The Interaction Between Zinc Oxide and Titanium Dioxide in Water

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Abstract

A mechanism is proposed for the reaction between zinc oxide and titanium dioxide in water. Between certain limits of weight ratios of zinc oxide and titanium dioxide definite increases in viscosity, pH, and sedimentation volumes with time have been observed which support the belief that tridimensional structures are formed from the individual particles. The same mechanism may be responsible for some of the thickening in emulsion paints containing these mixed pigments.

ZINC OXIDE and titanium dioxide are major pigments used in oil-based paints. However, incorporation of these pigments into linseed oil emulsion paints caused a rapid increase in viscosity to values above the desired range. This increase can easily be eliminated by leaving the zinc oxide out of the paint formulation, but ZnO imparts advantages difficult to find in other materials. These advantages include improved mildew resistance, better through-dry of the paint film, reduction of film degradation by adsorpition of ultraviolet light, and low cost (3). Therefore a study of the effects of ZnO on other components of emulsion paints seemed desirable for a better understanding of the reactions involved. This paper deals with the interaction between ZnO and TiO_2 in water without the addition of dispersing agents.

Experimental

Lead-free Azo ZZZ-55 zinc oxide (American Zinc Sales Company, Columbus, O.) and Ti-Pure R-510 titanium dioxide (Pigments Department, E. I. duPont de Nemours and Company, Wilmington, Del.) were used throughout, except when otherwise indicated. The distilled water used came from a common source supplied to the laboratories through block tin lines.

Viscosities were measured with a Brookfield model RVF viscometer at 20 rpm. All measurements were made at 25C and spindle No. 3 was used exclusively. The pH values were obtained with a Beckman model G pH-meter equipped with a glass electrode and a saturated calomel electrode. All pigment suspensions were prepared by weighing into a pint jar ZnO and TiO_2 in the right proportions to total 180 g. Thereafter 335 g of distilled water were added. Each glass jar had a bakelite screw cap with waxed paper insert. The paper inserts had to be replaced by rubber pads since chemicals extracted from the paper greatly influenced the rate of interaction. Special care had to be taken to eliminate any detergent or dispersing agents from the jars because any trace of these materials affected the rate of interaction.

A study of pH of pigment slurries in water revealed that ZnO suspensions (35% by wt) had a pH of 7.2 which was constant with time and independent of the lot number of the ZnO used. The pH of 35% TiO_2 suspensions was also constant with time but varied between 7.15 and 7.60, depending on the lot of TiO_2 used.

When a 35% suspension of a mixture of ZnO and TiO_2 was prepared, the pH changed rapidly in a matter of hours and reached an equilibrium value of 9.2 after several days. Also, the viscosity increased much more rapidly than for either the ZnO or TiO_2 suspension.

A series of 20 suspensions was prepared containing 35% solids and varying ratios of ZnO and TiO_2. The pint jars were placed horizontally in a Gump shaker (200 rpm and 2½ inch eccentricity) agitated simultaneously for 1½ hr at 25C, and stored at the same temperature. The viscosity and pH of each sample were measured initially and thereafter twice a week. Typical results are shown in Figures 1 and 2.

Figure 1 shows that a minimum in the viscosity-composition curve (η_0) was obtained at zero time. By adding the proper viscosities taken from the viscosity vs. concentration curves for the individual pigment suspensions (Figure 3), a theoretical zero viscosity curve is obtained. This calculated curve and the measured data are compared in Figure 4. The calculated minimum is lower than the measured values because any interaction between ZnO and TiO_2 particles has been disregarded.

Figure 1 shows two peaks in the viscosity curve after some time (19 and 33 days). The positions of

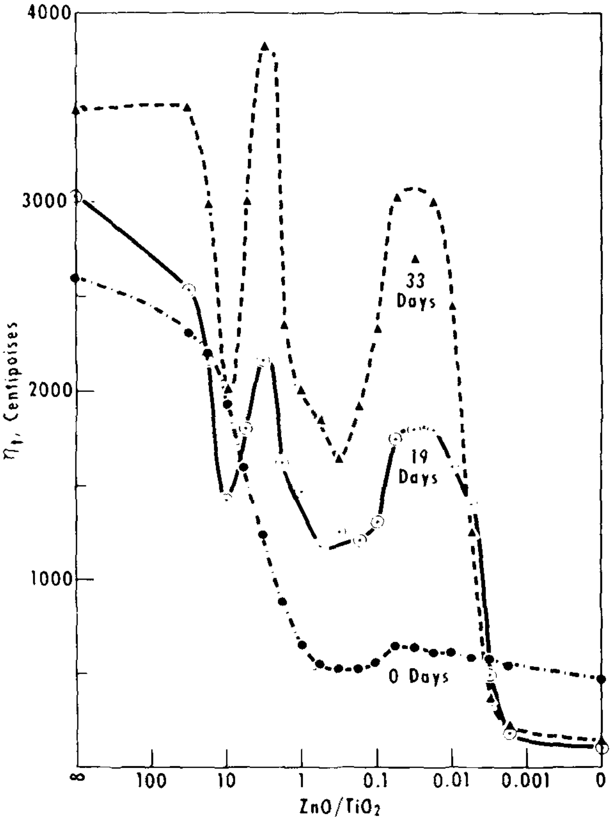

FIG. 1. Viscosity for pigment suspensions (35% solids) in water as a function of the pigment weight ratio, ZnO/TiO_2, at zero time and after 19 and 33 days.

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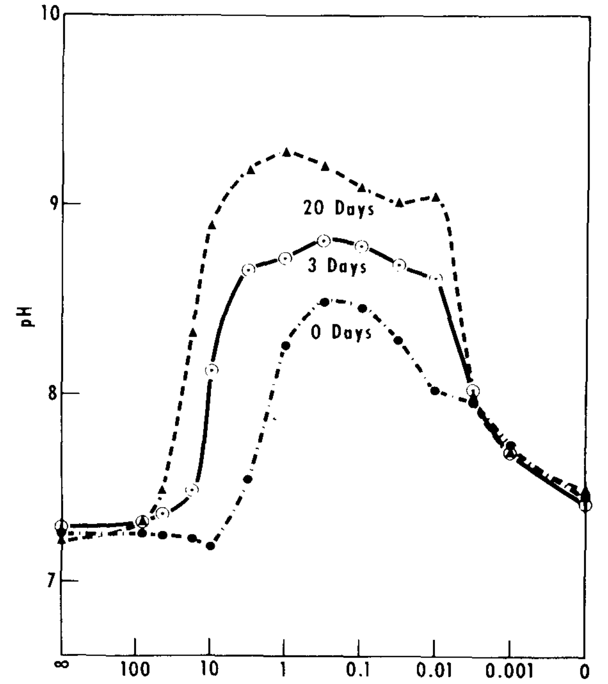

FIG. 2. The pH as a function of the pigment weight ratio, ZnO/TiO_2, at zero time and after 3 and 20 days.

the peaks fall at the ratio ranges of 1.8–3.2 and 0.018–0.032 and are essentially independent of the lot numbers of the pigments.

If η_t/η_o is plotted against the pigment ratios (Fig. 5), the viscosity increase takes place mainly in suspensions with pigment ratios between 10.0 and 0.0032. This increase is shown more clearly in Figure 6, where the viscosities are divided by the calculated zero-time viscosities of Figure 4.

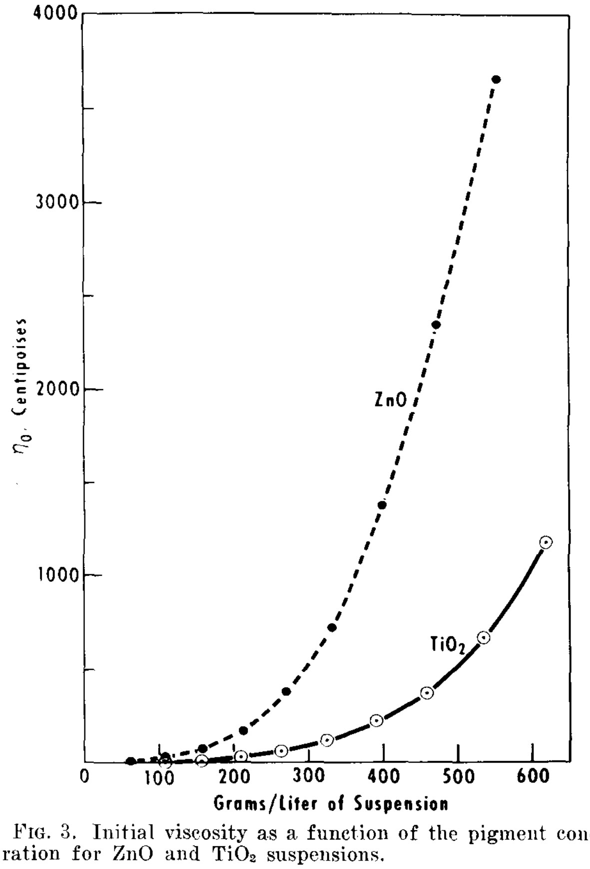

FIG. 3. Initial viscosity as a function of the pigment concentration for ZnO and TiO_2 suspensions.

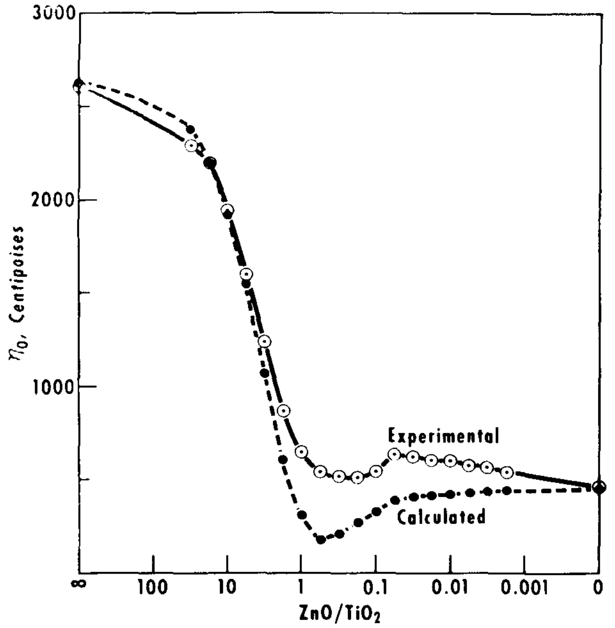

FIG. 4. Experimental initial viscosities for mixed ZnO and TiO_2 suspensions compared with a calculated curve obtained from viscosity-concentration curves of Figure 3.

The pH increase (Fig. 2) is believed to be caused by aggregates of pigment particles formed by a chemical bond between the surfaces of ZnO and TiO_2 particles, and is not due to the suspension effect. When the pH was measured both in the suspension and in the supernatant liquid, the difference was found to be less than one-tenth of one unit. The pH can be brought down to neutral by titration with HCl, but will increase again to values of around 8.0 in a matter of 24 hr. Since agitation of the aged slurries did not reduce their viscosity, further support for this kind of interaction is provided. Impurities in these commercial pigments were not responsible for their behavior because mixtures of pure grade, preanalyzed ZnO and TiO_2 (J. T. Baker Chemical Company, Phillipsburg, N. J.) also showed viscosity and pH increases.

A 35% suspension of B-991 zinc titanate (Titanium Alloy Manufactory Division, National Lead Company, Niagara Falls, N. Y.) had an equilibrium pH value of 9.2, which supports the assumption that the chemical

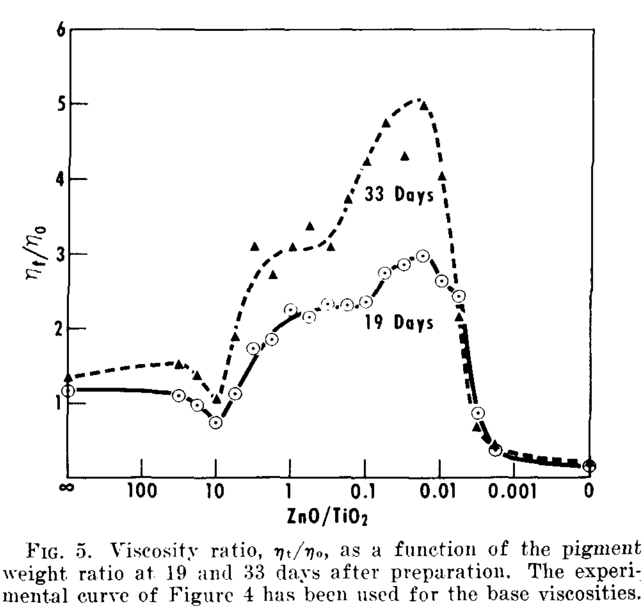

FIG. 5. Viscosity ratio, η_t/η_o, as a function of the pigment weight ratio at 19 and 33 days after preparation. The experimental curve of Figure 4 has been used for the base viscosities.

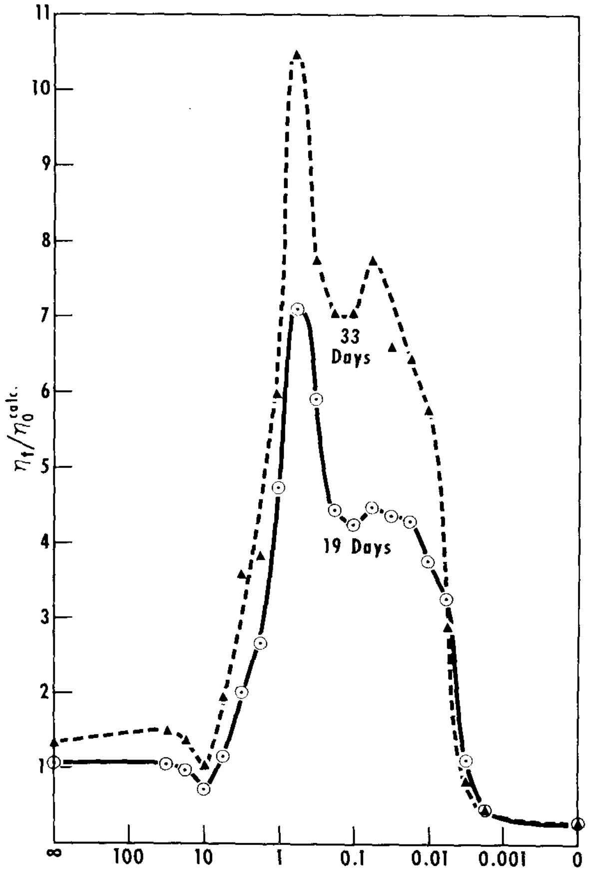

FIG. 6. Viscosity ratio, $\eta_t/\eta_o^{\text{calc.}}$ as a function of the pigment weight ratio at 19 and 33 days after preparation. The calculated curve of Figure 4 has been used for the base viscosities.

bond between ZnO and TiO$_2$ is of the zinc titanate nature. Also, the same behavior has been found for suspensions containing mixtures of ZnO and ASP-400 clay (Minerals and Chemicals Philipp Corporation, Menlo Park, N. J.) or wet ground mica (Mineralite Sales Corporation, Mineola, N. Y.); whereas, no reaction was indicated when these pigment extenders were used in combination with TiO$_2$. Mica, clay, and TiO$_2$ show strong negative charges when observed in an electrical field; but ZnO shows only a weak charge which can be either negative or positive in essentially neutral suspensions. However, at basic pH values ZnO is strictly negative.

Discussion

If the pigment particles are assumed to be spherical and of the same size for a given pigment, the total weight, W$_1$, of that pigment in the suspension can be expressed as

$$W_1 = \frac{4}{3}\pi r_1^3 n_1 \rho_1 \qquad \text{(a)}$$

where r_1 = the effective radius of the particles,
n_1 = the number of particles, and
ρ_1 = the density of the pigment.

The ratio of the total weight of the two pigments used in the suspensions can be written as

$$\frac{W_1}{W_2} = \frac{r_1^3 n_1 \rho_1}{r_2^3 n_2 \rho_2} \qquad \text{(b)}$$

in which W_1/W_2 = the pigment ratio ZnO/TiO$_2$ as used in the figures.

If no dispersing agent is used, the pigment particles in the suspension cannot be broken up into the elementary particles. Therefore, particle sizes as given by the pigment manufacturers cannot be used for this discussion. Coulter counter (1,2) measurements showed average particle sizes of approximately 1.0 micron for ZnO and 2.2 micron for the TiO$_2$ aggregates. Accepting these figures for our discussion the ratio of the radii of the ZnO and TiO$_2$ particles is assumed to be 0.5. If in addition the values of 5.6 and 4.2 g/ml are used for the densities of ZnO and TiO$_2$, respectively, Equation 2 can be reduced to

$$\frac{n_1}{n_2} = 6\frac{W_1}{W_2} \qquad \text{(c)}$$

From Figures 2, 5, and 6 it can be seen that at $W_1/W_2 = 10$, the pH is increased. This increase means there is an interaction, but at the same time the viscosity is not affected appreciably. From Equation C we find that for this pigment ratio $n_1/n_2 = 60$. Hence, there are enough ZnO particles to react with the TiO$_2$ particles and to coat them completely. Consequently, any further reaction between the two pigments is stopped. The same explanation can be used for w_1/w_2 = 0.0032 where there are 52 times more TiO$_2$ particles than ZnO particles; then the reverse condition exists. Between these ratios, tridimensional structures can be formed from the individual particles. These structures should, and in our opinion do, influence viscosity tremendously. The region in which the pH increases is much wider than that in which viscosity increases. (Compare Figures 2 and 6.) This deviation again points very strongly toward the described mechanism.

Additional evidence was obtained from sedimentation experiments. If these tridimensional structures build up, the sedimentation volumes should increase with time. To establish this point, 50 g of pigment with varying weight ratios of ZnO and TiO$_2$ were placed in 250 ml graduated cylinders and the cylinders filled with water. After shaking thoroughly the pigment was allowed to settle, and the sedimentation volumes were measured. When the measurements were completed, the pigment was redispersed, and

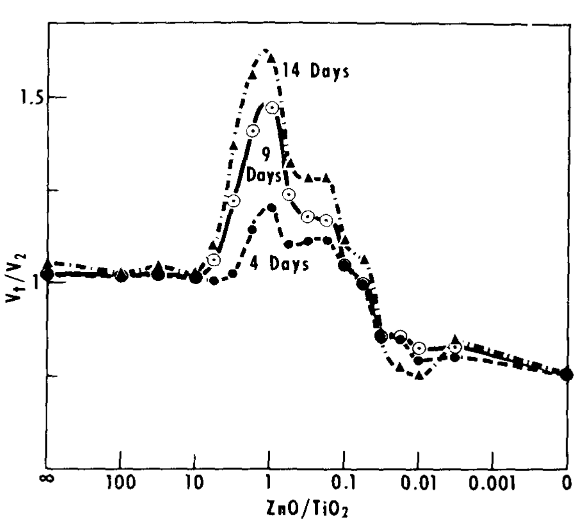

FIG. 7. Ratio of sedimentation volumes at 4, 9, and 14 days as a function of the pigment weight ratio, Zno/Tio$_2$. The sedimentation volumes at 2 days after preparation have been used as base values.

this procedure was repeated every few days. The results are shown in Figure 7 where the volume change, $V_t/V_{2\,days}$, is plotted vs. the pigment ratios. Again, the largest increase occurred in the same region of composition as observed previously. The decrease at low ratios results because all the pigment was not settled out at the time of measuring. However, this experiment proves definitely that tridimensional structures slowly build up between ZnO and TiO_2 and are unable to pack as closely together in water as do the individual particles.

Acknowledgment

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• *Letter to the Editor*

Glyceride Type Distribution Rule Calculations

With reference to the letter of Hammond and Jones on the calculation of Restricted Random Glyceride Distribution (1) I wish to state the following:

1) The principle underlying the calculation of glyceride type structure according to the Glyceride Type Distribution Rule (2a) (Restricted Random Distribution is an extension of the G.T.D. Rule to the detailed structure of the individual glycerides in the glyceride types) consists in the interchange, according to chance, of one saturated acid in the trisaturated glycerides factor (i.e., trisaturated glycerides required by chance distribution minus trisaturated glycerides actually present) with the unsaturated acids in the monosaturated and triunsaturated glycerides required according to chance distribution, the former being partly converted to disaturated glycerides and the latter to a mixture of mono- and disaturated glycerides. The proportions of disaturated glycerides thus formed from triunsaturated glycerides is uauslly small and may be left out for practical calculations (2a). The equations given (2b,1) are only for these practical calculations for usual ranges of saturated acid contents which is rarely between 60 and 67% with simultaneous minimum proportions of trisaturated glycerides.

2) When the percentage proportions of saturated acids to be thus interchanged with triunsaturated glycerides become equal to, or more than, one third of the latter, the non-trisaturated portion of the fat automatically becomes converted to a mixture of mono- and disaturated glycerides, and their proportions may be calculated as shown elsewhere (3). For natural fats with no trisaturated glycerides, and saturated acids between 61.8 and 66.6%, as also for various other possibilities, this is the procedure according to the G.T.D. Rule.

The possibility of triunsaturated glycerides having negative values and the glyceride types adding to more than 100% hence do not exist, according to the G.T.D. Rule as defined by the author (2a). This rule has now been found to hold good for as many as 70 different natural fats without a single exception so far.

3) The distribution suggested by Hammond and Jones (1) differs from the G.T.D. Rule in the following respects: a) The former assumes two separate independent equilibria, one for trisaturated glyceride formation and the other for non-trisaturated glyceride formation in the same droplet of depot fat, whereas there is only a single equilibrium according to G.T.D. Rule. b) The former does not take into consideration the fact that the proportions of mono- and diglycerides formed in the earlier stages will be those required according to chance distribution, whereas the latter takes care of this. As such, any partial agreement between the values by the two distributions appears to be purely fortuitous and is devoid of theoretical significance.

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