The Preparation of Organosols

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THE PREPARATION OF ORGANOSOLS

by

Wilfrid Francis White

A Thesis submitted to the Faculty of the Graduate School of Loyola University in partial fulfilment of the requirements for the degree of Master of Science.

Loyola University
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1938
VITA

Born in Chicago, Illinois on February 4, 1913. Preparatory education at St. Mel High School, Chicago. Student at Loyola University 1930-31, 1931-32, 1932-33, and 1934-35. Bachelor of Science received in June, 1935. Graduate Assistant in Chemistry at Loyola University from September 1936 to the present time.
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I. Introduction

There are numerous references in textbooks and in the literature concerning the preparation of colloidal dispersions of solid substances in organic liquids. For example, Holmes\(^1\) gives directions for the preparation of sols of arsenic trisulfide in nitrobenzene, copper sulfide in alcohol, and copper chloride in benzene. In addition, there are quite a few common commercial products composed of organic liquids carrying solid material in a state of subdivision within, or at least near, the colloidal range. Examples are paints, enamels, inks, and various pharmaceutical preparations. Hence, at first sight it would appear that organosols are quite common and that the methods of preparation are quite satisfactory. In the experience of the author, however, the stable organosols of record at the beginning of the work described in this paper were either dilute suspensions of very fine particles or very concentrated suspensions of large particles in viscous liquids. When the methods used to prepare dilute sols were modified in an attempt to make more concentrated ones, the products were not stable. Furthermore, the dilution of the concentrated sols resulted in precipitation of the solid phase. In an attempt to discover the principles governing the preparation of stable organosols of all concentrations

the author began the series of experiments described in this paper.

II. General Theory

The particles of a solid substance suspended in a liquid are subject to the following forces:

1. Those tending to keep the particles apart and evenly distributed throughout the liquid:
   A. The kinetic energy of the solid particles. This factor is the same for all particles at the same temperature, regardless of size. The velocity due to this energy varies as the square root of the reciprocal of the mass.
   B. The attraction between the solid particles and the liquid.

2. Those tending to bring the particles together and to cause separation into two phases:
   A. The attraction between the particles of the solvent.
   B. The attraction between the particles of the solute.
   C. The buoyancy of the solute due to displacement of the solvent.
   D. The force of gravity.

If 1 (B) is greater than the sum of 2 (A) and 2 (B) the substance will disintegrate spontaneously when placed in the
liquid and the particles will form a stable dispersion if the sum of \(2 \times C\) and \(2 \times D\) is less than \(1 \times A\). This is true in the formation of ordinary solutions and of the so-called hydrophilic colloids. If the solid substance does not disintegrate spontaneously, a homogeneous mixture can still be formed by overcoming \(2 \times B\) by mechanical grinding and then surrounding the particles with a third substance for which the resultant of \(1 \times B\), \(2 \times A\), and \(2 \times B\) is positive. The mixture will then remain homogeneous if \(1 \times A\) is greater than the sum of \(2 \times C\) and \(2 \times D\). The same result can be attained by building up the particles of the solid in the dispersion medium in the presence of the protective agent. The protection can be furnished either by a group of molecules or by a layer of adsorbed ions. Such is the picture in the case of stable hydrophobic colloids.

The solubility or dispersibility of a substance is a rough measure of the resultant of \(1 \times B\), \(2 \times A\), and \(2 \times B\). The vapor pressure of the solid and liquid, respectively, are indications of the magnitudes of \(2 \times B\) and \(2 \times A\). When the solid is insoluble in the liquid, \(1 \times B\) can be measured by determining the "wetting power" of the liquid for the solid.

When the molecules or ions of the solid are small the factor \(1 \times A\) is very large. Hence gravity has little or no measurable effect on the particles of such a solute and al-
most complete homogeneity is obtained. However, as the size
of the molecules is increased the factor 1 (A) diminishes
until it finally reaches the sum of 2 (C) and 2 (D). When
the factors promoting homogeneity dwindle to a point near the
value of the factors tending to cause separation into two
phases, it is possible to supply the difference by centri­
fuging. In the case of some substances (e.g., shellac) the
particles are so large that homogeneity is never attained,
despite the fact that the solid substance disintegrates spont­
aneously.

If it is assumed that the particles in a dispersion are
prevented from agglomerating or forming larger particles,
it is a simple matter to calculate the maximum size which will
remain in suspension indefinitely. Sufficiently small par­
ticles will have a motion due to kinetic energy large enough
to offset the attraction of gravity.

A spherical particle of radius \( a \) and density \( \rho_1 \) suspended
in a liquid medium of density \( \rho_2 \) will be acted upon by a
gravitational force \( G \), such that

\[
G = \frac{4}{3}\pi a^3 (\rho_1 - \rho_2) g \quad \text{dynes} \quad (1)
\]

If such a particle is moving in the liquid with a velocity
\( v \), Stoke's law gives for the force of liquid friction

\[
F = 6\pi n a v \quad (2)
\]
where $n$ is the viscosity of the solution. Since $G$ is constant for given conditions, while $F$ varies with the velocity of the particle, the sphere on falling will attain a constant limiting velocity $V_o$, such that

$$V_o = \frac{2g}{9n} \frac{(d_1 - d_2)}{a^2}$$  \hspace{1cm} (3)

Hence, in one second, the particle will fall $V_o$ units of distance.

The theoretical formula for the motion due to kinetic energy of large particles (Brownian movement) is

$$D^2 = \frac{RTt}{N \frac{3\pi n a}{}}$$  \hspace{1cm} (4)

where $D$ is the displacement parallel to any direction in $t$ seconds, $R$ is the gas constant, $N$ is Avogadro's number, and the other symbols have the same significance as above.

Hence in one second the particle will travel $\sqrt{\frac{RT}{N \frac{3\pi n a}{}}}$ units of distance in a vertical direction. Equating the two opposing distances, we find that for ordinary temperatures the critical radius is about $9 \times 10^{-5}$ cm. for $(d_1 - d_2) = 1$, and $4 \times 10^{-5}$ cm. for $(d_1 - d_2) = 10$. Hence, for all ordinary solids, permanent suspensions in organic liquids are theoretically possible if the particles are less than 0.5 microns in radius and are prevented from growing or agglomerating.\footnote{E.F. Burton in Alexander's "Colloid Chemistry", vol. 1} However, when the particle size ap-
proaches the maximum, the concentration will vary considerably with the depth, approaching zero at the surface of the liquid.

Perrin, while examining dispersions of mastic and gamboge in water, observed this concentration gradient and derived an equation which agreed very well with his data. He reasoned as follows: a particle suspended in a liquid is acted upon by the force of gravity. At the same time its Brownian movement that is, its tendency to diffuse, tries to balance this tendency to fall. The final result is that the particles distribute themselves in such a way that the concentration at the bottom is quite large, that at the top very small, and intermediate values occur between. This phenomenon has been detected even in true solutions where the depth is great, as in the atmosphere. By equating the tendency to diffuse as expressed by the osmotic pressure against the gravitational force, Perrin obtained an equation which showed the variation of concentration with the height in dilute sols. However, because of the fact that he had based his derivation on the osmotic pressure relations in dilute solutions, Perrin was not able to predict accurately the behavior of concentrated sys-

1 Kruyt (van Klooster), *op. cit.*, p. 148

Chemical Catalog Company, New York, 1926, p. 166

tems. Although there is general agreement that Perrin's equation needs revision, there is considerable difference of opinion concerning the correct interpretation of the deviations from his theory. Regardless, however, of the exact nature of the function, all theoretical considerations point to a considerable variation of concentration with the depth, especially in sols whose particles are near the size limit.

III. Discussion of Results

With these facts in mind and in the light of the experimental results reported in a later section of this paper, the preparation of organosols can be discussed as follows:

A. Preparation of Organophobic Sols

Since $1 \ (B) > 2 (A) + 2 \ (B)$, no difficulties are encountered in preparing these sols. Mere contact between solid and liquid results in spontaneous dispersion of the solute. The substances of this group are very important as protective agents which can be used in the preparation of the more difficult organophobic dispersions. Examples of substances which form organophilic sols are: natural and artificial resins, rubber, cellulose ethers and esters.

B. Preparation of Organophobic Sols

Here the situation is considerably different. There is no
appreciable attraction between internal and external phases to balance the individual cohesive forces. Hence, at the outset, a substance must be found which, by its attraction for both phases, will provide a link between them. This substance must be such that its particles completely surround the solid particle in order to prevent contact between particles and subsequent flocculation. In addition, the dispersed phase must be smaller than the limiting value as calculated above.

In the actual preparation of organophobic sols one has the usual alternatives of building up simple molecules to colloidal size or of tearing coarse particles down to the proper dimensions. In all cases the operation must take place in such a way that the protective agent can be introduced while the particles are below the maximum allowable size.

1. Condensation Methods

Perhaps the simplest method of building up molecular aggregates is by diluting a solution of the solid in one liquid by adding a second liquid in which the solid is insoluble, by this means a wide variety of organosols can be prepared. The method is most suitable for organic solids because a suitable combination of liquids can almost always be found.
This method, however, has the limitation that a mixed solvent always results.

Ordinary alcohol (95%), due both to the water content and to its own relatively high dielectric constant, dissolves considerable quantities of a wide range of electrolytes and permits the usual ionic reactions. By using this method a large number of insoluble substances can be prepared in a finely divided state. As in aqueous solutions, the particle size of the precipitate depends on the nature of the substance, the temperature, concentration, rate of mixing, and type of stirring.\(^1\) By proper regulation of these factors permanent alcoholic suspensions of various concentrations can be prepared when suitable protection is provided. The resulting sols are, however, always contaminated by the water and the other products of the reaction.

Sols prepared in alcohol by double decomposition reactions or by other methods can be purified as well as stabilized by taking advantage of the remarkable properties of ethyl cellulose. This substance, only recently available commercially, is the best protective agent the author has discovered to date. It is soluble in all of the common organic liquids with the exception of aliphatic hydrocarbons and it can be made

\(^1\)Kolthoff and Sandell: "Textbook of Quantitative Inorganic Analysis", Macmillan, New York, 1936, p. 93
soluble in them by adding a small amount of the ethyl ether of diethylene glycol. The presence of 5 percent water in alcohol does not seriously affect the solubility of ethyl cellulose. Hence, by mixing alcoholic solutions of the proper electrolytes containing ethyl cellulose, a wide variety of insoluble solids can be prepared in a colloidal state. Dilution with water will then coagulate the ethyl cellulose and make it possible to remove both protective agent and colloidal particles. The coagulum can be further purified by washing it with water (dialysis) and drying. The resulting mass can then be redispersed in almost any simple organic liquid or combination thereof. When one of the ions necessary for a reaction can be obtained in alcoholic solution and the other cannot, the method is still applicable if a solvent can be found for the second ion. If it dissolves in water, an alcoholic solution of the first ion and ethyl cellulose can be poured into an aqueous solution of the second ion. In this case precipitation and coagulation of the sol are accomplished in one operation.

The concentration and particle size of sols prepared by the condensation method are evidently limited by the solubility of the substances necessary to produce the desired solid. There are relatively few cases in which sols
containing more than a few hundredths of a gram of solid per cubic centimeter of solution can be prepared with particles below the maximum size. The particle size is smaller the better the mixing. With solutions of ethyl cellulose, apparently because of the viscosity and consequent slow rate of diffusion, it is almost impossible to mix quickly. For this reason, the particles in concentrated solutions grow to a size at which permanency is impossible. This is also the case when a gas is used to supply one of the ions necessary for the reaction, as in the precipitation of sulfides with hydrogen sulfide, chlorides with hydrogen chloride, etc. For the preparation of dilute sols, however, the condensation method is much simpler because it does not require elaborate apparatus.

In a few cases ionic reactions can be carried on in liquids other than alcohol. For example, arsenic and antimony sulfide sols can be prepared in xylene and nitrobenzene by passing hydrogen sulfide into solutions of the chlorides of those elements. In these cases rubber can be used as the protective agent.

2. Dispersion Methods

In cases where an inorganic solid cannot be formed in an organic liquid because of the insolubility of the reactants, it is necessary to use dispersion methods. In fact,
dispersion methods are almost universally applicable and can be used to prepare sols of any concentration up to a definite limit which is fixed by the solubility of the protective agent and by its power to coat the solid in question. Dispersion is accomplished by the use of suitable mechanisms, of which there are two types available: the differential roll mill and the colloid mill. Although these machines are often called "grinders", no appreciable reduction in particle size is accomplished. \(^1\) This is due to the practical impossibility of constructing a machine having plates or rolls which can be adjusted to move with a uniform gap of less than ten or twenty microns between them. Even when the plates can be adjusted to this minimum distance, as in the colloid mill, the machine cannot be used to grind hard substances because of the great wear involved. At best these machines can merely disperse homogeneously the primary particles of a solid. Hence the success of dispersion methods depends on the possibility of preparing the solid in the necessary size range by other methods. Fortunately this is possible in nearly every case. In fact, the only important commercial pigment which has defied all efforts to reduce it to colloidal dimensions is ultramarine blue.

\(^1\) Travis: "Mechanochemistry and the Colloid Mill", Chemical Catalog Company, New York, 1928, p. 159
Pigment manufacturers, especially, have investigated the factors governing particle size and are able to produce, within limits, any size desired. However, the opacity (and hence the covering power) of solids reaches a maximum at a definite particle size and it is this figure at which pigment makers aim. Opacity increases with subdivision down to about one-tenth micron and then drops off rapidly. This rapid decline is undoubtedly due to the fact that the particle becomes smaller than the wave length of light and hence is not as effective in impeding its progress, diffracting the light rather than absorbing it. For this reason pigment makers find it most economical to keep the size of their pigments below one micron and above one-tenth micron. How well they are able to do this is shown by the following table of the average particle size of commercial pigments:

Table I

Average Size of Commercial Pigments

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Radius (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon black</td>
<td>0.1</td>
</tr>
<tr>
<td>Lampblack</td>
<td>0.25-0.35</td>
</tr>
<tr>
<td>Lithopone</td>
<td>0.4</td>
</tr>
<tr>
<td>White lead</td>
<td>0.6-1.2</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>0.12-0.60</td>
</tr>
<tr>
<td>Titanium oxide</td>
<td>0.25-0.40</td>
</tr>
</tbody>
</table>
This means that permanent suspensions can be prepared if the dry pigment can be dispersed into individual particles in the presence of a suitable protective colloid.

As mentioned above, there are two types of machine in which colloidal dispersions can be made: the differential roll mill and the colloid mill. The former is designed to operate on a plastic mass and the latter on a thin fluid. Hence the colloid mill is suitable for dilute sols and the differential mill for concentrated ones. On the roll mill pigments are usually dispersed in the protective agent itself and the resulting mass is then dissolved in suitable solvents.

Although there are several kinds of colloid mill on the market, they all operate on the same general principle. The dispersion is due to hydraulic forces acting upon a thin film of fluid, which is forced between revolving plates. The principles involved are apparently an adhesion of certain portions of the liquid to each plate, which causes a tearing action on the particles in between.\(^1\) The plates are adjustable, usually with a minimum gap of about ten mi-


\(^2\)Travis: op. cit., p. 149

rons. Because of the terrific speeds involved (with proper design, about two miles per minute peripheral velocity) it is impossible to process systems containing particles whose individual diameters approach the gap distance. Such particles, even though relatively soft, destroy the blades in short order. If, however, the solid material is in the form of loosely packed aggregates of very small particles, the solid is deflocculated and dispersed by the severe shearing action. Even with very fine particles, however, considerable wear is suffered by the plates and they must be replaced from time to time.¹

Hence, in preparing dispersions with the colloid mill, the solid material in a very fine form must be mixed with a liquid and a protective agent and fed to the machine in a fluid condition. This requirement limits the concentration to about 15 or 20 percent solids. Also, because of the great heat developed (despite cooling systems), materials which are heat sensitive cannot be used. This consideration practically eliminates the use of nitro-cellulose as a protective agent, because of its tendency to decompose explosively at about 150°C. For this reason also, low boiling liquids cannot be used. If, however, ethyl cellulose is used as the protective agent the sol can be precipitated and redispersed

¹Travis, op. cit., p. 154
in the volatile solvent.

The differential roll mill is entirely different in design. As the name indicates, the machine is composed of two or more closely spaced rolls which revolve in opposite directions at different speeds. The rolls are made of substances which create considerable friction and are arranged so that they press against one another. The pigment is mixed with the protective agent and small amounts of suitable liquids and placed on the rolls in such a way that the mass is kneaded and sheared by the action of the rolls. In this type of machine the amount of dispersion depends largely on the nature of the grinding medium and in some cases the degree of dispersion is as good as that obtained by use of the colloid mill, despite the much smaller forces involved.

Many different grinding media have been used with the roll mill. Linseed oil is often used alone in the manufacture of printer's ink and paint bases. For other purposes natural or artificial resins are used with linseed oil or some other liquid. In mills provided with an internal heating system resins are sometimes used alone. In all of these cases, however, the product, while homogeneous as it leaves the mill, slowly separates into two phases on

1 Literature distributed by J.H. Day Co., Cincinnati, Ohio
standing. The reason, of course, is that the substances mentioned do not provide adequate protection for the particles. Microscopic examination of the precipitated pigment reveals that the particles have re-agglomerated.

The production of stable organosols thus depends on the use of an adequate protective agent as grinding medium or a constituent thereof. Up to the present time the only successful media which the author has discovered have been the cellulose compounds. These substances when used alone or with small amounts of plasticizer and when properly handled always give a product which remains homogeneous when diluted with any liquid in which the protective agent is soluble. In the case of ethylcellulose, this means that stable sols can be prepared in almost any organic liquid or mixture thereof.

In dispersing pigments in the cellulose compounds on the roll mill it is found that there is a definite limit to the amount of pigment which can be dispersed in a fixed amount of grinding medium.\(^1\) Practically, this limit corresponds to the first appearance of shortness in the bead when grinding. The limit varies with the pigment and seems to be almost independent of the cellulose compound which is used as the

\(^1\)Bulletin: "Ethyl Cellulose as a Grinding Medium", Hercules Powder Company, Wilmington, Delaware
grinding medium. Rough calculation shows that the amount of medium is proportional to the total area of the pigment particles. The following tables show these relations:

Table II

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon black</td>
<td>55/45</td>
</tr>
<tr>
<td>Iron blue</td>
<td>60/50</td>
</tr>
<tr>
<td>Chrome yellow</td>
<td>85/15</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>85/15</td>
</tr>
</tbody>
</table>

Table III

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Density</th>
<th>Diam. of particles</th>
<th>Particles per gram</th>
<th>Area/wt. Medium</th>
<th>Area/wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lampblack</td>
<td>2</td>
<td>0.1</td>
<td>(3 \times 10^{15})</td>
<td>(3 \times 10^5)</td>
<td>.82</td>
</tr>
<tr>
<td>Iron blue</td>
<td>3</td>
<td>0.15</td>
<td>(2 \times 10^{14})</td>
<td>(1.6 \times 10^5)</td>
<td>.50</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5.5</td>
<td>0.2</td>
<td>(5 \times 10^{13})</td>
<td>(0.6 \times 10^5)</td>
<td>.18</td>
</tr>
</tbody>
</table>

If an attempt is made to grind more than the limiting amount by diluting the cellulose grinding medium with a suitable solvent, it is found that the product does not yield completely stable sols. Apparently the excess pigment has not received a protective coating and hence agglomerates and settles out. It seems, therefore, that dispersions of pigments on the roll mill amounts to coating
the pigment particles with a uniform layer of cellulosic material, which then acts as a protective agent in solution. The approximate value of the area protected by one gram of ethyl cellulose has been checked roughly several times by preparing antimony sulfide sols of various concentrations by the condensation method in the presence of fixed amounts of ethyl cellulose and observing the concentration at which sedimentation first appears.

In review, the following conclusions have been reached:

1. Several methods are available for preparing stable organosols by suspending insoluble solid particles of the proper size in organic liquids and protecting them from agglomeration. This result had been predicted on theoretical grounds and the limit of particle size had been calculated.

2. The only protective agents effective near and up to the theoretical maximum particle size were the cellulose compounds. It should be stressed, however, that the work described in this paper was centered upon the larger size particles and that no special effort was made to stabilize particles in the lower colloidal range. At the same time it must be mentioned that stable sulfide sols have been prepared by condensation methods in xylene, using rubber
as the protective agent. However, these sols have not been investigated from the standpoint of possible compound formation between sulfide and rubber. All attempts to prepare sols by the dispersion method, using rubber as the protective agent, have failed.

IV. Cellulose Compounds as Protective Agents

Thus there remains the problem of explaining the unique effectiveness of cellulose compounds as protective agents. Now X-ray methods have revealed that cellulose itself is made up of chains of some eighty to one-hundred units of hexosan dimensions \( \text{C}_6\text{H}_{10}\text{O}_5 \), whose length is about ten Angstrom units. These chains are further joined in large bundles, the entire mass forming a web-like structure. Other studies have revealed that this peculiar arrangement is not destroyed in the formation of compounds of cellulose. It is also quite evident from the viscosity of solutions of these compounds that the forces which bind the cellulose chains in bundles are not completely neutralized in the process of solution. When cellulose compounds disperse they seem to swell by the action of the solvent until the fibers are separated and elongated to such an extent that they no longer possess the rigidity of solids, although they do not exhibit the complete fluidity of normal solutions of the same
Concentration. Hence such solutions can probably be regarded as made up of webs of loosely bound strands at least $10^{-5}$ cm in length, and perhaps longer. The mere presence of solvent molecules between the fibers must be regarded as causing a partial neutralization of the cohesive forces of the cellulose compound. If, now, a solid particle is interposed either by growing it from simple ions (which, because of their size can diffuse at will) or by mechanically forcing it into the web, the solvent is displaced and the web is caused to contract about the particle not by its attraction for the particle, but by its attraction for itself. This is in agreement with the observed fact that the protective action of the cellulose compounds is independent of the nature of the dispersed medium. If the bond between the particle and the protective agent were due to adhesive forces it would seem likely that this action would be selective.

V. Experimental Work

The experimental work was divided into two parts:

A. Dispersion Methods

The experimental work on organosol preparation began with attempts to disperse commercial pigments in organic liquids by grinding in an agate mortar. All such attempts failed to produce stable sols, but considerable differences were ob-
served in the various liquids with regard to the time required for complete settling of the pigment after grinding. The pigments used were titanium dioxide (Titanox-A; Titanium Pigments Corp., New York) and lead chromate (Light Chrome Yellow, A. Daigger and Sons, Chicago). Both pigments were ground in ethyl alcohol, iso-propyl alcohol, iso-butyl alcohol, amyl alcohol; the monomethyl, ethyl and butyl ethers of ethylene glycol; the ethyl ether of diethylene glycol, triethanolamine, acetone, benzene, toluene, xylene, kerosene, aniline oil, cresylic acid, and oleic acid. Rough quantitative measurements were made of the time of settling and the results can be generalized by means of the following list. The classes of liquids are arranged with respect to the time required for complete sedimentation, the shortest times being at the top:

1. Hydrocarbons
2. Acids
3. Amines
4. Amine-alcohols
5. Alcohols
6. acetone
7. Glycol ethers

The same order was observed for both pigments.
The two pigments used in the grinding experiments were guaranteed by their manufacturers to possess a primary particle size of less than 0.5 micron in radius and hence were theoretically capable of forming stable sols, if completely dispersed and prevented from re-agglomerating. In order to test the ability of pure liquids to stabilize suspended solids, a sample was sent to the Manton-Gaulin Manufacturing Company of Everett, Massachusetts, to be dispersed in one of their colloid mills. The sample was made up of 60 grams of titanium dioxide pigment in one liter of the ethyl ether of ethylene glycol. Since this liquid was a member of the class which gave the best results in the sedimentation experiments it was considered the most likely to produce a stable sol. The sample was processed three times through a colloid mill and the pigment was reported by the chemists of the Manton-Gaulin Company to have been dispersed into its primary particles as it left the mill. Within twenty-four hours, however, the pigment had settled completely. Microscopic examination showed that re-agglomeration had taken place.

Next, a series of tests were made on commercial products composed of solid particles suspended in organic liquids. In all cases the history of the product was obtained from the manufacturer. The products were all very viscous dispersions
and the tests consisted of a dilution of the material with a liquid which was compatible with the vehicle involved, sedimentation tests, and microscopic examination of the material (if any) which remained in suspension and the material (if any) which precipitated. The microscope used was a Leitz instrument arranged with overhead illumination and was capable of resolving objects greater than one micron in diameter, but not of measuring particles near that size. Hence it seemed possible to determine whether or not the pigments were dispersed into their primary particles. All of the materials tested contained pigments at least some of whose particles must have been below the maximum size for stable sols. The results are tabulated below:

**Table IV**

Examination of Commercial Sols

<table>
<thead>
<tr>
<th>Material</th>
<th>Pigment</th>
<th>Vehicle</th>
<th>Grinding Mill</th>
<th>Sedimentation time</th>
<th>Microscopic Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paint base</td>
<td>Chrome Yellow</td>
<td>Linseed oil</td>
<td>Ball</td>
<td>10 minutes</td>
<td>Clumps</td>
</tr>
<tr>
<td>Enamel</td>
<td>TiO₂</td>
<td>Toluene, cellosolve resin, cotton</td>
<td>Ball</td>
<td>5 hours</td>
<td>Some small clumps</td>
</tr>
<tr>
<td>Ink base</td>
<td>Iron blue</td>
<td>Linseed, resin, Roll ethocel.</td>
<td></td>
<td>No clear solution</td>
<td>No particles visible</td>
</tr>
<tr>
<td>Printer's ink</td>
<td>Lamp-black</td>
<td>Linseed, Roll drier, resin</td>
<td></td>
<td>6 hours</td>
<td>Clumps</td>
</tr>
<tr>
<td>Material</td>
<td>Pigment</td>
<td>Vehicle</td>
<td>Grinding mill</td>
<td>Sedimentation time</td>
<td>Microscopic Results</td>
</tr>
<tr>
<td>-------------------</td>
<td>---------------</td>
<td>-------------</td>
<td>---------------</td>
<td>--------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>Aniline ink</td>
<td>TiO₂</td>
<td>Shellac alcohol</td>
<td>Roll</td>
<td>20 hours</td>
<td>Clumps</td>
</tr>
<tr>
<td>Special ink base</td>
<td>TiO₂</td>
<td>Ethyl cellulose</td>
<td>Roll</td>
<td>No clear solution</td>
<td>Single particles</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 months</td>
<td></td>
</tr>
<tr>
<td>Same</td>
<td>Chrome yellow</td>
<td>same</td>
<td>same</td>
<td>same</td>
<td>same</td>
</tr>
<tr>
<td>Same</td>
<td>Iron blue</td>
<td>same</td>
<td>same</td>
<td>same</td>
<td>No particles visible</td>
</tr>
<tr>
<td>Same</td>
<td>Lamp-black</td>
<td>same</td>
<td>same</td>
<td>same</td>
<td>same</td>
</tr>
</tbody>
</table>

Finally, to test the performance of the colloid mill, a solution of 50 grams of cethyl cellulose in one liter of a 50-50 mixture of the ethyl ether of ethylene glycol and toluene was mixed with 60 grams of titanium dioxide pigment and was sent to the Manton-Gaulin company to be processed in one of their mills. The product was found to be stable after two passages through the mill.

Hence it seemed that the most effective protective agents were the cellulose compounds and that the only mills which give stable sols are the colloid mill and the differential roll mill. These generalizations were confirmed in private correspondence from the R. B. H. Lacquer Base Company of Bound Brook, New Jersey; the Cook Paint Company of Detroit, Michigan; and the Hercules Powder Company of Wilmington.
Delaware to the author. The same companies also supplied much of the information included in the section in which methods for the preparation of organosols by dispersion methods are discussed.

B. Condensation Methods

A series of alcoholic solutions were made up with the following salts: antimony trichloride, arsenic trichloride, cadmium nitrate, cobalt chloride, copper acetate, nickel chloride, and silver nitrate. In each case one gram of the salt was added to 20 cubic centimeters of 95% alcohol. All of the salts dissolved completely. To each solution one gram of ethyl cellulose was added and in all cases a clear solution was obtained by shaking for several minutes. Dry hydrogen sulfide was passed into each solution rapidly and with constant agitation until no more gas was absorbed. The solutions were poured into separate portions of water and the precipitated masses of ethyl cellulose and sulfides were washed thoroughly with several portions of hot water. Each coagulum was then dried and divided into 5 equal portions which were dissolved respectively in alcohol, cellosolve, benzene, ethyl acetate, and chloroform. In all cases stable sols were produced. Stable sols of silver chloride in the same liquids were prepared by passing dry hydrogen chloride into a solution of silver nitrate containing ethyl cellulose,
precipitating, washing, drying, and dispersing as above.

The procedure was then varied somewhat by pouring a solution of one gram of barium thiocyanate and one gram of ethyl cellulose in twenty cubic centimeters of alcohol into an aqueous solution of sodium sulfate. The resulting coagulum was washed, dried, and dispersed as before. Stable sols of barium sulfate were obtained. This method was repeated, using a solution of lead acetate and ethyl cellulose in alcohol and an aqueous solution of potassium chromate. The resulting sols were again stable.

Several experiments were then made with solutions of varying ratios of ethyl cellulose to precipitated solid. It was found that there is a definite limit to the amount of solid which a given amount of ethyl cellulose will stabilize. When an insufficient amount of protective agent is present, coarse, unstable dispersions result. Microscopic examination of the precipitate reveals large clusters of particles as compared to the individuals of stable sols.

An attempt at a quantitative measurement of the stabilizing limit was made with arsenic trisulfide sols. A 5% solution of ethyl cellulose in alcohol was divided into twenty cubic centimeter portions and varying amounts of antimony trichloride were added to them. The amount of antimony trichloride was varied from 0.1 gram to 3 grams.
It was found that all sols containing more than about 1.4 grams of antimony trisulfide (calculated from the antimony trichloride added and assuming complete conversion) contained coarse aggregates. Since each sol contained one gram of ethyl cellulose, the minimum weight ratio of protective agent to suspended solid was about 0.7. Since the size of the particles was not known, however, the results were not regarded as quantitatively significant since the protective action is undoubtedly a surface phenomenon and the surface could not be determined in this experiment.
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