

EFFECT OF STRUCTURE OF DISPERSING AGENT  
ON EFFICIENCY OF WET GRINDING

by

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May 27, 1936

Professor George W. Swett  
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Cambridge, Massachusetts

Dear Sir:

I hereby submit a thesis entitled "The  
Effect of Structure of Dispersing Agent on  
Efficiency of Wet Grinding" as partial fulfill-  
ment of the requirements for the degree of  
Bachelor of Science.

Respectfully yours,

✓

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## TABLE OF CONTENTS

	Page
Summary	1
Introduction	3
Apparatus and Procedure	9
Results	12
Discussion of Results	13
Conclusion	15
Recommendations	16
Appendix	
Diagram of Apparatus	17
Literature References	18

## SUMMARY

The use of dispersing agents for producing dispersions of materials near or in the colloidal range is becoming very important in such industries as the rubber, ceramic, paint, ink, etc.

Very little is known about the action of these agents except that they are usually organic compounds with one or more water soluble groups on the main chain or ring. It is believed that the dispersing action is due to protection of the dispersed material because of adsorption of the dispersing agent on the surface of the particle.

It is the object of this investigation to determine the effect of the following on the dispersing action: Polarity of the molecule, various groups on the main chain or ring, molecular weight and surface tension.

The method used was to grind sulphur in a pebble mill with various organic compounds of known structure and to measure the relative specific surface of the dispersion produced by using a Klein turbidimeter. Lowering of surface tension was measured by the du Nouy tensimeter.

It was found that a long chained high molecular weight compound with a water soluble group on the main ring had the greatest dispersing action, that methyl and hydroxyl groups had little effect when added to the chain and that the amino

group added considerable to the dispersing action of the compound. It was also found that surface tension lowering did not aid dispersing action unless the dispersing agent was adsorbed.

## INTRODUCTION

The increased activity and the special properties of materials comminuted to a particle size near or in the colloidal range have resulted in the increased use of such materials in many industries, of which outstanding examples are the rubber, paint, ceramic and ink.

A common method used in reducing a substance to this particle size is wet grinding using water, as the dispersing medium.

It has been found that if grinding is carried out in water alone, the particles will reach a certain limiting size, depending upon the material being ground, after which the particles will stick together and form flocks. Further grinding will not reduce the particle size beyond this point.<sup>1</sup>

Wet grinding with the addition of water-soluble substances such as glucose, urea,<sup>3</sup> and lactose<sup>4</sup> has been found to aid the formation of dispersions of indigo, aniline blue, sepia, sulphur, selenium, etc.

It is the present practice to add "dispersing agents"<sup>5</sup> to the mixture of solid and water that is to be ground. The only information that could be found in the literature was that they generally were organic compounds of a chain or ring structure with one or more water soluble groups which usually were either a sulfonic or carboxylic acid.<sup>5</sup>

Most of the dispersing agents are capillary active substances (wetting agents) which aid grinding by thoroughly wetting the particles to be ground with the dispersing medium and displacing adsorbed air films which would interfere with the grinding by causing the particles to float on the dispersing medium.<sup>1</sup> The dispersing agents which are capillary active also aid grinding by preventing flocculation. To account for this we must consider the surface energy of the system.

Surface energy is a function of surface area and surface tension.<sup>5</sup> In a colloidal dispersion, the specific surface of the dispersed material is extremely large and therefore considerable surface energy is to be associated with colloidal systems.<sup>5</sup> Harkins<sup>6</sup> states that a colloidal system may be defined as one in which the surface energy is appreciable in comparison with the heat of fusion of the material present as the dispersed phase.

Since the energy of any system tends to approach a minimum, the surface energy acts to decrease the surface of the dispersed particles by causing them to stick together, thus bringing about flocculation,<sup>1</sup> and since surface energy is also a function of surface tension, a substance which reduces the surface tension of the system reduces the surface energy, thus decreasing flocculation.

A dispersing agent which is surface active, will



concentrate in the interface between the dispersed solid and the dispersing medium according to Gibb's Law of Surface Concentration.<sup>7</sup> Therefore, surrounding each particle is a concentrated layer of the dissolved dispersing agent which helps to prevent the surface of the particles from coming in direct contact with each other.

On account of the extremely large surface exposed when the particles are near or in the colloidal range, adsorption of the dispersing agent is an important factor in determining the stability of the dispersed material.

Let us consider the oriented wedge theory of emulsions<sup>8,9,10</sup> which holds that the emulsifying agent concentrated in the interface in a mono-molecular layer in such a way that the group which has an affinity for water will stick out into the water phase while the group which exerts an attraction for the oil is adsorbed on the surface or submerged in the organic liquid which is being emulsified.

By analogy we can picture the molecules of the dispersing agent with one end adsorbed on the surface of the particle and the other end projecting into the water forming an oriented layer of molecules around the particle.

Since most of the dispersing agents are salts either of sulfonic or carboxylic acids they must ionize to some extent. To extend the concept referred to in the above paragraph it is generally accepted that ions are adsorbed

by the particle. After the adsorption of the ions, the particles behave somewhat like the ion itself. It can be shown experimentally that if a direct current is passed through the solution, the particles will migrate to the anode if the adsorbed ion is negative and to the cathode if the adsorbed ion is positive.<sup>1</sup>

The present picture<sup>11,12,13</sup> of a colloidal particle is a charged particle surrounded by a balancing ionic atmosphere of opposite charge. According to this theory, a particle would consist of a neutral nucleus of the dispersed material, an inner layer of ions adsorbed on the surface of the particle and an outer layer of ions which have a charge opposite to the adsorbed ions. This outer sheath consists of a diffuse layer of charges the density of which diminishes from a maximum near the fixed inner layer to a small value in the rest of the liquid.<sup>14</sup>

It is the mutual repulsion of the like-charged particles which is responsible for the stability of the sol. This force of repulsion is determined by the potential difference between the outer and inner layers rather than by the absolute electrical charge on the particles.<sup>5</sup> When this potential difference becomes zero, or too low to overcome the attractive forces between the particles, coalescence occurs. The addition of electrolytes will cause the potential to decrease and finally cause flocculation.

Brownian movement may give the particles enough velocity to overcome the mutual repulsion and thus cause coalescence. This factor becomes more noticeable as temperature increases and as viscosity of the solution and size of the particles decrease.<sup>15</sup>

The above discussion of the factors influencing the stability of a colloidal system may seem to digress from the subject of the thesis. However, since practically nothing could be located in the literature concerning the effects due to the structure of dispersing agents, the author felt that a knowledge of the factors affecting the stability of a colloidal system was a necessary background for the interpretation of the experimental work.

It was decided to start with low molecular weight compounds, the structure of which was definitely known, and to determine the effect of the following on their dispersing action: polarity of the molecule, various groups, namely methyl, amino, hydroxyl, and sulphonic acid, lowering of surface tension, and molecular weight.

Polarity has been shown to have considerable effect on many properties of compounds. Schmidt<sup>16</sup> points out that dissociation of acids, velocity of chemical reactions, optical activity and solvent effect may be correlated with the type and magnitude of the dipoles present in the molecule. However, a quantitative interpretation has only been

worked out for simple molecules. The effects caused by the bending of chain structures are not fully understood.<sup>19,20</sup>

Limited by this and the fact that the dipole moments of only a relatively few compounds have been measured. The only satisfactory compounds which could be found with equal dipole moments<sup>19,20</sup> were p-amino phenol and p-cresol. A comparison between the effects produced by the amino and methyl groups could also be determined at the same time by the use of these compounds.

After grinding with these compounds it was found that apparently the amino group had considerable effect on the dispersing action. Because of this, and because it was found, as mentioned previously, that the presence of a water soluble group is necessary, it was decided to use amino sulphonic acids for the remaining determinations.

## APPARTUS AND PROCEDURE

The laboratory procedure consisted essentially of the following steps:

1. Grinding sulphur in a pebble mill with a dispersing agent and using water as the dispersing medium.

2. Determining the per cent total solids in the resulting dispersion by drying a weighed sample of the dispersion.

3. Obtaining the relative specific surface of the dispersion by using a Klein turbidimeter.

4. Determining the lowering of surface tension caused by the dispersing agent.

Several trial runs from one to six hours were made to determine the shortest time necessary to give a dispersion which, from its appearance, was relatively fine. It was found that three hours grinding would give a satisfactory dispersion using 100 grams of sulphur, 100 ml. of water and 2 grams of dispersing agent. In all cases it was found necessary to add more water at the end of the run to remove the dispersion sticking to the pebbles. This amount varied from 25 to 175 ml.

The pebble mill was a common type laboratory jar mill with a volume of 0.24 cubic feet. The volume occupied by the pebbles was about 55% of the total volume. This volume of pebbles was found by Gow, Guggenheim, Cambell

and Coghill<sup>17</sup> to be the optimum amount for wet grinding. The weight of pebbles occupying this volume was seven pounds.

The determination of per cent solids was made by weighing a sample of about one gram into a two inch crystallizing dish and drying at a temperature between 90 and 95°C. to constant weight. It was found that if drying was carried out above the temperature range mentioned, the sulphur vaporized.

The relative specific surface of the dispersion was obtained by using a Klein suspension turbidimeter. The apparatus consists of a light tight box in which a light source is placed above a photronic cell which is connected to a micro-ammeter outside the box (See Fig. 1). A dispersion placed between the light and photo-cell will decrease the intensity of the light reaching the cell. If we denote the light intensity through the clear dispersing medium and tray by  $I_0$  (measured in micro-amperes) and the intensity through the dispersion by  $I_d$ , the specific surface ( $S$ ) is found to be expressed by the following equation. 18,19

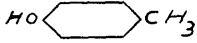
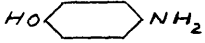
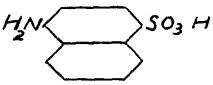
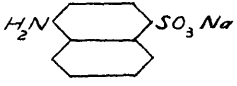
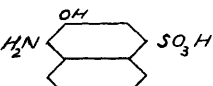
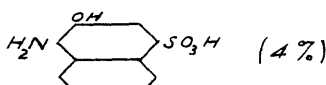
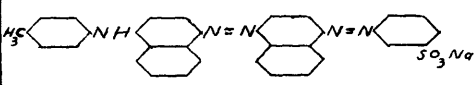
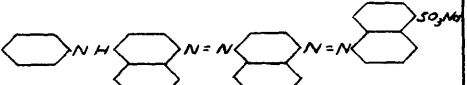
$$S = k \log \frac{I_0}{I_d}$$

This apparatus was originally designed to measure the specific surface of cement, consequently a procedure had to be worked out for sulphur dispersions. Since no sample of sulphur could be obtained which had a known specific surface, the relative specific surface  $\frac{S}{k}$  was determined for each dispersion. The procedure for obtaining  $\frac{S}{k}$  is to weigh out a sample of the dispersion which is equivalent to 3 grams of total solids.

Add enough water to make the sum of the water added plus the water in the dispersion equal to 6 grams; add 96 grams of glycerine and disperse. Take 2 grams of this dispersion and add 100 grams of glycerine, Weigh out 25 grams of this final mixture into a turbidimeter tray and place in the turbidimeter.  $I_0$  is obtained by weighing 25 grams of glycerine into a tray and taking the micro-ammeter reading.

Surface tension measurements were made with a du Nouy tensimeter. Distilled water was measured, then 2% solutions of the dispersing agents. The difference between the two readings divided by the reading obtained from the distilled water was taken as the per cent reduction in surface tension.

RESULTS

Run	Dispersing Agent	Relative Specific Surface	Mol. Wgt.	Reduction of Surface Tension in 2% Sol.
1	None	1.0	-	-
2		1.2	108	47.0
3		4.8	109	0
4		1.5	223	6.3
5		1.1	245	43.0
6		2.0	239	9.2
7		2.9	239	-
8		11.9	673	26.0
9		11.6	708	26.0



## DISCUSSION OF RESULTS

From the grinding with p-cresol and p-amino phenol it was found that the polarity had little effect on dispersing action. The dipole moments of both compounds are of the same order of magnitude<sup>20</sup> yet the relative specific surface of the dispersion made by using p-amino phenol was four times that of the dispersion obtained from p-cresol. Further evidence is obtained by comparing the results of runs 4 and 6. The polarity of 6 is less than 4 (run numbers are also used to denote the dispersing agent used) due to the counter-acting force of the negative OH with the positive NH<sub>2</sub> groups, yet a finer sulphur was obtained by using 6.

From runs 2 and 3 we can conclude that the amino group adds considerably more to the dispersing power of the compound than the methyl group. The addition of a hydroxyl group to the ring has little effect on the dispersing power as is shown by runs 4 and 6. When a long chain is substituted for the two hydrogens of the amino group, the dispersing power increases about ten times. This is seen by comparing run 5 with runs 8 and 9. A methyl group on the end of the chain does not affect the dispersing power (compare 8 and 9).

The property of a substance to lower surface tension does not necessarily signify that it is a dispersing agent. Comparing 2 and 3 we notice that 3 which does not reduce the surface tension of water is a better dispersing agent

than 2 which reduces the surface tension considerably. Again, comparing 4 and 5 we find that they both produce a dispersion of about the same fineness, yet 5 reduces the surface tension 37% more than 4.

Molecular weight seems to be important when the weight is added by a long chain (see 8 & 9) but an increase of 5% in molecular weight of 9 over 8 has no effect on dispersing action. However, an increase of over 100% in molecular weight did not improve the dispersing power of 4,5, and 6 as compared with 3. In this case, the increase in molecular weight was not due to the addition of a chain to the molecule.

## CONCLUSIONS

1. Polarity in the molecule has little or no effect on the dispersing action.

2. That it is a large molecule with a long chain structure which is adsorbed readily and firmly on the dispersed particle, and it is this chain in oriented position on the particle which is responsible for the stability of the dispersed material.

3. That surface tension lowering aids the dispersing action only when the compound is readily adsorbed.

4. That the addition of methyl and hydroxyl groups to the molecule of the dispersing agent does not increase the dispersing action.

### RECOMMENDATIONS

1. That the dispersing agents used in this thesis be used to grind a metallic oxide and the nature of the charge determined and compared with the sulphur sols produced using the same dispersing agents.

2. That other groups with long chains be investigated.

3. That the effect of concentration of dispersing agent be studied with the view of seeing if dispersing agent acts as its own flocculating agent.

4. That dispersing agents which are salts of di and tri valent metals e.g. calcium and aluminum be investigated.

(The author intends to continue with this thesis next year for partial fulfillment of requirements for the degree of Master of Science)

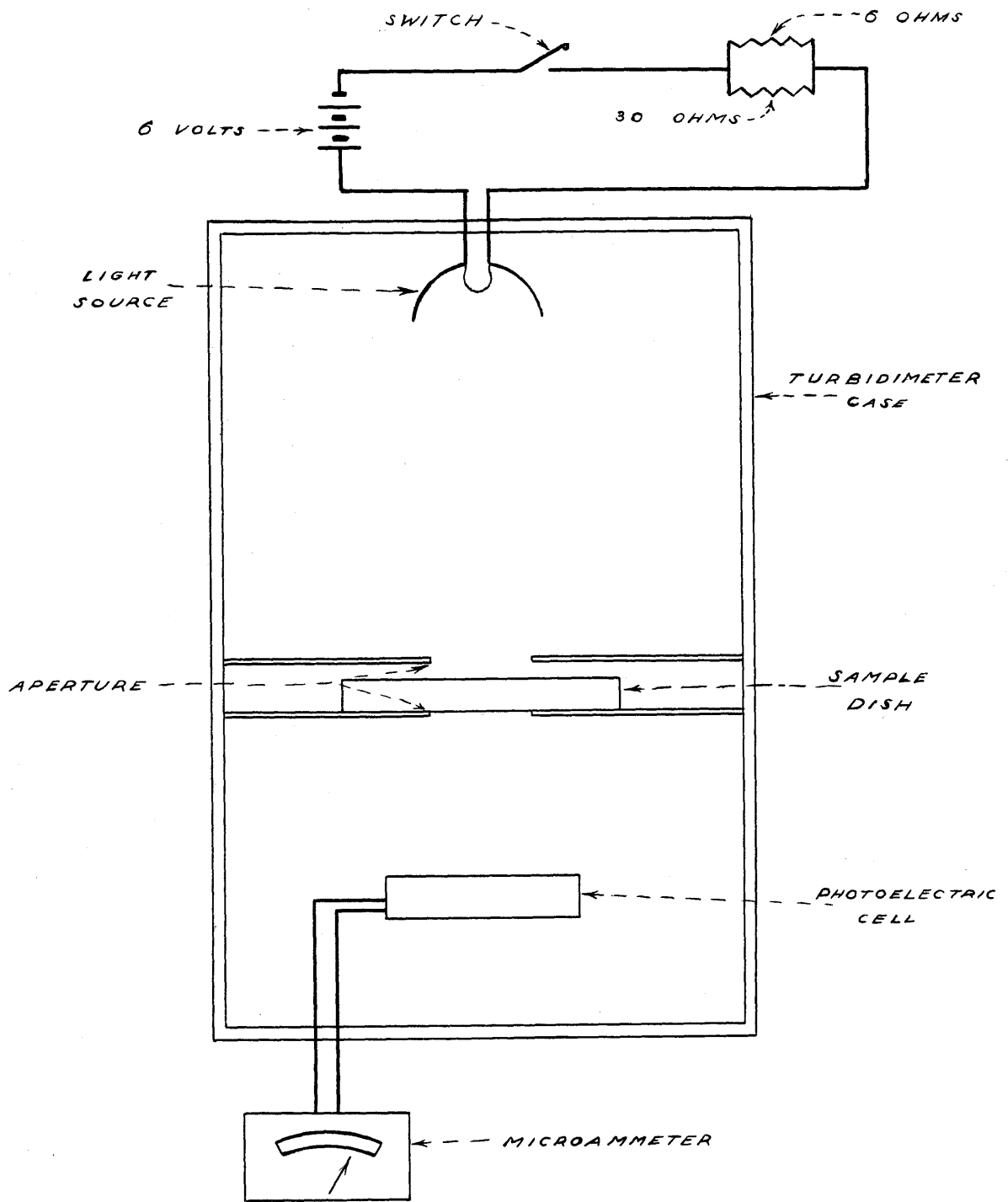


Fig. 1. - DIAGRAM of TURBIDIMETER

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