The  $pH$  value of the aqueous pigment suspension is of some importance in evaluating the facility or failure of a pigment to transfer. Low  $pH$  values hinder transfer and prolong mixing time. For most pigments it appears desirable to adjust the  $pH$  of the slurry to values above 6. It should be recognized, however, that factors other than an optimum  $pH$  value for facilitating transfer need consideration. Alteration of the  $pH$  of the slurry often results in a change in hue of the pigments; further, addition of an alkali to raise the  $pH$  forms water-soluble soaps which act as emulsifying agents and effectively prevent coalescence of the emulsified oil.

For most pigments the proper reagent, added at the initial stages of mixing, shortens the cycle and frequently results in a more complete transfer. The early patents on sodium soaps for this purpose have been noted. Brown<sup>27</sup> mentions the use of lead soaps. Manganous borate is

<sup>27</sup> R. V. Brown, U. S. Patent 1,192,163 (July 25, 1916).

given in the disclosure of Fletcher,<sup>28</sup> and alkali and alkaline earth salts and hydroxides are listed by Broeker.<sup>29</sup> The compounds of the latter group undoubtedly react with the acid components of the oil to form soaps. An old plant practice was to add barium chloride, often as the dry salt.

Amine soaps have many advantages over the metallic soaps, and a number of patents deal specifically with such compounds as aids in promoting flushing. Holton<sup>30</sup> uses triethanolamine soaps. Ryan and Fischer<sup>31</sup> specify the higher amines, either as the free amine or in combination with fatty acids, e.g., mono-amylammonium ricinoleate. Morrison and Perkins<sup>32</sup> claim a petroleum nitrogen base. Other amines of utility, mentioned by Yee,<sup>33</sup> are benzylamine and cyclohexylamine derivatives. These are stated to be especially effective in flushing iron blue, which is one of the less tractable pigments.

Lecithin is useful also in making flushed colors. Curado<sup>34</sup> claims lecithin for the purpose of facilitating flushing; Saunders and Downs<sup>35</sup> incorporate lecithin into the pigment-vehicle paste for the purpose of imparting greater fluidity to flushed pigment-vehicle pastes which have not been completely dehydrated. These inventors state also that lecithin makes the base pastes more compatible with reducing vehicles, and Curado notes that this compound contributes to drier stability in printing inks.

Surface-active agents of the cationic type are specified by Sloan and Patterson.<sup>36</sup> Many examples are listed; these fall into the following classes: (1) aliphatic quaternary ammonium or phosphonium hydroxides or salts; (2) ternary sulfonium salts; (3) long-chain betaines; (4) inorganic acid salts of amines; and (5) long-chain amines rendered water soluble by introduction of hydroxyl or carboxyl groups. Moilliet<sup>37</sup> utilizes essentially the same cation-active compounds, but adds, in addition, a surface-active material which assists in breaking the emulsion and in

<sup>28</sup> H. P. Fletcher, U. S. Patent 1,317,784 (October 7, 1919); Reissue 15,298 (March 7, 1922).

<sup>29</sup> J. F. Broeker, U. S. Patent 1,832,476 (November 17, 1931).

<sup>30</sup> E. C. Holton, Canadian Patent 321,447 (April 12, 1932).

<sup>31</sup> L. W. Ryan and E. K. Fischer, U. S. Patent 2,126,925 (August 16, 1938); Brit. Patent 469,559 (July 27, 1937).

<sup>32</sup> J. O. Morrison and B. H. Perkins, U. S. Patent 2,282,527 (May 12, 1942).

<sup>33</sup> E. G. Yee, U. S. Patents 2,271,323; 2,271,324 (January 27, 1942).

<sup>34</sup> J. G. Curado, U. S. Patents 2,252,702 (August 19, 1941).

<sup>35</sup> H. F. Saunders and C. D. Downs, U. S. Patent 2,117,366 (May 17, 1938).

<sup>36</sup> C. K. Sloan and G. D. Patterson, U. S. Patent 2,192,954 (March 12, 1940); cf. Brit. Patent 499,334 (January 23, 1939).

<sup>37</sup> J. L. Moilliet, U. S. Patent 2,219,395 (October 29, 1940).



gathering the pigment-vehicle granules into a coherent mass. As examples of these compounds, the following are mentioned: turkey-red oil, sodium cetyl sulfate, sodium dodecyl sulfate, sulfonated oleic acid, and isopropyl naphthalene sulfonate.

Frequently the color transfers without difficulty, but the separated water retains an appreciable quantity of suspended color. The addition of salts of barium or aluminum often serves to coagulate the suspended material. Brown and Roberts<sup>38</sup> find that phosphoric acid or a mono-alkali metal phosphate performs the same function for organic pigments.

In the procedure described by Martone<sup>39</sup> pigment pastes of high solids content are treated with a deflocculating agent to increase the fluidity and facilitate mixing; a precipitant for the deflocculating agent is added either before or during the flushing operation. This is a variant on the emulsification procedure noted previously. As deflocculating agents, Martone mentions hydrocarbon sulfonates, alkyl-aryl sulfonates, and stearyl trimethyl ammonium bromide. Precipitants are salts of calcium, iron, or aluminum.

### Dehydration

Removal of the water entrained in the pigment-vehicle paste is a troublesome operation. Reference has been made to the procedures of heating under vacuum and passing the paste over heated rolls. A distillation process using toluene as the "displacing fluid" is described by de Stubner.<sup>40,41</sup> Vesce<sup>42</sup> prepares a transparent iron oxide color dispersion by means of a distillation procedure. Colloidally dispersed iron hydroxide is mixed with an aqueous emulsion of an alkyd resin dissolved in a volatile organic solvent immiscible with water; subsequent azeotropic distillation leaves the pigment dispersed in an anhydrous vehicle.

In one method described by de Stubner,<sup>43</sup> wet pigment cakes are dehydrated by extracting with a water-miscible dehydrating agent (e.g., alcohol) with the product retaining some of the dehydrating liquid. This material is suitable for formulation with nitrocellulose. The dehydration of both pigment and nitrocellulose in a single operation is also described.<sup>44</sup>

Another dehydration sequence described by de Stubner<sup>45</sup> depends on

<sup>38</sup> R. G. Brown and R. R. Roberts, U. S. Patent 2,379,678 (July 3, 1945).

<sup>39</sup> T. A. Martone, U. S. Patent 2,238,275 (April 15, 1941).

<sup>40</sup> E. C. de Stubner, U. S. Patent 1,955,738 (April 24, 1934).

<sup>41</sup> E. C. de Stubner, U. S. Patent 2,149,282 (March 7, 1939).

<sup>42</sup> V. C. Vesce, U. S. Patent 2,384,579 (September 11, 1945).

<sup>43</sup> E. C. de Stubner, U. S. Patent 1,866,017 (July 5, 1932).

<sup>44</sup> E. C. de Stubner, U. S. Patent 1,795,764 (March 10, 1931).

<sup>45</sup> E. C. de Stubner, U. S. Patent 1,965,764 (July 10, 1934); Reissue 21,032 (March 21, 1939).

the gradual initial removal of water in a heated mixer and on further additions of aqueous pigment "at such a rate that the water in the dispersion is separated continuously as vapor. . . ."

Modified air-drying procedures are used also, and, although these variants are not strictly in the class of flushed colors, they are nevertheless often included. Verbyla,<sup>46</sup> for example, mixes aqueous pigment pulps with water-soluble oils and dries the composite. Gessler<sup>20</sup> emulsifies oil with a pigment slurry by means of triethanolamine soaps, breaks the emulsion, and subjects the pigment-oil paste to vacuum drying. The product is a pulverulent powder which forms a paste on rubbing or compression. In another variant, fine-grained, easily dispersible pigments are made by Vesce<sup>47</sup> by adding volatile solvents (petroleum naphthas, toluene, higher aliphatic alcohols, etc.) to aqueous pigment pastes with any one of a wide variety of surface-active agents, followed by air drying. Shiva<sup>48</sup> adds hydrous gels (starch, silica gel, aluminum hydroxide, etc.) to a water-wet pigment pulp, dries under vacuum, and incorporates a suitable oil.

Some of the unit operations of the flushed color process are adaptable to continuous operation methods. Although engineering research and development work have been done on the subject, there is no detailed description of any integrated operation. One of the earliest suggestions for continuous processing, given in a disclosure by Moses,<sup>49</sup> relates to white lead and utilizes both pulp and dry pigment without specifically indicating a flushing process. Another operation, that of a centrifuging process, intended primarily for dry color manufacture as described by Marquis,<sup>50</sup> is also adaptable and has been used to a limited extent for the separation of water from flushed color pastes. Osborne<sup>51</sup> describes a method for continuously dehydrating an emulsion of vehicle and color pulp. This is a field of process engineering in which numerous developments may be expected.

## Properties of Flushed Colors

### Strength

One of the most controversial of all aspects of the manufacture of flushed pigments has been the difference in tinting strength in comparison with dispersions made from dry color. Beakes<sup>52</sup> gives some data

<sup>46</sup> A. E. Verbyla, U. S. Patent 1,870,186 (August 2, 1932).

<sup>47</sup> V. C. Vesce, U. S. Patent 2,268,144 (December 30, 1941).

<sup>48</sup> R. N. Shiva, U. S. Patent 2,155,103 (April 18, 1939).

<sup>49</sup> A. S. Moses, U. S. Patent 1,371,926 (March 15, 1921).

<sup>50</sup> B. Marquis, U. S. Patent 2,239,492 (April 22, 1941).

<sup>51</sup> C. A. Osborne, U. S. Patent 2,378,786 (June 19, 1945).

<sup>52</sup> H. L. Beakes, *Am. Ink Maker*, **17**, No. 11, pp. 19, 21, 23 (November, 1937).

on the subject, and his figures refute, for the most part, the claims sometimes made for exceptional increases in tinting strength. The data in Table I are assembled from average values for a variety of experiments and show differences beyond experimental error.

TABLE I. STRENGTH DIFFERENCE IN FLUSHED COLOR DISPERSIONS COMPARED WITH DRY COLOR DISPERSIONS

(Average values based on bleach tests.)

Color	Beakes	Fischer & Gans	St. Louis Club
Chrome yellow, light	-5 to 0	....	0 to +10
Chrome yellow, medium	-8 to +5	0 to +2	0 to +10
Chrome orange	....	....	"Sl. weak"
Iron blue	-35 to 0	-5 to -10	0 to +15
Peacock blue (hydrate lake)	....	-5 to 0	....
Victoria blue (P.T.A.)	....	0 to +5	....
Malachite green (P.T.A.)	....	0 to +5	....
Barium lithol toner	....	0 to +5	....
Hansa toner	....	0 to +5	....
Para toner	-25 to 0	....	0
Toluidine toner	-25 to +5	+5 to +10	0 to +12
Phloxine toner	....	+5 to +8	....
Chrome green, light	-5 to 0	....	+6
Chrome green, medium	0 to +10	....	....
Chrome green, dark	0	....	+15

References: H. L. Beakes, *Am. Ink Maker*, **17**, No. 11, pp. 19, 21, 23 (Nov. 1937); E. K. Fischer and D. M. Gans, p. 324 in *Colloid Chemistry*, Vol. VI, J. Alexander, Editor, Reinhold Publishing Corp., New York, 1946; St. Louis Club, *Nat. Paint, Varnish and Lacquer Assoc., Sci. Sect., Circ. 568*, pp. 299-307 (1938).

Several pigments show an apparent loss of strength during the flushing operation. In processing as a dry color, iron blue reaches its maximum strength during the drying process, when, presumably, oxidation of the compound is completed; during flushing, however, not only is such oxidation prevented but reduction reactions with the oxidizable oils forming the vehicle may occur. This view is given further support by the fact that the strength of a flushed iron-blue composition increases when applied in a thin film, as in paint and printing ink, and allowed to dry. Color lakes of the peacock-blue type, in which a dye is precipitated on an aluminum hydrosol base, frequently show loss in strength because of desorption of the dye during flushing.

Other colors that show no appreciable gain or loss are chrome yellows and several of the organic toners. One color, usually marketed in flushed

form, is alkali reflex blue, and, although considerable progress has been made in developing a soft grinding dry color of this type, it is probable that the flushed form will continue to have an evident advantage in strength. Phloxine toner is a color that is consumed in relatively large quantities in both dry and flushed forms. Flushing this color appears to confer a real but smaller advantage.

Comparison of the microscopic appearance of dry grind and flushed color dispersions is in accord with the data from tinting strength determinations. The presence of oversize aggregates in the dry grind of alkali blue and phloxine toner may be noted in typical products. Dry grind and flushed color dispersions of the other colors will usually reveal inconsequential differences. Photomicrographs of comparable flushed and dry color dispersions have been reproduced.<sup>3,53</sup> Flushed pigment dispersions rarely contain sizeable aggregates, and the particles present in the oil dispersion are essentially unchanged from those of the aqueous slurry or pulp. It is for this reason that flushed pigment dispersions are usually rated as of superior texture. Some flocculation may be observed in the microscope mounts, but this is in part an incident in preparation.

The difference in strength of flushed pigments requires additional explanation, particularly in view of variations in testing methods. The only valid comparison is, of course, that of a flushed product against the same lot of dry pigment dispersed under optimum conditions. A hand-mulled pigment dispersion will usually be considerably weaker than the flushed color. Similarly, a dry color ground on a roll mill that has been improperly set, or in a composition of too low viscosity, or on a mill that is mechanically in poor condition is, of course, incompletely dispersed. A more subtle error arises from differential flocculation of the pigments in the tinting mixture as a result of trace quantities of moisture in the flushed color. Thus, if the moisture present in the pigment paste causes the white pigment (zinc oxide or titanium dioxide) in the bleaching dispersion to flocculate, the effectiveness of the white pigment is appreciably diminished and the flushed pigment will appear to have a higher tinting strength. All these errors in testing will lead to the same result: the dry color will appear weaker, and the laboratory technician will be misled if he concludes that the flushed color is inherently of greater tinting strength. It is probable that the conflicting statements on strength gained by the flushing process can be largely attributed to artifacts of the kind noted above.

<sup>53</sup> St. Louis Club, *Nat. Paint, Varnish Lacquer Assoc., Sci. Sect., Circ.* 568, 299-307 (November, 1938).

## Hue

Since colors are labile substances, it should be expected that dispersions made from flushed color and the same material dried and dispersed by mechanical means would differ. The changes in some pigments are quite marked and in one series of experiments,<sup>53</sup> the variations were found, not unexpectedly, to be related to the vehicle selected. The change in hue may become extreme if excessive and prolonged heating is employed to effect dehydration. The phosphotungstate acid lakes, in particular, are sensitive and a considerable loss in strength accompanies a "dirtying" of the color. Chrome yellow and orange pigments usually shift to slightly redder hues; para toner has been noted to change to a bluer tone, but some toluidine toners, particularly the light shades, are apt to be slightly yellower in the flushed form. Eosine toner varies more capriciously, some samples appearing yellower than the dry standard. Iron blue usually appears slightly redder. On the average, however, with skilled control of processing, the shift in hue is uniform for successive lots and is no greater than variations from standard in processing dry colors. Some compensation can be made by formulating the color to allow for hue changes during processing, and this expedient is employed if a standard is to be matched.

The relative hiding power of flushed pigments has been studied. In two series of tests, most dispersions prepared by flushing were observed to exhibit somewhat lower opacity than equivalent dry pigment dispersions.<sup>53,54</sup> There is some disparity in these and other reports, probably because of differences in experimental conditions. Weathering of paint films prepared with the two types of dispersions showed only slight variations. Gloss retention and light fastness were observed to be equivalent.

## Commercial Utility

Although pigment dispersions made by some variation of the flushing process have been used since about 1900, the commercial utility of the products is still actively discussed. May<sup>55</sup> stated the prevailing view that certain pigments, processed to advantage by this method, will remain standard items. Among these are alkali blue, lithol rubine, and scarlet 2R. Wolfe<sup>56</sup> notes that in printing ink technology, flushed colors

<sup>53</sup> Detroit Club, *Nat. Paint, Varnish Lacquer Assoc., Sci. Sect., Circ.* 568, 427-30 (1938).

<sup>54</sup> L. E. May, *Am. Ink Maker*, 17, pp. 16-18, 45 (November, 1937).

<sup>56</sup> H. J. Wolfe, "Printing and Litho Inks," 3rd Ed., MacNair-Dorland Co., New York, 1941; pp. 65-67.

have a definite but restricted place and can be used to advantage in gloss inks, colored news inks, certain classes of magazine inks, or in inks for which the selection of a vehicle is not a limitation.

In a general way the advantages and limitations of flushed pigments may be outlined as follows: (1) flushed pigments with few exceptions retain the particle-size characteristics of the pigments prepared in the aqueous system, and sintering of the particles or cementation by residual soluble salts during drying is avoided; (2) flushed pigment dispersions, in a few instances, have a higher tinting strength than equivalent dry colors, if the color is either deleteriously affected by drying or the particles form excessively hard aggregates which require an impracticable amount of grinding to develop full strength; and (3) the presence of a small amount of residual moisture in the dispersion accelerates livering reactions and increases the extent of flocculation of pigments, especially neutral or hydrophilic pigments. This has led to the frequent observation that flushed pigment dispersions are of higher consistency or body than equivalent dispersions made from dry pigments; the complaint has also been made that "seeding" is more frequently found in products formulated with flushed pigments.

The consensus of opinion is that skillful formulation minimizes the differences between equivalent dry and flushed pigment dispersions.



## Author Index

- Abbe, P. O., 304  
Abramson, H. A., 124  
Acheson, E. G., 229, 230, 250  
Acheson, G. W., 352, 354  
Adam, H. R., 83  
Adam, N. K., 75, 91  
Aldrich, H. L., 211  
Alexander, J., 227, 248  
Alfrey, T., 184  
Allan, B. W., 252  
Allen, A. O., 77  
Allen, E. R., 241, 242, 248  
Allen, R. P., 22, 53, 262  
American Society for Testing Materials,  
4, 7, 17, 51, 277  
Amon, F. H., 58, 114, 263  
Anderson, R. B., 16, 55, 61  
Andreason, A. H. M., 38  
Andrews, A. C., 127  
Andrews, L., 322  
Anthony, R. L., 115  
Archibald, W. J., 41  
Armbruster, M. H., 101  
Arnell, J. C., 43  
Arnold, J. E., 184, 210  
Arnold, K. A., 196  
Arrhenius, S., 176  
Asbeck, W. K., 278  
Auer, L., 243  
Austin, J. B., 14, 101  
Ayres, E. E., Jr., 142  
Azam, M. A., 277
- Babcock, G. R., 244  
Bailey, E. D., 49  
Baines, R. G., 325  
Baker, F., 176  
Baldwin, J. T., 242, 277  
Baltimore Paint and Varnish Production  
Club, 333  
Bancroft, W. D., 93  
Bangham, D. H., 91, 101  
Barksdale, J., 68
- Barnett, C. E., 15, 49, 68  
Barr, G., 148, 159  
Barrett, W. R., 300  
Barrick, G., 69  
Bartell, F. E., 79, 84, 86, 91, 111, 213,  
277  
Bate, A. E., 83  
Baum, L. A. H., 49, 178  
Bauman, G. P., 157  
Beakes, H. L., 292, 359, 360  
Beams, J. W., 41  
Bechtel, W. G., 192  
Beilby, G. B., 122, 259  
Bekk, J., 219  
Bell, S. H., 87  
Bellows, H. A., 280  
Benson, G., 108  
Benton, A. F., 29  
Berberich, O. P., 221  
Berger, R. W., 25  
Berggren, B., 79  
Bergmann, L., 264, 265  
Berkman, S., 119  
Bernard, H., 253  
Berry, C. E., 243  
Bernstein, I. M., 53, 263, 295, 355  
Biddle, S. B., Jr., 38  
Bikerman, J. J., 121, 219, 220  
Billings, E., 65  
Bingham, E. C., 147, 148, 152, 173, 174,  
175, 209  
Bircumshaw, L. L., 183  
Birks, L. S., 47  
Biscoe, J., 47  
Bishop, O. M., 248  
Bissell, E. S., 269  
Blaine, R. L., 42  
Blakeman, W. N., 242, 254  
Blodgett, K. B., 85  
Blom, A. V., 112  
Bloomquist, C. R., 18, 110, 111  
Blott, J. F. T., 78  
Boggs, J. K., 244



- Bogin, C. D., 213, 214  
 Böhner, G., 249  
 Bolthof, H., 208  
 Bondy, C., 265  
 Bonney, R. D., 282  
 Booge, J. E., 209, 243, 244, 253  
 de Booy, J., 176  
 Borger, C. J., 144  
 Borries, B. V., 20  
 Boss, A. E., 244  
 Bowles, R. F., 219, 286  
 Boyd, G. E., 34, 78, 98, 101  
 Braddicks, R., Jr., 263  
 Bramaio, L., 61  
 Bray, R. I., 58, 69  
 Bredée, H. L., 176  
 Breinig, R. M., 241  
 Bridgman, P. W., 260  
 Bridgman, W. B., 41  
 Bridgwater, E. R., 243  
 Brill, H. C., 253  
 Brill, R., 46  
 British Rheologists' Club, 155, 219  
 Brizzolara, A. A., 244  
 Broeker, J. F., 357  
 Brooks, V. S., 34  
 Broughton, G., 177  
 Brown, C., 40  
 Brown, H. M., 325  
 Brown, O. J., Jr., 69, 114  
 Brown, R. G., 358  
 Brown, R. V., 356  
 Brown, T. F., 113  
 Brubaker, D. G., 20, 25, 55  
 Bruce, H. D., 209  
 Bruggeman, D. A. G., 117  
 Brunauer, S., 28, 29, 30  
 de Bruyne, N. A., 219  
 Buchdahl, R., 218, 221, 222, 263  
 Bunzl, M., 177  
 Burdick, H. E., 244  
 Burger, P. J., 250  
 Burgers, J. M., 155, 195  
 Burgess, K. E., 55  
 Burton, E. F., 24, 26, 142  
 Burton, R. L., 46  
 Burwell, E. C., 133  
 Burwell, J. T., 83  
 Busse, W. F., 220, 298  
 von Buzagh, A., 123  
 Cajar, H., 352  
 Calbeck, J. H., 37  
 Campbell, A. B., 309, 312, 313  
 Campbell, G. A., 241  
 Cardwell, P. H., 84  
 Carman, P. C., 42, 43  
 Carpenter, A. W., 299  
 Carr, W., 278  
 Castor, W. W., 242  
 Chamot, E. M., 23  
 Chapman, A. R., 132  
 Chatfield, H. W., 299  
 Chesters, J. H., 324  
 Cines, M., 58, 65  
 Clapham, J. E., 248  
 Clapson, W. J., 133  
 Clark, A., 18  
 Clark, G. L., 46, 263  
 Clayton, W., 338  
 Clewell, D. H., 15, 49, 68  
 Coghill, W. H., 259, 304, 309, 310, 312, 313, 324  
 Cohan, L. H., 115, 182  
 Cohen, H. R., 260  
 Cole, J. W., 196  
 Columbian Carbon Co., 54, 62, 64, 299  
 Conolly, S., 144  
 Conrad, C. M., 168, 192  
 Conrad, V., 297  
 Coolidge, C., 253  
 Coons, K. W., 226  
 Cooper, L. V., 222  
 Corrin, M. L., 136  
 Cosslett, V. E., 27  
 Couette, M., 159  
 Coughlin, J. J., 210  
 Cox, A. B., 85  
 Cragg, L. H., 155  
 Craig, T. J., 51, 286  
 Crawford, J. R., 147  
 Crossley, M. L., 248  
 Crouet, J., 244  
 Cunningham, E. N., 298  
 Cupples, H. L., 226  
 Curado, J. G., 357  
 Curtis, H. A., 87  
 Cutter, J. O., 87  
 Cyr, H. M., 243  
 Dahlen, M. H., 243  
 Dahlstrom, R., 97, 98, 99

- Daiger, W. H., 252  
Dalla Valle, J. M., 4, 11, 17, 42  
Damerell, V. R., 231  
Daniel, F. K., 197, 277  
Dann, C. M., 243  
Davies, J., 248  
Davies, N. S., 87  
Dawson, D. H., 146  
Dedrick, B. W., 280  
Denslow, R. R., 353  
Depew, H. A., 68, 108, 132, 245  
Deryagin, B., 121  
Desch, C. H., 77  
Detrick, S. R., 243, 247  
Detroit Paint and Varnish Production,  
Club, 237, 362  
DeVaney, F. D., 259, 304, 310, 324  
DeWitt, T., 56  
Dienes, G. J., 220  
Dieterle, H. F., 244  
Dietz, V. R., 28  
Dillon, J. H., 222  
Dobbin, R. E., 108, 263  
Donald, M. B., 113  
Dorsey, N. E., 74, 93  
Doss, K. S., 90  
Dourif, H., 352  
Downs, C. D., 357  
Draper, C. R., 132, 282, 290, 292, 326,  
335  
Dreher, E., 260  
Drogin, I., 299  
Droste, W. H., 210, 246  
Drummond, D. G., 25  
Dube, G. P., 126  
DuClaux, M. J., 176  
Duffey, P., 292  
Dunn, E. J., 21  
Duntley, S. Q., 49  
Dupré, M. A., 75  
Dyer, A. S., 129  
  
Eckert, A. C., Jr., 46  
Edser, E., 78, 123  
Eggert, J., 249  
Eide, A. C., 68, 132  
Eirich, F., 177  
Eley, D. D., 297, 298  
Ellis, C., 139, 216  
Ellis, G. H., 251  
Elm, A. C., 254  
  
Emmett, P. H., 16, 29, 30, 31, 32, 34, 56,  
58, 65  
Emödi, B. S., 15  
Endres, H. A., 243, 323  
von Engelhardt, W., 188  
Engle, L. S., 302  
Englehart, L. F., 221  
Epstein, B., 259  
Erickson, D. R., 245  
Erskine, A. M., 242, 243, 244, 252, 353  
Evans, R. M., 67  
Everett, H. J., 269  
Ewing, W. W., 35, 98  
  
Fahrenwald, A. W., 312  
Fairs, G. L., 23  
Fankuchen, I., 47  
Farr, H. O., 283  
Farrow, D. K., 192  
Fatzinger, E. A., 113  
Feldman, A., 75, 77  
Ferguson, A., 90  
Ferrise, L. J., 206  
Ferry, J. D., 168  
Fischer, E. K., 21, 55, 74, 107, 119, 125,  
129, 131, 133, 138, 145, 147, 155, 157,  
160, 163, 165, 168, 192, 206, 210, 216,  
225, 232, 280, 286, 292, 302, 304, 315,  
325, 343, 349, 350, 357, 360  
Fischer, H., 309, 310, 313  
Fletcher, H. P., 357  
Foster, L. V., 24  
Franceson, A., 117  
Fraser, H. J., 204  
Freeman, P. R., 223  
Freundlich, H., 24, 28, 29, 44, 86, 120,  
124, 125, 131, 177, 182, 183, 184, 189,  
192, 194, 195, 227  
Frey, C. M., 276  
Friedman, H., 47  
Friedrich, H., 246  
Frith, F., 47  
Fritts, S. S., 18  
Fromm, H., 261  
Fullam, E. F., 19, 22, 25, 54, 55  
Fuller, C. H., 260  
Fuller, M. L., 25  
Fürth, R., 44  
  
Gabor, D., 25  
Gage, F. W., 43, 244

- Gage, S. H., 23  
 Gallay, W., 111, 196, 222, 298  
 Gamble, D. L., 15, 49, 134, 184, 209, 213, 250  
 Gans, D. M., 34, 55, 66, 74, 92, 107, 109, 111, 112, 155, 231, 286, 343, 350, 353, 360  
 Garber, J. D., 206  
 Gardner, H. A., 51, 132, 148, 206, 207, 244, 277  
 Garlick, O. H., 325  
 Gaudin, A. M., 17, 42, 141, 258, 259, 312  
 Gayer, K., 231  
 Gearhart, F. B., 242  
 Geddes, J. A., 211  
 Gehman, S. D., 22, 23  
 Gerould, C. H., 25  
 Gessler, A. E., 66, 354  
 Giambalvo, V., 243  
 Gibbs, J. W., 78  
 Glaser, D. W., 113  
 Goepfert, W. F., 246  
 Goldenberg, N., 260  
 Goldman, P., 197, 277  
 Gooden, E. L., 18, 42  
 Goodeve, C. F., 184, 189  
 Gorin, M. H., 124  
 Gow, A. M., 309, 312, 313  
 Grady, L. D., 134, 213, 250  
 Graton, L. C., 204  
 Gravath, A. M., 26  
 Greager, O. H., 277  
 Green, H., 4, 10, 19, 20, 33, 54, 56, 57, 60, 105, 107, 108, 116, 148, 152, 157, 159, 163, 167, 175, 179, 180, 181, 183, 184, 185, 209, 219  
 Grenquist, E. A., 53, 108, 300  
 Greubel, P. W., 206, 244, 292  
 Griffith, A. A., 260  
 Groh, J. O., 42  
 Gross, J., 312, 313, 317  
 Grossman, H., 251, 354  
 Grunberg, L., 208  
 Guggenheim, M., 312  
 Guillien, R., 117  
 Guinier, A., 46  
 Gunther, F., 248  
 Gupta, N. N. Das, 27  
 Gurney, L. E., 160  
 Gwathmey, A. T., 124  
 Hager, C. R., 252  
 Hailwood, A. J., 248, 354  
 Hall, C. H., 22  
 Hall, R. E., 253  
 Hall, W. K., 55, 61  
 Haller, W., 112  
 Hamaker, H. C., 126  
 Hamm, F. A., 27  
 Hancock, A., 113  
 Hardinge, H., 311, 312  
 Hardy, W. B., 75, 94, 120, 121  
 Harkins, W. D., 21, 32, 34, 75, 77, 79, 83, 84, 85, 87, 91, 94, 97, 98, 99, 100, 101, 102, 107, 109, 111, 112, 119, 123, 125, 136, 137, 231  
 Harmon, C. G., 79  
 Harner, H. R., 37  
 Hartley, G. S., 135, 225  
 Harvey, E. N., Jr., 4, 13, 14, 15, 57, 58, 59, 65, 102, 129, 138  
 Harvey, W. T., 206  
 Haslam, G. S., 22, 213  
 Hatch, G. B., 228  
 Hatschek, E., 148, 165, 174, 192  
 Hauser, F. A., 40, 74, 126, 189, 227  
 Hawley, G. G., 25  
 Headley, W. N., 242  
 Heckert, W. W., 195  
 Hedrick, J. E., 127  
 Hemingway, H. J., 273  
 Henderson, H. B., 42  
 Hener, W., 260  
 Henglein, F. A., 259  
 Henneberry, G. O., 43  
 Henniker, J. C., 123  
 Henszey, W. H., 325  
 Hermans, P. H., 261  
 Hertel, K. L., 42  
 Hess, K., 261  
 Heymann, E., 193  
 Hillier, J., 24, 55  
 Hinkley, W. O., 38  
 Hochstetter, R., 352  
 Hochwalt, C. A., 214  
 Hofer, L. J. E., 55, 61  
 Hoffman, E., 247  
 Holley, C. R., 348  
 Holt, H. S., 253  
 Holton, E. C., 357  
 Hood, S. L., 323  
 Hoover, C. E., Jr., 346

- Hopkins, F. W., 290  
 Horning, S. C., 140, 252, 353  
 Houwink, R., 126, 148, 174, 210  
 Hucks, R. T., 274, 354, 355  
 Hudson, D. R., 204  
 Hukki, R. T., 259  
 Humbert, R. P., 54, 61  
 Hunt, J. K., 209, 213  
 Hurwitz, C., 323  
  
 Immerheiser, C., 248  
 Innes, W. B., 101  
 Irons, E. J., 83  
 Ismay, C. D., 350  
  
 Jacobsen, A. E., 37, 40, 55  
 Jarmus, J. M., 133, 214  
 Jarrett, M. E. D., 215  
 Jebens, W. J., 128  
 Jellinek, M. H., 47  
 Jerome, C. W., 107, 131, 232  
 Jessup, J. C., 351  
 Johnson, H. M., 241  
 Johnston, N., 222  
 Jones, A. D., 195  
 Jones, L. D., 248  
 Juliusburger, F., 189, 194  
 Jura, G., 32, 85, 91, 101, 102, 123  
  
 Kallmann, H., 123  
 Kammermeyer, K., 113  
 Kaufmann, W. E., 248  
 Kausche, G. A., 20  
 Kendall, S. W., 307, 310, 318, 323  
 Kent, J. W., 330  
 Kern, J. G., 248  
 Kewish, R. W., 184, 213  
 Keyes, W. F., 43  
 Kienle, R. H., 248  
 Kingsbury, F. L., 246  
 Kinney, S. P., 4, 12, 15  
 Klein, A., 38  
 Klemm, H. F., 220  
 Knoll, A., 77  
 Kohl, W. H., 24  
 Kohler, A. S., 113  
 Kranich, W. L., 157  
 Kriebler, J. G., 168  
 Krieger, K. A., 32  
 Kross, W., 183  
 Kruyt, H. R., 129  
  
 Kümmel, P., 133  
 Kunkel, W. H., 38  
  
 Labout, J. W. A., 184  
 Lacey, H. T., 135  
 Ladd, W. A., 26, 54, 108  
 Lamb, H., 162  
 Lambert, J. M., 220  
 Lampitt, L. H., 260  
 Land, W. E., 252  
 Landis, C. G., 55  
 Lang, J. W., 243, 247  
 Langmuir, I., 29, 125, 126  
 Larsen, D. H., 196  
 Laudenslager, H., 231  
 Lawrence, A. S. C., 138, 228  
 Lea, F. M., 42  
 Lecher, H. Z., 135  
 Lee, H. E., 312  
 Lee, W. B., 121  
 Leidheiser, H., Jr., 124  
 Lenher, S., 44  
 Lent, C. M., 133  
 Levey, H. A., 276  
 Levine, S., 126  
 Lewis, G. L., 119  
 Lewis, H. B., 261  
 Lewis, W. C. M., 125  
 Lightbody, A., 146  
 Likhtman, V. I., 264  
 Lindsley, C. H., 160, 163, 165, 168, 192  
 Livingston, H. K., 32, 34, 83, 84, 87, 90,  
 101  
 Livingston, N. F., 252  
 Lloyd, H. B., 50  
 Loeb, L., 124  
 Loomis, A. L., 264  
 Los Angeles Paint and Varnish Produc-  
 tion Club, 324  
 Loveland, R. P., 15  
 Lowe, G. M., 192  
 Lucas, R., 128  
 Lukens, A. R., 55  
 Lynch, W., 290  
 Lynn, J. E., 40  
 Lyons, E. J., 269  
 Lyons, W. J., 168, 192  
  
 MacInnes, D. A., 41  
 Mack, C., 110  
 Mackay, J. F., 115

- Maher, G. R., 354, 355  
 Malm, C. J., 211  
 Malysheva, D., 121  
 Manahan, M. L., 243, 245, 252  
 Marcot, G. C., 134, 252  
 Mardles, E. W. J., 111  
 Margaretha, H., 177  
 Marling, P. E., 214  
 Marquis, B., 359  
 Marsden, E., 278  
 Martin, G., 4, 260  
 Martin, S. W., 37, 39, 40, 141  
 Marton, C., 25, 27  
 Marton, L., 27  
 Martone, T. A., 358  
 Maslennikov, V. M., 264  
 Mason, C. W., 23  
 Mattoon, R. W., 136, 137  
 Mattson, R., 231  
 Maxwell, J. C., 149, 173  
 May, L. E., 362  
 McBain, J. W., 28, 121, 136, 137  
 McBain, M. E. L., 136  
 McCartney, J. T., 55, 61  
 McClellan, P. P., 108  
 McCutcheon, J. W., 226  
 McDowell, C. M., 113, 120  
 McKee, R. H., 136  
 McKinney, P. V., 263  
 McMahan, E. L., 242  
 McMillen, E. L., 87, 113, 119, 190, 210, 213  
 McMullen, E. W., 69  
 McNesby, J. R., 102  
 Mead, W. J., 196  
 Meerman, P. G., 55  
 Mees, C. E. K., 15  
 Meister, W. F., 243  
 Melmore, S., 203  
 Menihan, H. M., 15  
 Merrill, R. C., 136, 137  
 Merwin, H. E., 67  
 Metz, G. F., 305, 307  
 Miller, N. F., 83, 111  
 Mills, W. G. B., 318, 326, 327  
 Minich, A., 289  
 Mittelmann, R., 137  
 Moffatt, L. R., 177, 178  
 Moilliet, J. L., 357  
 Mooney, M., 184  
 Morris, T. C., 22, 23  
 Morris, V. N., 108  
 Morrison, J. O., 247, 357  
 Morton, G. A., 24  
 Moses, A. S., 359  
 Mott, R. A., 47  
 Mowlds, K. S., 251, 252  
 Moyer, L. S., 124  
 Mullin, C. E., 251  
 Murray, C. A., 77, 111  
 Nason, H. K., 222  
 Neale, S. M., 192, 208  
 Nelson, W. K., 250  
 New, G. F., 244  
 Newkirk, A. E., 140  
 Newton, I., 148, 149  
 New York Paint and Varnish Production Club, 52, 237, 287, 289, 337  
 New York Printing Ink Production Club, 206, 207, 292, 293  
 Nichols, J. B., 41  
 Nissan, A. H., 208  
 North, W. B., 51  
 Northwestern Paint and Varnish Production Club, 254  
 Nottage, M., 121  
 Nurse, R. W., 42  
 O'Brien, H. C., 26  
 O'Brien, R. J., 248  
 O'Brien, W. J., 242  
 Odén, S., 36  
 Oeser, E., 245  
 Offutt, H. H., 65  
 Olsen, V. R., 325  
 O'Neal, G. M., 242  
 Opp, C. J., 220  
 Oppermann, C. F., 243  
 Osborne, C. A., 359  
 Osterhof, H. J., 86  
 Ostwald, Wo., 112, 190  
 Othmer, D. F., 354  
 Overbeek, J. T. G., 126  
 Palit, S. R., 138  
 Pall, D. B., 346, 347  
 Palmer, G. B., 351  
 Paquin, M., 243  
 Park, C. R., 108  
 Parks, R. Q., 323  
 Parmelee, C. W., 79

- Parts, A., 117  
 Patterson, G. D., 209, 213, 246, 247, 252,  
     **357**  
 Patterson, H. S., 106  
 Pearson, H. C., 281  
 Pease, D. C., 92  
 Pechukas, A., 43  
 Pederson, K. O., 41  
 Peiker, A. L., 248  
 Perkins, B. H., 244, 247, 357  
 Perrott, G. St. J., 4, 12, 15  
 Perry, J. W., 226  
 Peterson, K. W., 252  
 Pfund, A. H., 49  
 Philippoff, W., 148  
 Pickett, O. A., 254  
 Pierce, E., 144  
 Pigache, P. G., 250  
 Plauson, H., 338  
 Plechner, W. W., 68, 133, 244  
 Poiseuille, J. L. M., 149  
 Poncelot, E. F., 258  
 Poser, M., 24  
 Prebus, A. F., 54  
 Price, C. W., 87  
 Price, D., 226  
 Promnitz, O., 326  
 Pryce-Jones, J., 184, 185, 196  
 Puddington, I. E., 111, 196  
 Purdy, J. M., 52  
  
 Rabinow, J., 128  
 Ramage, A. S., 241, 351  
 Ramberg, E. G., 24  
 Rammler, E., 258  
 Randolph, W. G., 245  
 Rao, B. S., 90  
 Rawitzer, W., 183  
 Ray, R. C., 260  
 Rayleigh, Lord, 324  
 Razouk, R. I., 101  
 Read-Baker, G. W., 276, 282  
 Rebinder, P. A., 263, 264  
 Redd, O. F., 326  
 Reed, C. E., 189  
 Reed, R. F., 220  
 Reiner, M., 152, 163, 168  
 Reising, J. A., 127, 140  
 Renold, A., 197  
 Reynolds, O., 194  
 Rhodes, F. H., 128  
 Rhodes, H. D., 46, 263  
 Rice, O., 228  
 Richards, P. H., 136  
 Rickard, T. A., 83  
 Rideal, E. K., 29, 189  
 Riegel, E. R., 268, 276, 296  
 Rigden, P. J., 43  
 Risse, F., 243  
 Ritchie, E. J., 69  
 Rittenhouse, G., 18  
 Riwlin, R., 163  
 Roberts, L. E., 112  
 Roberts, R. R., 358  
 Robertson, C., 308  
 Robertson, R. H. S., 15  
 Robinson, F. B., 135  
 Robinson, J. V., 177  
 Robison, H. E., 40  
 Rochow, T. G., 55  
 Röder, H. L., 184, 195  
 Rodewald, C. W., 184  
 Rogers, S. R., 299  
 Rollason, E. C., 50  
 Rolle, C. J., 325  
 Roller, P. S., 14, 41  
 Romberg, J. W., 222  
 Romwalter, A., 39  
 Roon, L., 289  
 Rose, H. E., 50  
 Rosen, N., 292  
 Ross, C. L., 332  
 Ross, I. K., 332  
 Rossman, R. P., 65, 108, 262, 263  
 Rothen, A., 41, 122  
 Roundy, P. V., Jr., 41  
 Routh, J. I., 261  
 Rowley, H. H., 101  
 Royer, G. L., 248  
 Rudd, H. W., 326  
 Rupp, E. M., 276  
 Rushton, J. H., 269  
 Russell, J. L., 189  
 Ryan, C. J., 245  
 Ryan, L. W., 77, 107, 109, 111, 128, 231,  
     325, 357  
 Ryan, P. J., 327  
  
 Saal, R. N. J., 78, 184  
 St. Louis Paint and Varnish Production  
     Club, 360, 361  
 Sass, S., 25

- Saunders, B.; 215  
 Saunders, H. F., 357  
 Saunders, L.; 35  
 Saweris, Z., 91  
 Sawyer, R. H., 69, 253  
 Schachman, H. K., 40  
 Schmidling, G. T., 64  
 Schmiel, E. M., 272  
 Schmutzler, A. F., 354  
 Schoenfeld, F. K., 53, 262  
 Schofield, R. K., 184  
 Schroeder, A. J., 354  
 Schuhmann, R., Jr., 258  
 Schultz, F. J., 246  
 Schuster, M. C., 22, 25, 55  
 Schwartz, A. M., 226  
 Schweyer, H. E., 4, 38, 49, 177, 178, 222  
 Scott Blair, G. W., 148, 155, 168, 175, 184, 195, 196  
 Scully, S. A., 66  
 Searle, G. F. C., 160  
 Seidel, G. R., 252  
 van Selms, F. G., 129  
 Sharratt, E., 50  
 Shaw, B. T., 54, 61  
 Sheets, G. H., 195  
 Shepherdson, A., 354  
 Sheridan, E., 302  
 Sherrington, A., 277  
 Shillaber, C. P., 23  
 Shiva, R. N., 359  
 Shoulejkin, W., 68  
 Shutt, R. S., 110, 111  
 Siegel, A., 241, 242, 243  
 Silver, B. R., 243  
 Silverman, M., 352  
 Simha, R., 177  
 Sloan, C. K., 139, 246, 247, 357  
 Smith, A. E., 26  
 Smith, C. M., 42  
 Smith, D., 33, 56, 57, 60, 61  
 Smith, G. P., 124  
 Smith, H. DeW., 155  
 Smith, H. L., 211  
 Smith, J. E., 44, 45  
 Smith, N. D. P., 54, 59, 60, 61, 62, 63  
 Smith, W. R., 58, 65, 69, 262, 263  
 Snell, F. D., 226  
 Snyder, J. W., 254  
 Soday, F. J., 111  
 Sollner, K., 18, 264, 265  
 Solomon, E., 47  
 Sonsthagen, L. A., 295  
 Soyenkoff, B. C., 127  
 Sparrow, E. E., 335  
 Speakman, J. B., 106  
 Star, D. E., 310  
 Staudinger, H., 260  
 Steele, F. A., 119, 242  
 Steinberg, M., 115  
 Steynour, H. H., 39, 113  
 Stener, E., 261  
 Sterbenz, A. F., 292  
 Stewart, A., 354  
 Stillwagon, S. C., 281  
 Stokes, S. C., 299  
 Stone, H. E., 244  
 Strakhovskii, G., 121  
 Strom, C. O., 335  
 de Stubner, E. C., 273, 358  
 Stutz, G. F. A., 49, 64, 254  
 Sullivan, R. R., 42  
 Sullivan, R. W., 244  
 Sullivan, W. F., 37, 40, 55  
 Sulman, H. L., 85  
 Sumner, G. G., 37  
 Sutherland, J. B., 127  
 Sutton, J. B., 247  
 Svedberg, T., 41  
 Sward, G. G., 51, 148, 206, 277  
 Sweitzer, C. W., 244, 300  
 Swerdlow, M., 61  
 Swindells, J. F., 206  
 Szymanowitz, R., 230  
 Taggart, A. F., 17, 305, 322  
 Taylor, A. M., 132  
 Teller, E., 30  
 Teller, F., 248  
 Thimm, J. E., 218, 221  
 Thomas, A. W., 227  
 Thomas, C. A., 111  
 Thomas, P. J., 245  
 Thompson, M. S., 248  
 Thornhill, F. S., 58, 69, 263  
 Thyne, A. W. F., 278  
 Tilleard, D. L., 54, 59, 60, 61, 62, 63  
 Todd, J. D., 352  
 Todd, W., 248  
 Tollenaar, D., 208  
 Toronto Paint and Varnish Production Club, 113, 143

- Toulmin, H. A., 243  
 Travis, P. M., 338  
 Traxler, R. N., 49, 177, 178, 221, 222  
 Treloar, L. R. G., 194  
 Tripp, V. W., 192  
 Trivelli, A. P. H., 15  
 Tucker, G. R., 250  
 Tuley, W. F., 250  
 Turkevich, J., 55  
 Turner, J. L., 68  
  
 Ullmann, E., 44  
 Underwood, E. M., 305, 307  
 Updike, R. L., Jr., 18  
 Urbanic, A., 231  
 Usher, F. L., 113, 120  
  
 Valko, E. I., 44, 45, 47  
 Van Antwerpen, F. J., 226  
 Vance, A. W., 24  
 Vand, V., 177  
 Van Loo, M., 213, 278  
 Van Norman, E., 27  
 Vansomeren, H. S., 50  
 Vasel, G. A., 282  
 Vendl, M., 39  
 Venstrem, E. R., 263  
 Venuto, L. J., 134, 143, 326  
 Verbyla, A. E., 303, 359  
 Verdery, R. B., 220  
 Vervecy, E. J. W., 126  
 Vesce, V. C., 254, 358, 359  
 Vinograd, J. R., 26, 137  
 Voet, A., 117, 218, 220, 283, 327  
 Vogel, M. R., 246, 254, 300  
 Vogt, M. J., 231  
  
 Wachholtz, F., 117, 208  
 Wack, P. E., 115  
 Wadell, H., 11, 16  
 de Waale, A., 119, 184, 193  
 Wagner, L. A., 49  
 Waldie, W. A., 355  
 Walker, W. C., 53  
 Walton, C. W., Jr., 111  
 Wampner, H. L., 213, 242  
 Ward, A. G., 223  
 Waring, R. K., 210  
 Wark, I. W., 85  
 Warren, B. E., 46, 47  
 Watson, J. H. L., 14, 26, 27  
  
 Webb, W. A., 222  
 Wehrle, P. W., 335  
 Weidinger, A., 261  
 Weidlich, W. A., 273  
 Weisberg, H. E., 241  
 Wells, P. V., 49  
 Weltmann, R. N., 157, 159, 179, 180, 181,  
     183, 184, 185, 188  
 Wendt, B., 249  
 Wenzel, R. N., 84  
 Werthan, S., 113  
 Westbrook, E. I. E., 223  
 Whatmough, W. H., 355  
 Wheeler, G. B., 325  
 White, T. A., 29  
 Whitfield, G. W., 184  
 Whitwell, J. C., 168  
 Whytlaw-Gray, R., 106  
 Wicker, C. R., 211  
 Widmer, G., 144, 245  
 Wiegand, W. B., 26, 108, 134, 246, 300  
 Wien, R. H., 113  
 Wiggam, D. R., 301  
 Wilcock, D. F., 70, 184, 213  
 Williams, J. W., 41  
 Williamson, R. V., 158, 192, 195, 209,  
     213  
 Willstaetter, M., 123  
 Wilson, A. D., 250  
 Wilson, J. N., 26  
 Windebank, C. S., 177  
 Winding, C. C., 157  
 Winkler, H. G. F., 182, 188  
 Winslow, W. M., 127  
 Wint, R. F., 210  
 Withington, W. H., 305  
 Wohlers, H. E., 243  
 Wolfe, H. J., 206, 216, 292, 362  
 Wollman, E., 176  
 Wood, R. W., 264  
 Wooley, A. D., 84  
 Work, L. T., 4, 113  
 Wornum, W. E., 276, 282  
  
 Yee, E. G., 357  
 Young, C. B. F., 226  
 Young, T., 80, 81  
 Young, T. F., 74, 83  
  
 Zakoschikova, E. P., 264  
 Zapp, R. L., 244, 302



Zettlemoyer, A. C., 53  
Zimmer, G. F., 281  
Zimmerman, J., 206  
Zipper, P., 281  
Zschimmer, B., 248

Zsigmondy, R., 23, 24  
Zucker, M., 221  
Zuidema, H. H., 79  
Zussman, H. W., 253  
Zworykin, V. K., 24, 25, 55

# Subject Index

- Absorption, definition of, 28  
oil, 276-278
- Acetate dyes, dispersion of, 251
- Acetylene black, particle size of, 58
- Adherence of particles, 105
- Adhesion tension, 86-88  
measurement of, 86-87  
and oil absorption, 277  
and settling volume, 111
- Adhesion, work of, 75-76, 81, 90, 101-102
- Adsorption, 28-35, 101-102  
assumptions for calculation of specific surface data, 30, 32-33  
Brunauer-Emmett-Teller equation for, 30  
definition of, 28  
experimental techniques, 30-33  
of gases and vapors, 28-34  
Harkins-Jura equation for, 33  
and interfacial energy, 101-102  
Langmuir equation for, 29  
method for particle-size measurement, 12, 28-35  
molecular areas in, 32-35  
from solution, 34-35, 231  
and spreading coefficient, 102  
of water vapor, 33  
and work of adhesion, 102
- Age-hardening of asphalt, 221
- Aggregate(s), 5-7  
breakdown during dispersion, 7, 22, 230  
on colloid mill, 343  
during mixing, 274  
on roll mills, 53-54, 238-240, 266, 282, 289-292, 303  
on stone mill, 333-336  
by ultrasonic radiation, 265  
of carbon black, 46, 53-54, 262-263  
definition of, 4-6, 104-105  
in dispersions, 40, 50-54, 249, 303, 361  
of dyes, 45  
formation of, 5-6
- Aggregate(s), in paint films, 50, 144  
in paints, 249  
removal by centrifuging, 249, 266  
size, estimation of, 40, 45-47, 50-54
- Aggregation, prevention of, 224, 247-249
- Aging of dispersions, 201-203, 250
- Air-liquid interface, 74-75
- Albumin as a protective colloid, 251
- Aluminum benzoate in pigment processing, 254
- Aluminum hydrate in roll-mill dispersion, 293
- Amicron, 23
- Amides as dispersing agents, 233-235, 245
- Amines as dispersing agents, 232-236, 244, 245-247, 255, 302, 357
- Amphipathic molecule, definition of, 225-226
- Angle of contact, 74-94; *see also* Contact angle
- Antimony oxide, particle size of, 56
- Apparent viscosity, definition of, 157-158
- Aqueous dispersions, 243, 249-253
- Artifacts in electron microscopy, 27, 107
- Asbestine, particle size of, 56
- Asphalt dispersions of mineral powders, flow of, 177-178, 222
- Attractive forces, 120-124
- Ball mill(s), 304-328  
cascading of grinding medium, 309, 325, 328  
centrifuging of grinding medium, 309-312  
charge of grinding medium, 313-314  
charging ratios for dispersion, 314-316, 328  
commercial practice in operating, 325-327  
construction of, 305-307  
contamination in, 323-324  
critical speed of, 310-311

- Ball mill(s), deformation of balls in, 324-325  
 diameter and rate of dispersion in, 318-319  
 for dispersion of carbon black, 326-327  
 temperature during operation, 320-321, 327  
 types of, 305  
 viscosity of dispersion, 318-321, 325, 328  
 voids in ball charge, 314-315  
 wear of grinding media, 322-325
- Banbury mixer, 280, 297
- Barium resinate in pigment processing, 242
- Barium sulfate, heat of immersion data for, 98-100
- Barytes, particle size of, 56
- Beads of carbon black, 6, 65-66, 134-135, 321
- Bentonite, particle size of, 61
- Benzidine base as a dispersing agent, 236, 246, 302
- Benzidine yellow, particle size of, 59  
 in roll-mill dispersion, 293
- Blanc fixe, particle size of, 56
- Bonding of single metal crystals, 123-124
- Borneol as a deflocculating agent, 254
- Bronziness of pigments, 241
- Brownian motion, 36, 106, 107, 141-142
- Buhrstone for mills, 306, 330
- Burnt sienna, particle size of, 57
- Cadmium orange in roll-mill dispersion, 293
- Cadmium red in roll-mill dispersions, 293, 301
- Cadmium yellow in roll-mill dispersion, 293
- Capillary viscometer, 159
- Carbon black, aggregates of, 46-47, 53-54, 65-66, 262-263  
 alkaline earth metal soaps as dispersing agents for, 244  
 amines as dispersing agents for, 235-236, 245-246, 302  
 beads of, 6, 65-66, 134-135  
 benzidine base as a dispersing agent for, 236, 246, 302  
 conductivity of dispersions of, 113-116
- Carbon black, copper soaps as dispersing agents for, 236, 244, 246, 302  
 density of, 65, 262  
 dispersions, flow of, 179-180  
 dispersion, in ball mill, 320-321, 326-327  
 in colloid mill, 343-344  
 on roll mills, 235, 293, 300, 302  
 dye intermediates as dispersing agents for, 246  
 jetness and particle size, 69  
 nickel soaps as dispersing agents for, 244, 302  
 particle size of, 58, 64-66, 263  
 pellets, 65-66, 134-135  
 soaps as dispersing agents for, 236, 244, 246, 302  
 structure by x-ray diffraction, 46  
 water adsorbed by, 96-97
- Carboxy methyl cellulose as a protective colloid, 247
- Cascading of balls in mill, 309, 325, 328
- Casein as a protective colloid, 251
- Catacting of balls in mill, 309, 325
- Cationic surface-active agents in dispersion, 247
- Cavitation during ultrasonic radiation, 265
- Cellulose, depolymerization during grinding, 260-261
- Centrifugal sedimentation for particle-size measurement, 39-41
- Centrifuging of balls in mill, 309-312
- Centrifuging for removal of aggregates, 249
- Channel black, *see* Carbon black
- China clay, particle size of, 61
- Chrome green in roll-mill dispersion, 293, 301
- Chrome orange, particle size of, 57, 63  
 in roll-mill dispersion, 293
- Chrome yellow, particle size of, 57, 63  
 dispersions, flow of, 179-180  
 in roll-mill dispersion, 293, 301-302
- Chromium naphthenate in pigment processing, 243-244
- Clay suspensions, deflocculation of, 230
- Clays, particle sizes of, 61-62
- Clearance between grinding surfaces on mills, 266-267, 286-287, 296, 335-336, 343-345

- Cobalt naphthenate as a dispersing agent, 231
- Coconut oil in pigment processing, 244
- Cohesion, work of, 75
- Colloid mill, 338-346, 353  
action of, 342-346  
clearance between rotor and stator, 267, 343-345  
construction of, 340-342  
dispersion with, 238, 342-346, 353  
history of, 338-340  
operating speeds of, 343  
sizes of, 341
- Colloidal carbon, *see* Carbon black
- Colloidal graphite, 229-230, 249-250
- Comminution, process of, 258-267
- Compaction of powders, 262-263
- Conductance of dispersions, 113-116
- Cone mills, 337-338, 346
- Consistency, 150-159, 173-223, 224; *see also* Plastic flow  
of asphalt compositions, 177-178, 221-222  
common terms for, 147, 154-156  
control with surface-active agents, 225  
definition of, 174  
inferred from oil-absorption data, 278  
of lacquers, 208-216  
and mill operation, 266-267, 288-290, 296-298, 318-321, 325, 328, 337, 344-346  
of paints, 208-216  
of pigment dispersions, 173-190, 194-205, 231-240  
of printing inks, 216-221  
of starch pastes, 192-193
- Contact angle, 79-94, 350  
data for various systems, 83-86  
difficulties in measurement of, 88-90, 93  
Dupré's equation, 75, 81  
implications of, 90-94  
measuring methods for, 81-82, 93  
nomenclature of, 92  
Young's equation for, 80-81
- Contamination from ball and pebble mills, 323-324
- Contamination from roll mills, 291, 295-296
- Conversion units, table of, 2
- Copper oleate as a dispersing agent, 231, 236, 244, 246
- Couette viscometer, 159; *see also* Viscometer, cylindrical rotational
- Crushing, 259-261, 266, 276
- Crystal lattice distortion during grinding, 260
- Crystals, acicular, orientation during grinding, 261
- Deformation of balls during grinding, 324-325
- Deformation and flow of plastics, 222
- Deflocculating agents, *see* Surface-active agents
- Deflocculation, 105, 224, 230; *see also* Flocculation  
definition of, 105  
and dilatant flow, 197, 203  
index of, 118
- Degradation of polymeric substances during grinding, 260-261
- Dehydration of flushed-color dispersions, 352-353, 358-359
- Density of carbon black, 65, 262
- Depolymerization during grinding, 260-261
- Detergent, definition of, 225
- Dextrin as a protective colloid, 248, 250
- Diachysis, 120
- Diameter, arithmetical mean, 10, 11  
average, 9  
effective, 11, 35  
harmonic mean, 9  
length average, 10, 11  
mean length, 10, 12  
mean surface, 10, 12  
mean volume, 10, 12  
median, 10, 11  
modal, 10, 11  
nominal, 10, 11  
mean volume-surface, 10, 12  
weight-mean, 10-12
- Diatomaceous earth, particle size of, 55, 61-62  
for prevention of hard settling of pigments, 133
- Diatoms, shapes and dimensions of, 55, 61-62
- Dielectric constant of dispersions, 116-118

- Diffusion method for particle-size measurements, 44-46
- Dilatancy, 170-172, 194-205
- Dilatant flow, 170-172, 194-205  
 of carbon-black dispersions, 197, 250  
 characteristics of, 194-196  
 of chrome-yellow dispersions, 197  
 in colloid-mill operation, 345-346  
 and concentration of disperse phase, 195-205  
 definitions of, 153-154, 157, 194-195  
 and deflocculation of the disperse phase, 203  
 equations for, 167-168  
 examples of, 154, 195-202  
 in grinding, 261-262, 289, 345-346  
 of iron oxide dispersions, 200-202  
 measurement of, 170-172, 195-203  
 and packing volume of the disperse phase, 203-205  
 and particle shape, 204  
 and particle size, 195-196  
 of printing ink, 220  
 of quicksand, 203  
 in roll-mill operation, 289  
 of starch suspensions, 195, 197-201  
 and thixotropy, 203-205  
 of zinc oxide dispersions, 197
- Dispersibility, 249-250, 262
- Dispersing agent, definition of, 225; *see also* Surface-active agent
- Dispersion, general, 1-2, 6, 261-267
- Disc mills, 329-346
- Dispersol dye dispersions, 251
- Dough mixer(s), 271-275  
 construction of, 271-272  
 for dispersion of pigments, 248-249, 272-275, 351-353  
 for flushing process, 351-353  
 operation of, 272-275  
 for preliminary mixing, 272, 300  
 vacuum-jacketed, for dehydration, 352-353
- Drier dissipation, reduction of, 247, 254
- Dry grinding of solids, 258-261
- Duplex films, 94-95
- Dye(s), acetate, dispersion of, 251  
 crystallites, size of, 47  
 intermediates as deflocculating agents, 246  
 particle size of, 45, 47
- Dye(s), solubilization of, 136-138
- Edge-runner mill, 275-276
- Elasticity, 222
- Electric charge on suspended particles, 105-106, 124-128, 140, 228
- Electron microscopy, 24-27  
 artifacts in, 26-27  
 comparison with optical microscopy, 24  
 depth of field in, 24  
 dispersion of powders for, 25-27  
 limits of resolution, 24  
 mounting media for, 26  
 particle-size data from, 14, 58, 59-66  
 preparation of specimens, 25-27  
 references to published electron micrographs of powdered solids, 54-55  
 specimen changes in, 27  
 wavelength equivalent of electron beam, 24
- Electrophoresis, 124-127
- Elutriation method for particle-size measurement, 41-42
- Emulsification process for flushed colors, 354-355
- Emulsifying agent, definition of, 225; *see also* Surface-active agent
- Emulsions, photographic, 15, 265-266  
 stability of, 119
- End-effect correction for rotational viscometer, 163-165
- Energy, surface, 74-79, 94-95, 97-103
- Energy of adhesion, 99-101
- Energy of immersion, 97-100
- Entrained air, in dispersions, 202-203, 250, 295  
 effect on optical properties, 69-70  
 in flotation, 132
- Eosine toner, particle size of, 59, 67  
 flushed form of, 360-362
- Estimation of aggregate size, 40, 45-47, 50-54
- Ethyl abietate as a deflocculating agent, 254
- False body, 209
- Fatty acids in pigment processing, 241-243, 356
- Fatty alcohol sulfates in pigment processing, 232-236

- Fenchyl alcohol as a deflocculating agent, 254
- Fibrillation of dispersed particles, 127
- Film pressure, 88, 90-91, 101-102
- Films, duplex, 94-95  
monomolecular, 30, 33, 35, 94-96, 99, 112, 228-229, 231, 257  
polymolecular, 94-95, 123, 257
- Fineness gauges, 52-53
- Five-roll mill, 280-281, 284-285, 290-292
- Floating of pigments in mixtures, 138-144; *see also* Flooding
- Flocculation, 104-135  
in aqueous suspensions, 125-126, 131  
and Brownian motion, 107  
of carbon black in rubber, 108, 115-116  
characteristics of, 104-105, 115-116  
and conductivity of dispersions, 113-116  
control with surface-active agents, 224-257  
definition of, 104-105  
and dielectric constant of dispersions, 110-118  
form factor in, 117-118  
and flooding of pigments in mixtures, 138-144  
free energy change in, 119  
and hiding power, 146  
by immiscible liquids, 128-135  
induced by electrostatic field, 127-128  
induced by magnetic field, 107, 127-128  
and opacity of dispersions, 145-146  
in paints and lacquers, 133-134, 215-216  
and plastic flow, 116, 128-129  
in printing inks, 134  
and settling of dispersed particles, 109-113, 133, 230-231  
and thixotropy, 189-190  
and tinting strength, 361, 363  
and yield value, 116, 128-129, 189-190
- Floccules, 104-105, 106
- Flooding, 138-144  
Brownian motion in, 141  
control of, 143-144  
and electric charges, 140  
and flocculation of dispersed particles, 140  
and particle size, 143-144
- Flooding, and plastic flow, 140  
reduction with matrix pigments, 144, 245  
and tinting-strength errors, 142, 359-361
- Flotation of ores, 131-132
- Flow, common terminology of, 147, 154-156  
dilatant, 153-154, 170-172, 194-205  
of dispersions, 156, 176-182, 208-223, 231-237  
Newtonian, 152, 157, 159, 206  
of oils, 206-208  
plastic, 152-153, 173-182  
pseudoplastic, 153, 190-194  
thixotropic, 152-153, 182-190, 193, 203, 210-211  
types of, 150-154
- Flowout of paints and lacquers, 211-216
- Fluorescent dyes, 63-64
- Flushed color and pigment dispersions, 6, 135, 348-363  
commercial utility of, 362-363  
dehydration of, 352-353, 358-359  
emulsification process for, 354-355  
hue variations in, 362  
properties of, 359-363  
reagents for, 356-358  
strength of, 359-361  
theory for, 349, 350  
vehicles for, 135, 355
- Foam process for treating pigments, 248
- Forces between dispersed particles, 118-138
- Forces, long-range, 120-124
- Gelatin as a protective colloid, 248
- Glass beads for grinding, 308  
as size standards, 18
- Glue as a protective colloid, 248, 251
- Gloss retention in flushed pigments, 362
- Gloss white in roll-mill dispersion, 293
- Glycerine as a dispersion medium, 232-236
- Graphite, colloidal, 229-230, 249-250  
heat of immersion data for, 100
- Gravure printing ink, 216-219
- Grinding, dry, of crystalline substances, 259-260  
new surface in, 259  
of polymers, 260-261

- Grinding, dry, of proteins, 260-261  
 wet, *see* Dispersion, Ball mills, Pebble mills, Roll mills, Disc mills, Cone mills, and Colloid mill  
 with surface-active agents, 263-264
- Grindometer, 53
- Guignet green in roll-mill dispersion, 293
- Gums as protective colloids, 134, 241, 248, 250
- Hansa yellow, particle size of, 59, 67  
 in roll-mill dispersion, 293
- Heat of immersion, 97-101, 146
- Hemoglobin as a protective colloid, 251
- Hiding power, 69, 144-146, 362
- High polymers, rheology of, 222
- High-temperature dispersion, 132-133, 327
- Hue variations of flushed colors, 362
- Hydrophilic surface, definition of, 91, 93-94
- Hydrophobic surface, definition of, 91, 93-94
- Hydrotrophy, 136
- Hysteresis loop in flow curve of thixotropic material, 152-153, 184-188
- Image distortion, electron microscope, 27  
 optical microscope, 20
- Impactoids, 263
- Inuline base as a dispersing agent, 246
- Infrared reflectance of dispersions, effect of steel contaminant, 323-324
- Infusorial earth, particle size of, 61-62
- Inkometer, 220-221
- Inositol hexaphosphoric acid as an ion-sequestering agent, 253
- Interface, air-liquid, 74-75  
 definition of, 73  
 liquid-liquid, 75-77  
 solid-liquid, 77, 79-103
- Interfacial energy, 74-79, 94-95, 97-103
- Interfacial tension, 75-77, 128-131
- Ion sequestration, 253
- Iron blue, dispersion of, 233, 293, 301-302, 343-344  
 particle size of, 57, 62, 69
- Iron mill, 337-338
- Iron oxides, energy of adhesion data for, 102
- Iron oxides, dilatant flow of suspensions of, 197, 200-203  
 particle size of, 57, 62
- Iron powder, energy of adhesion data for, 102
- Jetness of carbon-black dispersions and particle size, 69, 300
- Kieselguhr, particle size of, 61-62
- Lacquers, leveling of applied films, 211-216  
 orange peel of, 212-216  
 viscosity of, 211  
 flocculation of pigments in, 132, 214-215
- Lampblack, particle size of, 58, 65
- Lead chromate, particle size of, 57, 63
- Lecithin, as a dispersing agent, 231-236, 237, 302, 357  
 as a flocculating agent, 131, 189, 232-233
- Leveling of paint and lacquer films, 210-216
- Licorice as a protective colloid, 248
- Light fastness of flushed colors, 362
- Light microscope, *see* Optical microscopy
- Light transmission and flocculation, 145-146
- Lignin sulfonate as a protective colloid, 251
- Limestone in asphalt dispersions, 178
- Linseed oil varnish, vehicle for dispersion, 232-236  
 viscosities of, 206-208
- Liquid-liquid interface, 75-77
- Lithographic printing ink, flocculation of pigment in, 134
- Lithographic varnish, viscosity standards, 206-208
- Lithol red toner, particle size of, 59, 66  
 in roll-mill dispersion, 234, 293
- Lithol rubine, particle size of, 59  
 in roll-mill dispersion, 293
- Lithopone, particle size of, 56
- Madder lake, particle size of, 59
- Magnesium carbonate in roll-mill dispersion, 293
- Magnesium oxide, particle size of, 47

- Magnetic field, flocculation of particles**  
in, 107, 127-128
- Malaxation, 268
- Mastication, 268
- Matrix pigments, 144, 245
- Metal powders, coating of, 242, 245  
work of adhesion, data for, 102
- Methyl cellulose as protective colloid, 247
- Methyl cellulose sols, pseudoplastic flow  
of, 190-194
- Micelles, 135-138, 227-228
- Microscopy, electron, 24-27; *see also*  
Electron microscopy  
optical, 19-23; *see also* Optical micro-  
scopy
- Mills for dispersion, 268-347  
ball and pebble, 304-328  
colloid, 338-346  
disc, 329-346  
Dodge, 280-281  
edge-runner, 275-276  
five-roll, 280-281, 284-285, 290-292  
iron, 337-338  
Kinson, 280  
Neal, 279-280  
Plymouth, 280-281  
pot, 337-338  
single-roll, 282-283  
stone, 329-337  
three-roll, 280-281, 283-296  
two-roll, 280-281, 296-303
- Mineral oil as vehicle for dispersion, 232-  
236
- Mixers, 268-278, 296-297  
change-can, 270-271, 351  
dough, 270-275, 351-353  
edge-runner, 275-276  
impeller, 269-270  
pony, 270-271
- Mixing, 268-278, 351-353
- Molecular areas of adsorbed molecules,  
32-35
- Molybdate orange, particle size of, 69  
in roll-mill dispersion, 293
- Mounts for electron and optical micro-  
scopy, 20-23, 25-27
- Naphthenates in pigment processing, 244
- Newtonian flow, 152, 157, 159, 206
- Nickel soaps, dispersing agents, 244, 302
- Nigrometer, 69
- Nitrocellulose, dispersions in, 273-274,  
299-302
- Noise level of operating ball mill, 311-312
- Offset printing, 217
- Offset printing inks, flocculation of pig-  
ment in, 134
- Oil absorption, 276-278
- Oil viscosities, 206-208
- Oils in pigment processing, 244
- Oleophilic surface, definition of, 93-94
- Oleophobic surface, definition of, 93-94
- Optical microscopy, 19-23  
comparison with electron microscopy,  
24  
depth of field in, 19-20  
dispersion of powders for, 20-23  
effect of particle shape on image, 20  
limits of resolution, 19-20  
mounting media, 21-23  
for oversize particles, 50-51  
particle-size counting technique, 21-22  
preparation of specimens for, 20-23
- Optical properties of dispersions, 67-70,  
145-146
- Orange mineral, particle size of, 57  
in roll-mill dispersion, 293
- Orange peel of lacquers, 212-216
- Ore flotation, 131-132
- Oversize particles (aggregates), size esti-  
mation of, 40, 45-47, 50-54, 303
- Packing and dilatant flow, 203-205
- Packing of grinding media in ball mills,  
316-317, 324
- Packing of spheres, 203-204, 316-317
- Packing volumes of particles, 203-204
- Paint, distribution of pigment in dry film,  
144-145  
false body of, 209  
floating of pigments in, 138-144  
flooding of pigments in, 138-144  
flow properties of, 208-216  
gloss of, 133-134, 145  
leveling of films, 210-216  
pigment-concentration gradient in dry  
film, 144-145  
plasticity of, 128  
rheological properties of, 208-216  
settling of pigments in, 113, 132-134  
surface irregularities, 212-213



- Paint, thickness of film, 213-214  
 thixotropy of, 210-211, 213-216  
 types of, 208-209  
 water in, 133, 214  
 yield value of, 209-211
- Para red toner in roll-mill dispersion, 293
- Particle, concept of, 4-7  
 diameter, definition of, 8-9
- Particle shape, 9  
 and dilatancy, 204  
 effect on image in microscopy, 20  
 effect on settling, 35-36, 38-39  
 and optical properties, 68  
 and plastic flow, 178, 180  
 and thixotropy, 188-189
- Particle size, 3-72; *see also* Aggregate  
 average diameters, 8-16  
 control of, 225  
 distribution, for carbon black, 65  
 for chrome yellow, 14  
 for lampblack, 65  
 and flooding of pigments in mixtures,  
 140-144  
 measuring methods, 16-54  
 adsorption of gases and vapors, 28-  
 34  
 adsorption from solution, 34-35  
 diffusion, 44-46  
 elutriation, 41-42  
 fineness gauges, 52-53  
 microscopy, electron, 24-27  
 microscopy, optical, 19-23, 50  
 microscopy, ultra-, 23-24  
 permeability, 42-44  
 sedimentation, 35-41  
 sieving, 17-18  
 tinting strength, 47-48  
 turbidimetry, 48-50  
 x-ray diffraction, 46-47  
 and optical properties of dispersions,  
 15, 67-70, 145-146  
 projective area, 15  
 standards for, 18
- Peacock blue, particle size of, 59, 66  
 in roll-mill dispersion, 293  
 strength of, flushed, 360
- Pebbles for grinding, 307-308
- Pebble-grit stone for mills, 331
- Pebble mill, 304-328; *see also* Ball mill
- Penetrating agent, definition of, 225
- Peptization, 104
- Permeability method for particle-size  
 measurements, 42-44
- Persian orange lake in roll-mill disper-  
 sion, 293
- pH of slurries during flushing, 356
- Phloxine toner, flushed form of, 360-362  
 particle size of, 59, 67
- Phosphates in pigment processing, 243,  
 253  
 as ion-sequestering agents, 253
- Phosphorescent pigments, particle size  
 of, 63-64
- Phthalic acid derivatives in pigment  
 processing, 244
- Phthalocyanine pigments, particle size  
 of, 59, 66  
 crystallization of, 66
- Pigment(s), *see also listings under names  
 of pigments*  
 aggregates, 4-6, 40, 50-54, 249, 303,  
 361  
 ball-mill dispersion of, 308-328  
 coating of, 229, 241  
 colloid-mill dispersion of, 342, 346  
 concentration gradient in dry paint  
 films, 144-145  
 dispersion of, general, 258-267  
 dispersions, rheology of, 173-205  
 flocculation and deflocculation of, 104-  
 146, 227-239  
 flooding of, 138-144  
 flushing of, 348-363  
 matrix, 144, 245  
 particle size of, 54-72  
 pebble-mill dispersion of, 308-328  
 resinated, 241-242  
 roll-mill dispersion of, 285-303  
 separation from vehicle for analysis,  
 135  
 settling of, 35-41, 109-113, 132-133,  
 138-143, 230-231  
 soft-processing, 6, 135, 224, 247  
 stone-mill dispersion of, 333-337  
 surface-active agents in processing,  
 224-257  
 for thixotropic dispersion, 252  
 wetting of, 73, 79-103, 224, 227-232
- Plastic flow, 150-152, 154, 156, 157, 163-  
 166, 168-170, 173-182  
 of asphalt dispersions of mineral pow-  
 ders, 172-178, 221-222

- Plastic flow, causes of, 116, 128-131, 175-176  
 coefficient of, 157  
 of concentrated pastes, 222-223  
 definition of, 149, 157, 173-174  
 of dispersions, 156, 176-182, 208-223, 231-237  
 equations for, 152, 176-182  
 measurement with rotational viscometer, 162-182  
 in mill operation, 266-267, 288-290, 296-298, 318-321, 325, 328, 337, 344-346  
 of paints, 208-216  
 of pigment dispersions, 176-182  
 of plastics, 222  
 of printing inks, 216-221  
 of rubber compositions, 222  
 and thixotropic flow, 189-190  
 and yield value, 174-176  
 Plastic mixing, 268, 271-275  
 Plastics, rheological properties of, 222  
 Plasticity, definition of, 174; *see also* Plastic flow  
 Plastometer, 222  
 Polar-non-polar molecule, definition of, 225  
 Polishing, surface changes in, 122, 259  
 Polymers, changes during grinding, 260, 301  
 Polymolecular films, 94-95, 123, 257  
 Polymorphism of pigments, 27  
 Polystyrene, depolymerization during grinding, 260  
 Polyvinyl alcohol as a protective colloid, 247  
 Ponderomotive effects in dispersions, 127  
 Porcelain balls for grinding, 307-308  
 Powdered pigment dispersions, 303  
 Power equations in viscometry, 168  
 Pressure, roll, 297-298  
 Pressure-displacement cell, 86-87  
 Printing inks, 133, 216-221  
 flocculation of pigments in, 134  
 lithographic, treated pigment for, 252  
 moisture-set, treated pigment for, 245  
 requirements for, 216  
 rheological properties of, 216-221  
 tack of, 219-221  
 types of, 217  
 viscosity of, 217-219
- Printing processes, 217  
 Protective colloids, 136, 203, 226-228, 230, 247-251  
 Proteins, changes in structure during grinding, 260-261  
 as protective colloids, 248, 251  
 Pseudoplastic flow, 153-154, 157-158, 190-194, 289  
 characteristics of, 153, 190-192  
 of cuprammonium sols of cellulose, 192  
 definition of, 151, 153-154, 190, 192  
 equations for, 167-168  
 examples of, 154, 192-193  
 of methyl cellulose sols, 192-193  
 rate of shear in, 192  
 of starch pastes, 192-193  
 and structural viscosity, 190
- Quartz, changes in crystal structure during grinding, 260  
 Quartz balls for grinding, 308  
 Quartz suspensions, thixotropy of, 189  
 Quasi-viscous flow, 192  
 Quaternary ammonium compounds as surface-active agents, 245-247  
 Quicksand, 203
- Rate of shear, 149-154  
 and dilatant flow, 194-195  
 limiting, 208  
 in measurements on plastics, 221  
 and pseudoplastic flow, 192-194  
 in roll mill, 286, 289  
 in rotational cylindrical viscometer, 165-166  
 and thixotropic breakdown, 152-153, 184-188
- Red lake C, particle size of, 59  
 in roll-mill dispersion, 293  
 Resinates, metallic, as dispersing agents, 241-242  
 Rheology, definition of, 147; *see also* Flow, Viscosity  
 Rheological measurements, 147-223  
 Rheopexy, 189  
 Rhodamine toner, particle size of, 59  
 Rittinger's law, 259  
 Roll pressure, 297-298  
 Roll mill(s), 279-303  
 action of, 285-290  
 breakdown of aggregates by, 290, 292

- Roll mill(s), clearance between rolls, 267, 286-287, 296  
 compaction of powders by, 292  
 comparison of three- and five-roll types, 291-292  
 construction of, 283-284  
 contamination from, 291, 295-296  
 dehydration of dispersions, 301, 303, 353  
 five-roll type, 284-285, 291-292  
 history of, 279-281  
 knife, take-off, 295  
 output of, 287-291  
 pigment-vehicle ratios for, 292-293, 301  
 single-roll, 281-283  
 sizes of, 284-285, 296-297  
 speed ratios of rolls, 290-291, 297, 299  
 three-roll type, 280-281, 283-284  
 two-roll type, 280-281, 296-297  
 types of, 279-285, 296-297  
 uni-roll, 281-283
- Rotational viscometer, 159-173; *see also* Viscometer, cylindrical rotational
- Roughness factor, 16
- Rubber, carbon-black aggregates in, 53-54  
 mill, 296-303  
 processing of, 298-299  
 test procedures for, 298-299
- Rubbone, 299
- Rugosity, 15
- Salicylic acid as a deflocculating agent, 253
- Saponin as a protective colloid, 248
- Sedimentation of dispersed particles, 109-113, 132-133, 141-142, 230-231, 253  
 and adsorption, 231  
 centrifugal, 39-41  
 control of rate of, 132-133  
 effect of particle shape on, 38-39  
 gravitational, 36-38, 230-231  
 and heat of vaporization of suspending liquid, 112  
 for particle-size measurement, 36-41  
 and Stokes' law assumptions, 35-36, 38-39
- Seeding, 263, 363
- Sequestering of ions, 253
- Settling of dispersed pigments, 109-113, 132-133, 138-143, 230-231, 253; *see also* Sedimentation
- Shearing during dispersion, 259, 266, 268, 279, 282-290, 296, 333-337, 342-344
- Sieves, standard, 17
- Sieving, 17-18
- Silica, heat of immersion data for, 98-100  
 in asphalt dispersions, 178
- Silicones in pigment processing, 254
- Size-distribution curves, 7-8, 14, 68  
 carbon black, 65  
 chrome yellow, 14  
 lampblack, 65  
 titanium dioxide, 68
- Skewness of size-distribution curves, 7-8, 13
- Slate in asphalt dispersions, 178
- Slipping of balls and pebbles during mill operation, 309, 311-312
- Smokes, 106
- Soaps, as dispersing agents, 244, 302  
 as flattening agents, 243  
 as flushing agents, 356-358  
 as leafing agents, 244  
 in pigment processing, 239-244, 356-358  
 for prevention of hard settling, 133
- Soft-grinding pigments, 6, 135, 224, 247
- Solid-liquid interface, 77, 79-103
- Solids, dry grinding of, 258-261  
 surface energy of, 77-79
- Solubilization, 135-138
- Specific sedimentation volume, 109
- Specific surface, 12, 15, 30-35; *see also* Particle size  
 by adsorption, 30-35  
 of carbon black, 65-66  
 of diatomaceous earth, 61  
 by permeability method, 43  
 of pigments, 56-59  
 of titanium dioxide, 59-60  
 of ultramarine blue, 63
- Sphericity, 16
- Spreading coefficient, 75-77  
 liquid-liquid, 75-77  
 and sedimentation volume, 110-111  
 solid-liquid, 77, 101-102
- Spreading of liquids on solids, 91-97
- Spreading pressure, 88, 90-91

- Stability of emulsions, 119  
 Stability of suspensions, 119-120  
 Stannic oxide, heat of immersion data, 98-100  
 Starch, depolymerization during grinding, 260  
 Starch pastes, pseudoplastic flow of, 190-194  
 Starch suspensions, dilatant flow of, 194-205  
 Stearic acid as a leafing agent, 242  
 Steel balls for grinding, 308  
 Stokes' law, 35-36, 109  
 Stone mill, 329-337  
   action of, 333-337  
   and breakdown of aggregates, 334  
   clearance between running stones, 335-336  
   construction of, 329-332  
   dimensions of dressed stone, 332  
   history of, 329  
   output of, 333-337  
   speed of, 332  
   and viscosity of dispersion, 337  
   wear of, 335  
 Stormer viscometer, modification of, 160-162  
 Structural viscosity, 190  
 Sulfonates as dispersing agents, 232-237, 358  
 Sulfosuccinic esters as surface-active agents, 231-236  
 Supercentrifuge, 40  
 Supersonic radiation, *see* Ultrasonic radiation  
 Surface-active agents, 224-257, 356-358  
   classification of, 226-227  
   and coating of particles, 229, 241  
   and comminution, 237-239, 263-264  
   definition of, 225  
   deflocculating action of, 131, 137, 227-230  
   in dyeing, 45, 47  
   and efficiency of mill operation, 237-239, 289, 302, 328, 345  
   and electrophoresis, 127  
   in flushing process, 356-358  
   methods for addition to dispersions, 239-240  
   in pigment dispersion, summary, 255-257  
 Surface-active agents, in pigment manufacture, 239-257  
   quantity required for monomolecular coating, 228-229  
   and solubilization, 135-138  
   theories for action of, 131, 137, 227-230  
 Surface energy, 74-79, 94-95, 97-103  
 Surface forces, 120-124  
 Surface roughness, 15  
 Surface, specific, 12, 15; *see also* Specific surface  
 Surface tension, 74-75, 227  
   and adhesion tension, 86  
   calculated from heat of sublimation, 79  
   of glass, 79  
   of liquids, 74  
   measurement of, 74-75, 82  
   of metals, 79  
   of solids, 77-79  
   of waxes, 79  
 Suspensions in air, 105-106  
 Tack, printing ink, 219-221  
   relation to viscosity, 220  
 Take-off knife on roll mill, 295  
 Tall oil in pigment processing, 244  
 Tannin as a dispersing agent, 230, 250  
 Temperature effects during dispersion, 261-262, 303, 320-322, 351-353, 362  
 Terpene derivatives as deflocculating agents, 254  
 Texture of dispersions, 50-54, 361; *see also* Aggregate  
 Thixotropic breakdown of dispersions, 152-153, 184-188  
   coefficient of, 154, 188  
   measurement of, 183-188  
   by ultrasonic radiation, 265  
 Thixotropic flow, 152-153, 182-190  
   of concentrated pastes, 222-223  
   and dilatant flow, 203  
   and flocculation, 188-190, 193, 203  
   measurement of, 152-153, 173, 182-190  
   mechanism of, 189-190  
   of oils, 208  
   of paints, 210-211, 215  
   pigment for, 252  
   of rubber, 221-222

- Thixotropic flow, time factor in, 188, 190
- Thixotropy, 152-153, 182-190  
definition of, 182-183
- Tinting strength, 69  
effect of dispersing agents on, 237-238  
and flooding, 138-141  
of flushed colors, 359-361  
and hiding power, 69  
method for particle-size measurement, 47-48
- Titanium dioxide, dispersions, flow of, 179-180  
dispersion with surface-active agents, 236  
energy of adhesion data for, 100, 102  
heat of immersion data for, 98-101  
particle size of, 40, 56, 59-60, 68  
roll-mill dispersion of, 293, 301  
sedimentation of, 40-41  
specific surface of, 59
- Toluidine toner, particle size of, 59, 67  
properties of flushed, 360, 362  
roll-mill dispersion of, 293
- Turbidimetry, method for particle-size measurement, 48-50
- Typographic printing, 217
- Tube mill, 305
- Ultimate working unit, definition of, 7, 266
- Ultracentrifuge, 41
- Ultramarine blue, dispersion with colloid mill, 344  
dispersion with surface-active agents, 232  
thixotropic dispersion of, 187  
water-repellent, 244
- Ultramicroscopy, 23-24
- Ultrasonic radiation, 26, 264-266
- Ultraviolet reflectance of paints, effect of entrained air on, 69-70
- Vehicles for flushed colors, 355-356
- Velocity gradient, *see* Rate of shear
- Vermilion, English, particle size of, 57
- Victoria blue phosphotungstic acid lake, particle size of, 59
- Visco-elastic deformation, 221-222
- Viscometer(s), calibration with standard liquids, 166-167, 206  
capillary, 159
- Viscometer(s), Couette, 159  
cylindrical rotational, 150-151, 159  
accuracy of, 171-172  
advantages of, 148, 159  
application of, 173, 168-211, 231-237  
basic factor in operation of, 162-168  
end-effect correction for, 163-165  
equations for, 162-168, 188  
precision of, 172-173  
rate of shear in, 165-166  
torque in, 162-163  
falling ball, 159  
inkometer, 220-221  
MacMichael, 160  
parallel plate, 219-220  
Stormer, 160-162  
tackmeter, 219-220
- Viscosity, 148-159  
apparent, definition of, 157-158  
of asphalt compositions, 177-178, 222  
calculation of, 148-154, 162-168  
coefficient of, 149, 157  
definitions, 149-158  
of dispersions, 173-205, 231-240  
and flooding of pigments, 139-144  
inferred from oil-absorption data, 278  
of lacquers, 211  
limits, for operation of mills, 267  
and mill operation, 266-267, 288-290, 296-298, 318-321, 325, 328, 337, 344-346  
of oils, 206-208  
of paints, 209-211  
plastic, definition of, 157; *see also*  
Plastic flow  
during shearing, 297-298  
of printing inks, 216-221  
of rubber compounds, 221-222  
standards, 206-208  
structural, 190  
units of measurement, 154
- Voids in ball charge, 314-315
- Vulcanization of rubber compounds during milling, 299
- van der Waals' forces, 120-124
- Wagner turbidimeter, 49
- Water, adsorbed on powdered solids, 33-34, 95-97  
in carbon-black dispersion, 262

- Water, dispersion of pigments in, 243, 249-253  
floculating effect of, 111-113, 128-135, 231-237, 250, 363  
removal, from dispersions, 301, 351-353, 358-359
- Water-dispersible pigments, 248, 250
- Waxes in pigment processing, 253
- Wear of grinding media in ball and pebble mills, 322-325
- Wear of stone mill, 335
- Wedge-grit method for estimation of aggregate size, 51
- Wettability, 91, 93, 231
- Wetting, definition of, 73
- White lead, flow of dispersions of, 179-180  
flushing of, 348, 350-351  
particle size of, 56, 60  
in roll-mill dispersion, 293
- Whiting, particle size of, 56
- Work of adhesion, 75-76, 81, 90, 101-102
- Work of cohesion, 75
- X-ray diffraction method for particle-size measurement, 46-47
- Yield value, 152-157, 173-182  
alternative terms for, 152
- Yield value, change during dispersion, 232-236, 240, 319-322  
definitions of, 152-154, 174-175  
of dispersions, 128-130, 156, 180-181, 222-223, 231-240, 318, 344, 363  
equations for, 152, 163, 180-182  
and flocculation, 116, 128-131, 189-190  
and flooding, 140-141  
measurement of, 163, 172-176, 180  
and mill operation, 237-238, 289, 320, 328, 345  
of paints, 209-211  
of printing inks, 218-219
- Zeta potential, 124-126
- Zinc metal powder, energy of adhesion data for, 102
- Zinc naphthenate as a dispersing agent, 232-237, 240, 255-256
- Zinc oxide, energy of adhesion data for, 102  
flow of dispersions of, 180-182  
heat of immersion data for, 98  
particle size of, 49, 56, 60, 68, 182  
in roll-mill dispersion, 293, 301-302
- Zinc yellow, roll-mill dispersion of, 293
- Zirconium oxide grinding balls, 308



