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The Importance of Being Flocculated

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ABSTRACT

Current concepts of deflocculation in nonaqueous media are examined, and an extension of these is used to design a polymeric deflocculating agent of improved performance. The predicted performance improvement is experimentally verified.

The degree of flocculation is a major formulation variable which rarely is measured and controlled in the surface coating industry, yet the gain in opacity and tinting strength can be as much as 30% and the pigment saving possible by effective utilization of titanium pigments alone would be enormous. Many color problems are simply a reflection of the changing efficiency of one of the pigments changing its flocculation on storage or film formation.

The difference in settling behavior of dispersed and flocculated systems is so well known as to need no comment, but the paint industry seems very reluctant to apply controls which could effectively eliminate settling as a complaint. It prefers to simply add some

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*Deceased.

flocculating agents and hope that they will continue to function throughout process and formulation changes and production vagaries.

Low gloss and gloss drop on drying are a consequence of the flocculated particles in the film. Application properties—ease of brushing, spreading rate, brush marking, flow-out, and sagging—have all been related to the rheology of paints, which is influenced mainly by particle flocculation, but rheological properties are not being used as controls and only in rare instance, as far as the writers are aware, as formulating tools.

The mechanical properties of dried films have also been related to flocculation and we can quote a major improvement in chip resistance of an automotive mass production undercoat [1] obtained by low degrees of pigment flocculation. Again, although the formulation improvement has been accepted, the principle of flocculation control has been rejected.

MEASURING FLOCCULATION

It is implicit in any work in control of flocculation that there is available some method of measurement. Direct observational techniques with a microscope are at the best only qualitative and it is, therefore, necessary to measure the effects of flocculation rather than flocculation itself. Optical methods can be very precise, but require highly skilled techniques and are of doubtful value if too many variables are being studied.

We have found rheological methods to be a useful and reasonably quantitative method of assessing particle flocculation. Our chosen technique is based on the Casson plot [2] which gives a yield value and a viscosity at infinite shear. We relate yield value to the particle flocculation, and the viscosity at infinite shear to the Newtonian viscosity of the continuous phase, plus the hydrodynamic effect of the particle volume and to the crowding between individual particles.

Deflocculated pigment suspensions are characterized by low yield values, and an effective dispersant is one which gives a low yield value system at low levels of dispersant.

MECHANISM OF DEFLOCCULATION

In this paper we are dealing only with nonaqueous systems in which we have assumed the contribution of ionic stabilization is small, and that in practice deflocculation is achieved by steric barriers of adsorbed molecules. We have taken as a starting point our work with oleic and stearic derivatives and their adsorption onto titanium dioxide pigment, in which we were unable to achieve deflocculation in hydrocarbon media. We accepted this as showing that barriers thicker than 20 Å were necessary, and by review of current "dispersing agents" we placed the small molecules (metal soaps, monoglycerides, grinding aids) into a wetting agent-flocculation class and the higher molecular weight polymers into a dispersing-deflocculating category.

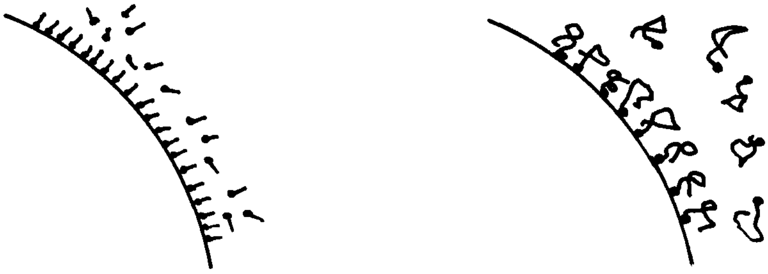
The ICI Paints Division (in the United Kingdom) developed dispersing agents which were the most effective agents available at that time, with high degrees of deflocculation, but their original monofunctionality (i.e., one polar group capable of strong adsorption per polymer chain) did lead to low weight efficiencies since even with highly polar groups, such as nitro, adsorption was not complete.

Dulux Australia Ltd. developed double comb agents which we postulated would overcome this defect by the use of multiple adsorption sites. It was found that efficiency of adsorption was much higher even if groups with low polarity were used. However, the postulated method of adsorption as a flat layer with all polar groups on the surface would give a steric barrier little larger than that of stearic acid, which the writers did not accept as being sufficient. We felt that the size of the steric barrier might be increased if the number of adsorption anchor unit sites were reduced below the accepted 25% for a double comb, and give a dispersant with high adsorption characteristics and a still larger steric barrier. The barrier could be formed by looped adsorption of the polymer chains as illustrated, and will in this paper be referred to as a V.W. dispersion (see Fig. 1).

There are three requirements for an efficient surface-active agent. First it should be adsorbed in such a way as to give a steric barrier of about 100 Å units. The second requirement is that the surface-active agent shall be highly soluble in the solvent. The third requirement is that to achieve a high efficiency per unit weight, adsorption must approach 100%. We postulate that these can be achieved with polymeric multianchor combs in which the effective anchor sites are placed at 100 to 150 units apart. This results in "loop" adsorption with most of the surfactant forming a solvated barrier round the pigment.

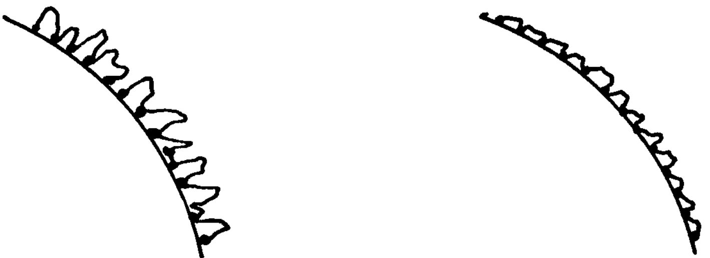
Optimum efficiency will be obtained at relatively low concentrations of anchors with highly polar anchor groups, but with less polar groups more anchors per unit length will be required to give an average of one effective anchor to every 100 to 150 units.

Summarizing, it is predicted that at low levels of effective anchors, adsorption will be inefficient, but high dispersibility can still be obtained. Furthermore, at high levels of anchor full adsorption will be achieved, but low levels of dispersibility result because the comb has been pulled down flat on the pigment surface. In between these two extremes an anchor content should exist which will result in looped V.W. adsorption and optimum dispersing characteristics. To test the hypothesis, it was decided to examine the effectiveness of polymeric dispersants containing varying numbers of anchor units.



Small monopolar(Stearic Acid)
Small Barrier-Flocculation
Single anchor-Low adsorption

Large Monopolar
Large barrier-deflocculation
Single Anchor-low adsorption



Large Multipolar
Large barrier-Deflocculation
Multi anchor-High adsorption

Large Multipolar(over anchored)
Small barrier-flocculation
Multi anchor-High adsorption

FIG. 1.

RESULTS AND DISCUSSION

Two series of surfactants were prepared. The first was comprised of copolymers of lauryl methacrylate and glycidyl methacrylate (GMA) in various proportions. These surfactants were used as solutions in xylol. In these surfactants the lauryl methacrylate portion would be highly solvated by xylol while the glycidyl methacrylate units were expected to form weak anchors onto the titanium dioxide particle surface. A second series of surfactants with more active anchor groups were prepared from the first series by opening the epoxide rings with p-nitrobenzoic acid.

The surfactants with GMA anchors were evaluated in dispersions of titanium dioxide (Austiox R-CR3) in xylol in which both of these components had been carefully dried before use. The volume fraction of titanium dioxide was 18.0% and the amount of surfactant used was 0.50% w/w on the pigment.

A more practical system was used to evaluate the surfactants with p-nitrobenzoic anchors. Again it was comprised of an 18% by volume dispersion of titanium dioxide in xylol, but in this case both components were used as obtained from commercial sources without further treatment. The concentration of surfactants used in these systems was 1.0% w/w of the pigment. The relative concentrations of the components in these dispersions were chosen solely on the grounds that they gave measurable differences in rheology as the number of anchor units in the surfactants was varied. Higher concentrations of surfactants gave almost fully deflocculated systems with all agents.

It was decided to determine the degree of deflocculation in each system using rheological measurements. According to Casson's theory [2], the apparent viscosity of a flocculated system should be given by the equation:

$$\eta = [\eta_{\infty}^{\frac{1}{2}} + (\gamma/D)^{\frac{1}{2}}]^2$$

where η_{∞} is the high shear viscosity, D is the shear rate, and γ is the yield value of the system. Preliminary experiments showed that plots of the square root of the apparent viscosity against the reciprocal of the square root of the shear rate were indeed linear between shear rates of 100 and 500/sec. The yield value, γ, should be a measure of the deflocculation of a system.

The rheological results obtained for the dried dispersion with the lauryl methacrylate-glycidyl methacrylate surfactants are shown in Fig. 2. In this diagram the yield values for the dispersions are plotted against the percentage of glycidyl methacrylate anchor units. A minimum exists in this plot. This minimum indicates that the optimum composition for this series of surfactants is at about 20% of glycidyl methacrylate units.

The results for the undried dispersions with the p-nitrobenzoic acid modified surfactants are shown in Fig. 3. In this case the p-nitrobenzoate groups are considered to be the predominant source of anchor groups, though unreacted glycidyl groups are present. For this reason the yield values have been plotted against the percentage of p-nitrobenzoate modified units. A distinct minimum exists, indicating that the surfactant with about 10% of these units is the optimum for deflocculation.

The existence of the minimum in these plots is predicted by the V.W. hypothesis. In two further experiments we then attempted to confirm the theoretical explanation of these maximum dispersing efficiencies. According to our postulate, the initial increase in dispersing efficiency of a surfactant as the anchor content is increased as a result of a greater degree of adsorption.

Adsorption determinations were made in two of the undried dispersions, A and B. A sample of each dispersion was centrifuged and the content of the clear layer was measured.

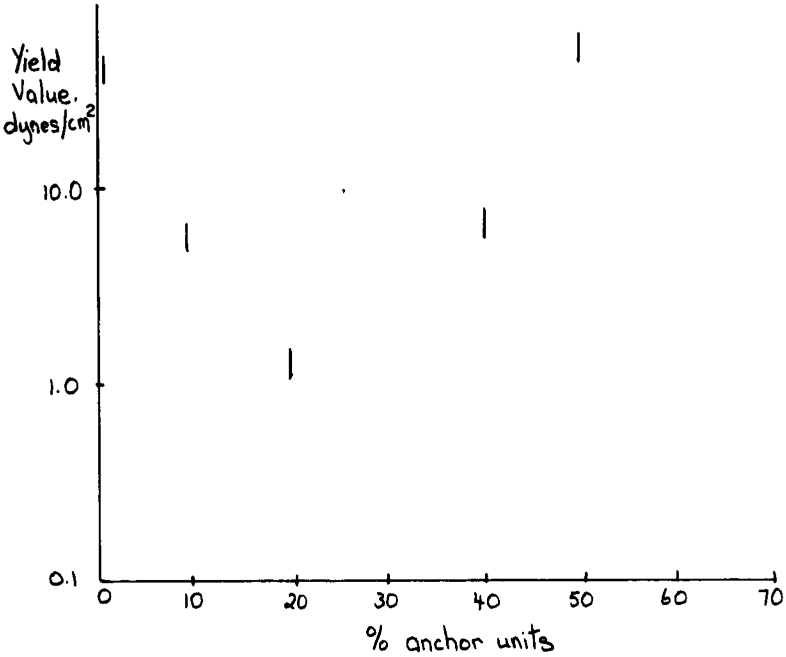


FIG. 2. Rheological results obtained for the dried dispersion with the lauryl methacrylate-glycidyl methacrylate surfactants. The yield values for the dispersions are plotted against the percentage of glycidyl methacrylate anchor units.

The results which are recorded in Table 1 show that the surfactant with no strong anchor units is not as extensively adsorbed as the surfactant with the optimum anchor content. This is in agreement with the theory, and thus confirms that deficiencies in the dispersing agents with few or no anchor units per molecule are possible.

As the anchor content of a surfactant is increased beyond the optimum value, the theory predicts a decrease in dispersing efficiency associated with a smaller steric barrier.

The data given by Thomas [3], relating the volume fraction of the dispersed phase (and adsorbed layers) to the relative viscosity of the dispersion (dispersion viscosity/continuous phase viscosity), was used to compare the sizes of the steric barriers in two of the undried systems (B and C). The high shear viscosities of these dispersions were determined by extrapolating the apparent viscosities according to Casson's theory. The viscosities of the continuous

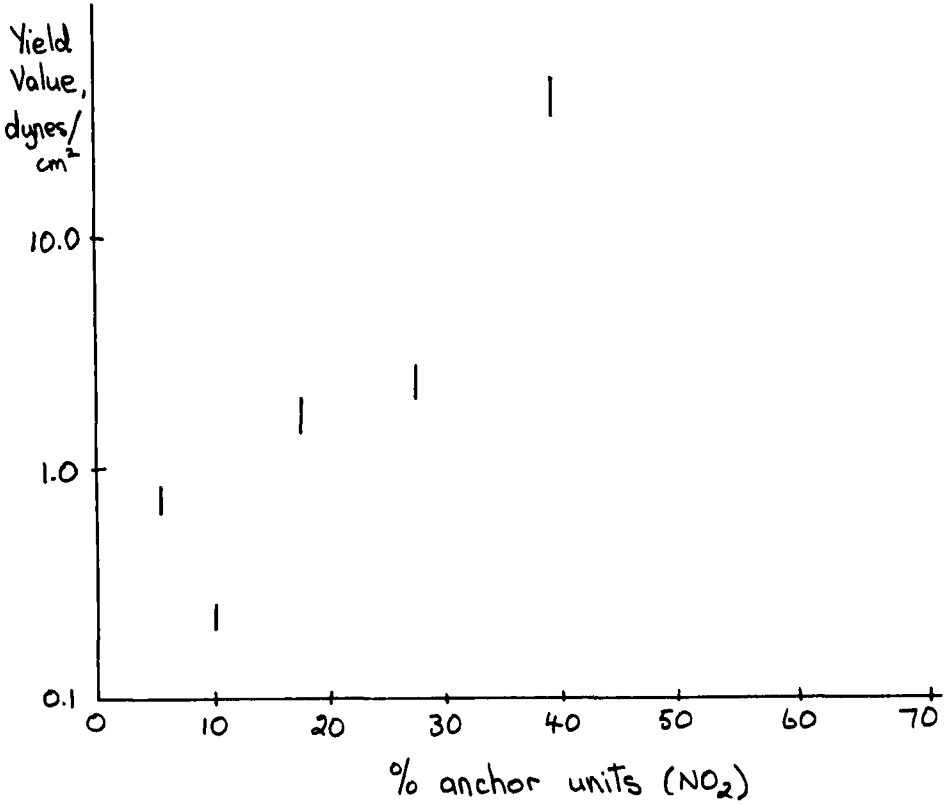


FIG. 3. Results for the undried dispersions with the p-nitrobenzoic acid modified surfactants.

TABLE 1. Adsorption of Surfactants on Undried TiO_2 from Undried Xylol Solution

Dispersion	Surfactant	% Anchor units (NO_2)	% of Surfactant adsorbed
A	LMA:GMA copolymer	0	15
B	LMA:GMA copolymer, ring opened with p-nitrobenzoic acid	8.42	84

TABLE 2. The Effect of Anchor Group Concentration on the Relative Viscosity of Undried TiO_2 in Undried Xylol

Dispersion	Surfactant	% Anchor units (NO_2)	High shear viscosity	Relative viscosity
B	LMA:GMA copolymer ring opened with p-nitrobenzoic acid	8.42	3.40	5.19
C		27.3	2.47	3.82

phases were measured at 25°C in an Ostwald tube after recovery by centrifuging from the dispersions.

We would have liked to compare completely surfactant free systems with the optimum dispersion (B) and the overanchored system (C), but the surfactant-free basic system was too viscous, and so we were limited in this experiment to comparing the relative viscosities of systems B and C.

The results are given in Table 2, showing distinct increase in relative viscosity for the dispersed system B. Following Thomas's data, this indicates an increase in particle volume concentration as the most likely explanation. If the specific surface areas of the TiO_2 is about 10 m/g, then dispersion B has an adsorbed layer about 60 Å^2 thicker than dispersion C.

Although considerably more measurements along these lines must be made, this does indicate that a large number of strong anchor groups tends to pull the surfactant molecule onto the particle surface. This allows the particles to approach each other to a point where the attractive forces are capable of flocculating the system.

SUMMARY

The above experimental evidence is consistent with the V.W. postulate put forward to explain polymeric surfactant efficiency.

1. Dispersion efficiency passes through a maximum as anchor concentration increases.
2. The lower dispersion efficiency at low concentrations of anchor group is consistent with the low degree of adsorption found.
3. The lower dispersion efficiency at high concentrations of anchor group can be explained on the evidence showing a smaller adsorbed layer due, we believe, to flatter adsorption of the molecule.

4. The large difference in optimum anchor concentration between glycidyl and nitro groups is probably related to their polarity.

The results of this admittedly small amount of experimental work do show that the V.W. postulate mechanism of deflocculation is possible and does explain observations that current theories do not. A more extensive examination of the postulate in order to solve the most vexing problem in the paint industry is justified.

EXPERIMENTAL

Synthesis of Dispersing Agents

Two series of dispersing agents were prepared, the first comprised copolymers of lauryl methacrylate (LMA) and glycidyl methacrylate (GMA) in various proportions. The polymerization was carried out in a 2:1 mixture of ethyl acetate and butyl acetate using azodiisobutyronitrile as initiator. The solution was refluxed for 8 hr after which the polymer concentration closely approached the calculated value. The solvent was then removed and replaced by xylol which had been dried over sodium sulfate and subsequently distilled.

The second series of surfactants was prepared from the first series by opening the epoxide rings with p-nitrobenzoic acid. This was performed in the original ethyl acetate/butyl acetate solvent. The esterification was continued until the acid number fell below 0.1 g KOH/g. Again the solvent was removed and replaced by dry xylol.

Preparation of TiO_2 Dispersions

Dispersions containing 18% TiO_2 by volume in xylol plus the appropriate surfactant were prepared by ball milling for 16 hr in polyethylene jars containing half-inch diameter porcelain pebbles. For the surfactants with GMA anchors, the TiO_2 and xylol were carefully dried before use and the surfactant content was 0.5% by weight on the pigment. For the second series of surfactants with p-nitrobenzoic anchors, both the TiO_2 and xylol were used as obtained without drying and the surfactant content was 1.0% of the weight of the pigment.

Rheological Measurements

Measurements of apparent viscosities at various shear rates were made at 25.0°C on an Epprecht Rheomat fitted with an "O" cup.

The results for viscosity (η) as a function of shear rate (D) were fitted to Casson's equation [2]:

$$\eta^{\frac{1}{2}} = \eta_{\infty}^{\frac{1}{2}} + (\gamma/D)^{\frac{1}{2}}$$

to calculate the yield stress (γ) and the high shear viscosity η_{∞}.

The viscosities of the continuous phases of the dispersions were measured at 25.0° C in an Ostwald u-tube viscometer after centrifuging the dispersions to remove the titanium dioxide.

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