excess NaOH catalyst was increased from 10 to 100%. At a reaction temperature of about 300C nearly comparable yields of cyclic acids were obtained at solvent ratios of 6, 3, and 1.5:1. At all temperatures, the best yields occurred at the highest solvent ratio.

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Reactivity of Zinc Oxide and Titanium Dioxide in the Presence of Dispersing Agents[1]

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Abstract

The effect of various dispersing agents on the interaction between zinc oxide and titanium dioxide in water was investigated. Addition of conventional dispersing agents to suspensions of zinc oxide and titanium dioxide reduces initial viscosities but increases the rate of interaction; however, ethylene glycol reduced interaction. Higher concentrations of dispersing agents caused foaming of the suspensions and caking of the pigments. If organic dispersing agents are replaced by inorganic phosphates, pigment interactions, foaming, and caking can be prevented in suspensions containing as much as 61% solids by weight.

Introduction

MIXTURES of zinc oxide and titanium dioxide show a rapid increase in pH and viscosity when dispersed in water without dispersing agents or other chemicals. These increases are due to a chemical interaction causing the formation of tridimensional structures (2). In 35% suspensions the interaction is most pronounced when the weight ratio of ZnO and TiO_2 is in the order of 1:2. This pigment ratio coincides with that in practical paint formulations. The pH shifts from near neutral to an equilibrium value of 9.2, and the viscosity increases by a factor of 10 in a period of 1 month after preparation.

In many emulsion paint formulations pigment interactions have been avoided by eliminating zinc oxide and using mercury compounds or other chemicals to obtain mildewcidal properties. However, other advantages obtained from the use of zinc oxide, such as better through-dry of the paint film, reduction of film degradation by U.V. absorption, and low cost, are lost.

Preliminary experiments showed that the addition of conventional organic dispersing agents did not prevent pigment interactions. Therefore a detailed study of pigment suspensions in a variety of dispersing agents was undertaken to obtain more information on the reactivities of the various components. This work showed that inorganic phosphates prevent the interaction between ZnO and TiO_2.

Experimental

Suspensions with 35 and 50% solids were prepared by weighing dry pigments into glass jars. Dispersing agents were dissolved in distilled water to the highest concentration used in a particular series of suspensions. The solution and additional water were added to the dry pigment in the right proportions necessary to obtain the desired percentage solids and dispersing agent concentration. This procedure was not successful at the 61% solids level because the dry pigment volume was too large for the containers used. Therefore, the pigments were added slowly to the dispersing agent solutions.

All suspensions were shaken for 1½ hr at 25C in a Gump shaker, and pH and viscosity measurements were carried out as described previously (2). For viscosities between 1,000 and 5,000 cp spindle No. 3 was used exclusively with the Brookfield RVF viscometer at 20 r.p.m. Below 1,000 cp spindle No. 2 was used for better precision, and spindle No. 4 was used for values above 5,000 cp only.

In the series containing ethylene glycol the pigments were shaken in the water solution before the ethylene glycol was added to prevent the formation of a stable foam.

The titrations were performed by adding a 25% commercial stock solution of dispersing agent from a micro-burette to the pigment slurry, which was stirred continuously with a Premier DD Dispersator. The Dispersator was stopped during the actual pH measurements, and more dispersing agent was added only after the pH value had become constant. The specific pigment grades and the particular dispersing agents used are given although this naming should not be construed as an endorsement over similar materials from other manufacturers:

Azo ZZZ-55 zinc oxide (American Zinc Sales Co.) and Ti-Pure R-510 titanium dioxide (Pigments Department, E. I. duPont de Nemours & Co.) were used exclusively.

Tamol 731 (sodium salt of carboxylated polyelectrolyte) and Acrysol A-1, A-3, and A-5 (polyacrylic acid with varying molecular weight) are products of Rohm & Haas Co.

The modified dialdehyde starch used was prepared at the Northern Laboratory by oxidation of dialdehyde starch with chlorine in methanol solution (3). The sodium salt was obtained by titration of an aqueous solution of the product with sodium hydroxide to pH = 9.0, and subsequent evaporation of the water at 100C.

The poly-itaconate was prepared by polymerization of itaconic acid. Itaconic acid (20 g) was dissolved in a mixture of 25 ml dioxane and 25 ml of 0.5 N hydrochloric acid, and 0.25 g potassium persulfate
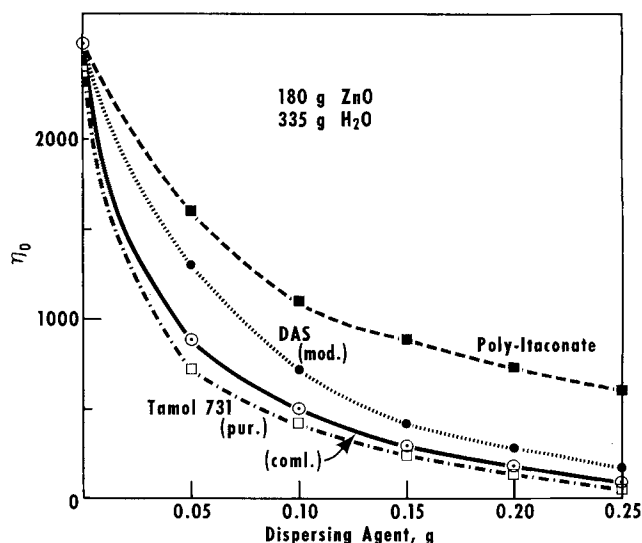
FIG. 1. Initial viscosities of 35% ZnO suspensions as function of the concentration of poly-itaconate, modified dialdehyde starch, and commercial and purified Tamol 731.

was added. After the reaction mixture was kept at 50C for 48 to 60 hr, it was slowly added to 1 liter of acetone. The polymer precipitated and was further treated as described by Marvel (1) and by Shepherd (4). The sodium salt was prepared by the same method as used for the dialdehyde starch.

A purified sample of Tamol 731 was obtained by precipitation of the acid from the commercial 25% stock solution. The solution (25 ml) was slowly added to 250 ml of 1 N hydrochloric acid. The precipitate was washed with 0.1 N hydrochloric acid solution and with water. The Tamol acid was then again dissolved in a sodium hydroxide solution. The water was evaporated under the same conditions as described earlier. Sodium salts of the Acrysols were similarly prepared.

Results

Figures 1 and 2 show the effect of 0.0 to 0.25 g of dispersing agent on the initial viscosity of suspensions containing 180 g of ZnO and 335 g of water. The following polymeric products were tested: poly-
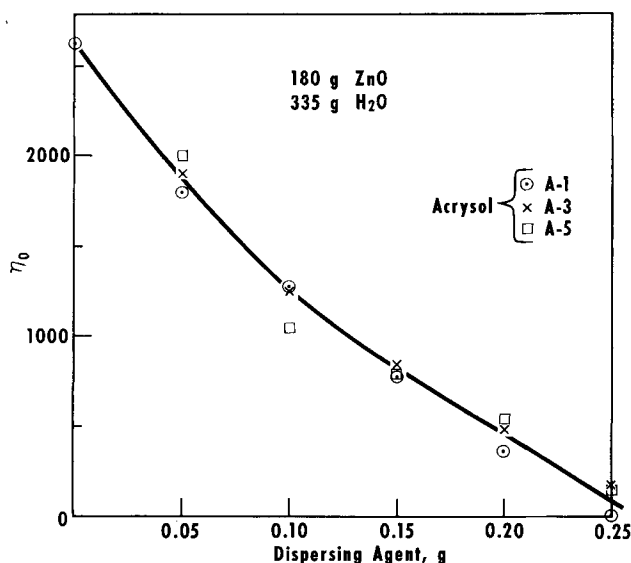

FIG. 2. Initial viscosities of 35% ZnO suspensions as function of the concentration of Acrysol A-1, A-3, and A-5.
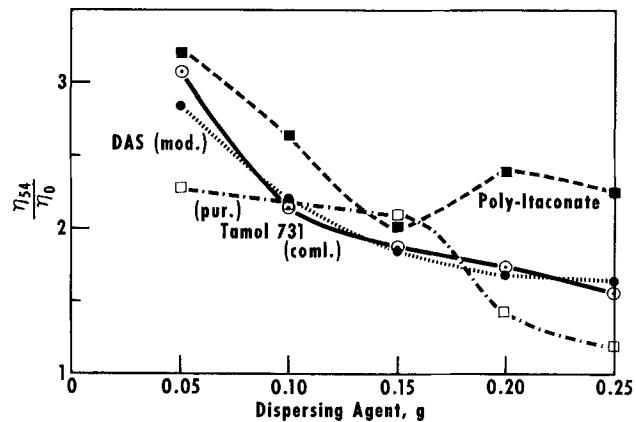

FIG. 3. Viscosity instability for 54 days as function of the concentration of poly-itaconate, modified dialdehyde starch, and commercial and purified Tamol 731.

itaconate, modified dialdehyde starch (DAS), Tamol 731, purified Tamol 731, and Acrysols A-1, A-3, and A-5. The Acrysols (Fig. 2) give a near linear dependency in contrast with the materials shown in Figure 1. Whereas a 35% ZnO suspension in water without any additives does not change viscosity appreciably with time, most of the dispersing agents produce a viscosity instability (Figs. 3 and 4). The instability is expressed as the ratio of the viscosity at 54 days to the initial viscosity. The only reasonably stable suspensions contain 0.2 g or more of purified Tamol 731 and are comparable with suspensions containing no additives.

Since the commercial Tamol was almost as effective as the purified sample, all further experiments were carried out with the commercial product.

The pH dependency on the dispersing agent concentration was determined by titration with Tamol. Three 50% suspensions were prepared containing (a) 300 g of ZnO, (b) 300 g of TiO$_2$, and (c) a mixture of 100 g ZnO and 200 g TiO$_2$. During the titrations of the ZnO and TiO$_2$ suspensions, the pH was measured after each addition of 0.1 ml of Tamol. For the titration of the mixture of ZnO and TiO$_2$ the pH measurements were made after the addition of each 0.05 ml. The results are shown in Figure 5. Sharp breaks were observed in the pH curves of ZnO and TiO$_2$ at 0.30 and 0.075 g Tamol, respectively. The arrows indicate the points at which the suspen-
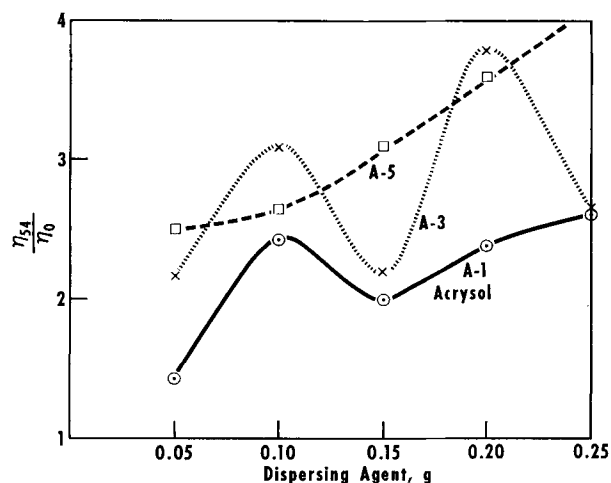

FIG. 4. Viscosity instability for 54 days as function of the concentration of Acrysol A-1, A-3, and A-5.
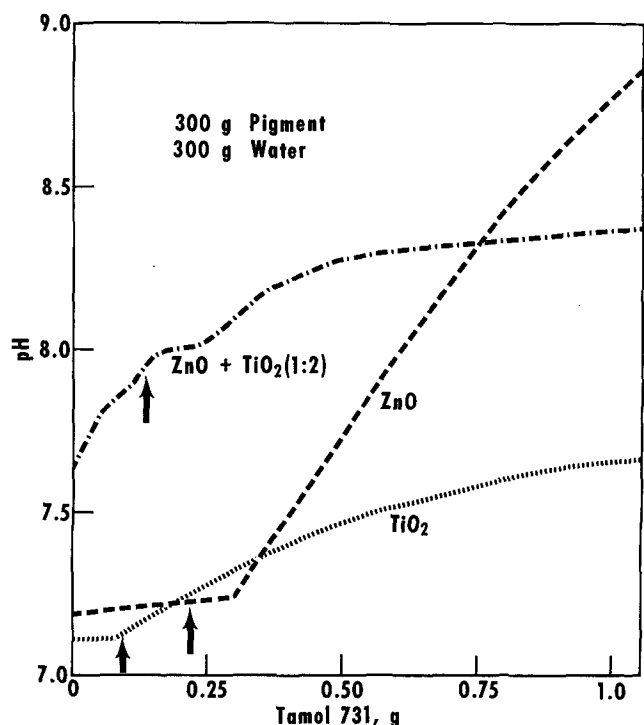
FIG. 5. Titration curves of 50% pigment suspensions with 25% commercial Tamol 731 solution. Arrows indicate the points of apparent rapid viscosity decrease.

sions appeared to become appreciably thinner. We believe this point of thinning should coincide with the break in the pH curve. With the ZnO suspension, this point appeared at a lower Tamol concentration because the Dispersator did not mix the highly viscous part of the suspension with the more liquid center.

The pH of the mixture of ZnO and TiO$_2$ started much higher and increased rapidly during the early stage of titration, because of pigment interaction (2).
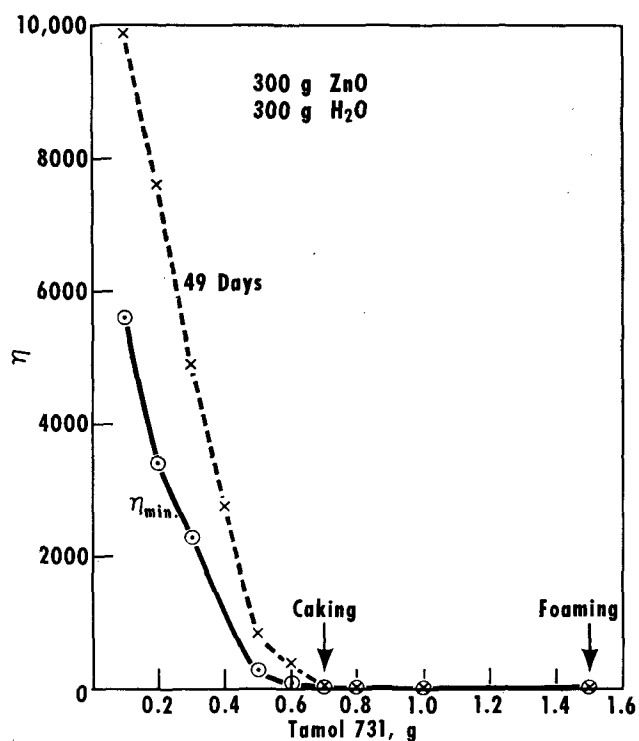

FIG. 6. Minimum and 49-day viscosities of 50% ZnO suspensions as function of the Tamol concentration.
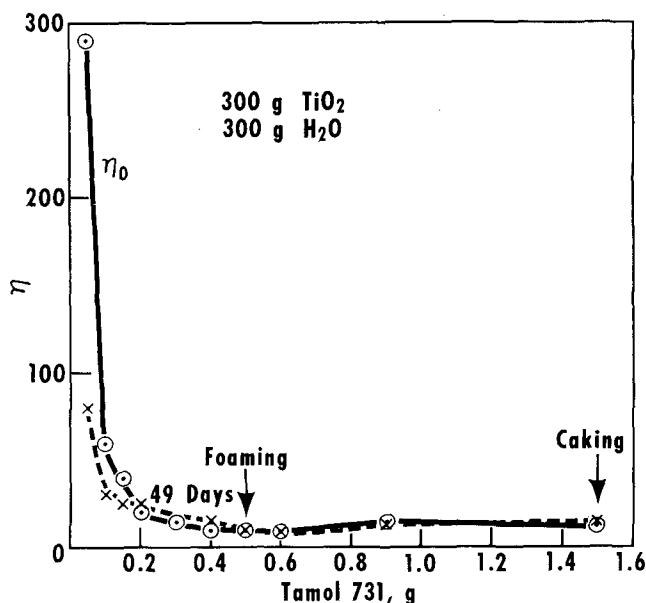

FIG. 7. Viscosities at 0 and 49 days of 50% TiO$_2$ suspensions as function of the Tamol concentration.

After 0.1 g of Tamol was added, this interaction slowed down and the curve resembled the composite of the minima in the individual pigment titrations. When 0.1 g of Tamol was added to 300 ml of water, the pH increased to approximately 10.0. From the titration curve of the ZnO-TiO$_2$ mixture it appears that up to a concentration of 0.2 g the Tamol is mainly absorbed on the TiO$_2$. Between 0.2 and 0.35 g of Tamol, a discontinuity parallel to the break in the ZnO titration curve suggests that in this region Tamol is adsorbed on the ZnO. At Tamol concentrations above 0.35 g the curve resembles the TiO$_2$ titration curve again.

The effect of Tamol concentration on viscosities of 50% ZnO and TiO$_2$ suspensions is shown in Figures 6 and 7. For ZnO suspensions the minimum viscosities are attained after 1 day. After that the suspensions containing less than 0.7 g of Tamol give a steady increase in viscosity. Above this concentration the pigment settles to the bottom of the container and forms a hard cake. When these cakes are redispersed, the same low viscosities occur. At a Tamol level of 1.5 g measurements became difficult because a stable foam formed, which could not be broken. In TiO$_2$ suspensions the viscosities decreased to low values in a few days and remained there for the entire period in which the suspensions were observed. Foaming was troublesome above the 0.5 g Tamol level, but caking of the pigment was only observed at the highest concentration tested. Evidently reactivity of ZnO is greatly increased in the presence of dispersing agents; TiO$_2$ is not affected this way.

Adding ethylene glycol to Tamol-dispersed suspensions of ZnO produces a definite effect on viscosity stability (Table I). All suspensions in this series contained 300 g of ZnO and 300 g of liquid, and the

TABLE I

Effect of Ethylene Glycol on Viscosity Increase η_{34}/η_2 for 50% Zinc Oxide Suspensions at Varying Tamol Concentrations

G H$_2$O/E.G.	G of Tamol 731 per 600 G of Suspension				
	0.2	0.4	0.6	0.8	1.0
300/0	1.6	2.3	2.7	2.0	1.1
285/15	1.6	1.6	1.2	1.3	1.1
270/30	1.2	1.3	0.9	1.1	0.9
240/60	1.4	1.7	1.1	1.3	1.0

TABLE II

Effect of Ethylene Glycol on Viscosity Increase η_{33}/η_1 for 50%
Suspensions of ZnO and TiO₂ (Wt Ratio = 1:2)

G H₂O/E.G.	G of Tamol 731 per 600 G of Suspension				
	0.2	0.4	0.6	0.8	1.0
300/0	8.1	7.4	5.0	7.3	90.0
285/15	5.5	4.7	3.9	5.4	10.7
270/30	5.3	6.1	2.1	6.1	40.7
240/60	7.6	10.3	3.3	63.3	15.6

Tamol content was varied between 0.2 and 1.0 g. The ethylene glycol concentration was varied from 0 to 20% by weight of the total added liquid phase. The glycol was added after the slurries were processed in a Gump shaker, otherwise a stable foam that formed interfered with viscosity measurements. At the highest Tamol level tested, the ZnO tended to cake at all glycol concentrations, but if the cakes were broken up and redispersed, viscosities were nearly equal to the initial values. The maximum stabilization without caking was with 10% ethylene glycol (based on total liquid phase) and 0.2% Tamol (based on pigment only).

The effect of ethylene glycol on interaction between ZnO and TiO₂ in the presence of Tamol is shown in Tables II and III. For this series the experiments were repeated with suspensions containing ZnO and TiO₂ in a weight ratio of 1:2. Table II shows the increase of the viscosity after the first 33 days. In every instance the largest increase took place during the first 6 days; thereafter the interaction slowed down considerably. This decrease in reactivity is shown in Table III where the viscosities at 6 days are used as basis for the viscosity increase at 33 days. Those values marked with a superscript "a" did not increase at all after the first 12 days. Again the best results were with 10% ethylene glycol (based on liquids only) and 0.2% Tamol (based on solids only). The viscosity increases only by a factor of 2.1 in 33 days, and no increase is indicated after the first 6 days. Unquestionably ethylene glycol does slow down the pigment interaction but does not prevent it entirely.

During the study of the effect of various electrolytes on the interaction between ZnO and TiO₂ it was discovered that the addition of phosphates produced an unsuspected result. The addition of 16.75 mmoles KH₂PO₄ and 9.93 mmoles NaOH (buffer solution with pH = 7.0) to 35% pigment suspensions with varying ratios of ZnO and TiO₂ gives the pH effect as shown in Figure 8. Viscosities for the entire series were low and constant with time. The pH values shown in Figure 8 are equilibrium values reached after several days. The pH of the 35% ZnO suspensions increased from 7.2 in water to 10.9 in the phosphate buffer, whereas the 35% TiO₂ suspension increased only 0.1 of 1 pH unit. The pH increase indicates that the phosphate ion is strongly adsorbed on the ZnO. If the phosphate ion is also adsorbed on the TiO₂, the mechanism must be different as indicated by the difference in pH increase. By this action the reactivity
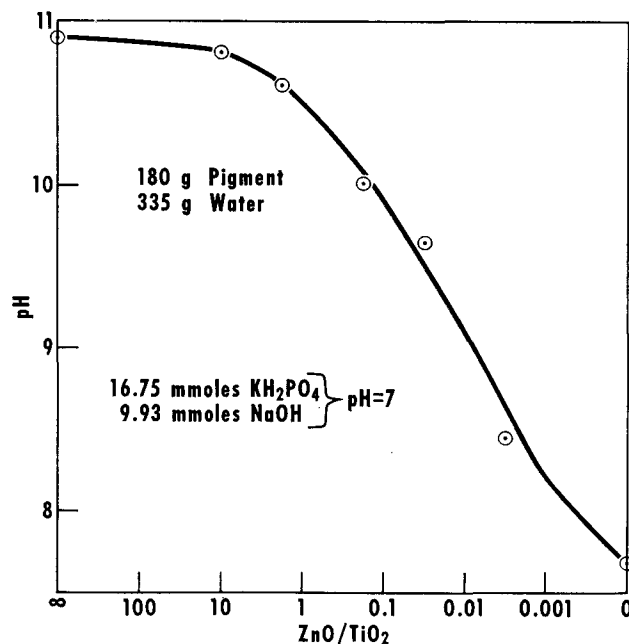

FIG. 8. pH versus ZnO/TiO₂ for 35% suspensions containing phosphate buffer.

of ZnO is reduced to a large extent, and interaction between the pigments is stopped.

After this discovery, a series of suspensions containing 61% by weight of a mixture of ZnO and TiO₂ in the ratio of 1:2 and varying KH₂PO₄ and NaOH concentrations was prepared. Four stock solutions containing 21.7 g of KH₂PO₄ each and 0.00, 1.33,

TABLE III

Effect of Ethylene Glycol on Viscosity Increase η_{33}/η_6 for 50%
Suspensions of ZnO and TiO₂ (Wt Ratio = 1:2)

G H₂O/E.G.	G of Tamol 731 per 600 G of Suspension				
	0.2	0.4	0.6	0.8	1.0
300/0	2.16	1.84	1.35	1.45	2.70
285/15	1.87[a]	1.34[a]	1.05[a]	1.11[a]	1.85
270/30	1.39[a]	1.44[a]	0.83[a]	1.19[a]	5.59
240/60	1.79	1.72	1.29[a]	1.51[a]	3.16

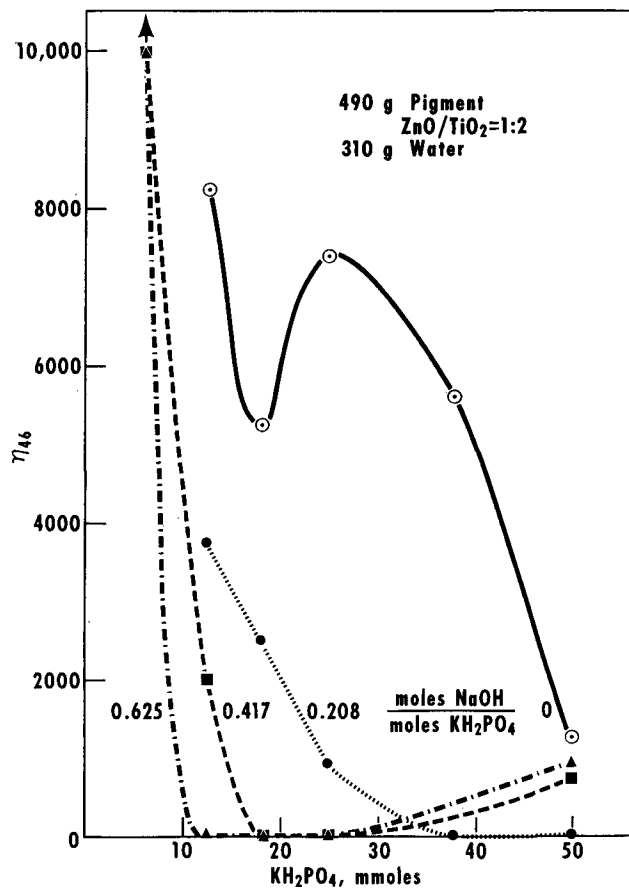[a] These suspensions did not change viscosity during last 21 days.

FIG. 9. Viscosities of 61% suspensions of ZnO/TiO₂ mixtures at 46 days as function of KH₂PO₄ concentration and varying ratios of NaOH and KH₂PO₄.
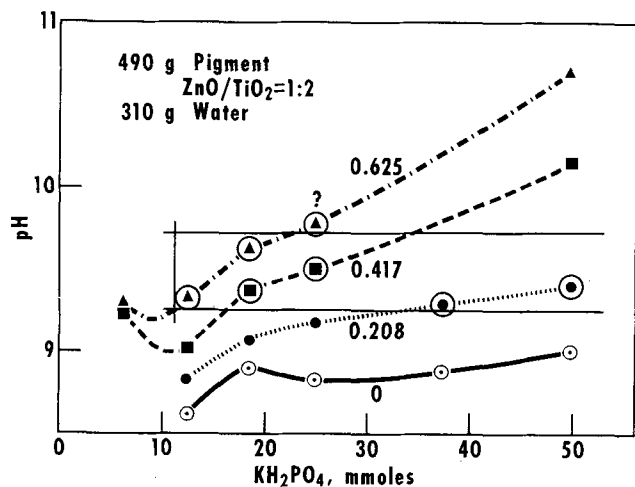
FIG. 10. pH as function of KH$_2$PO$_4$ concentration and varying ratios of NaOH and KH$_2$PO$_4$ for 61% pigment suspensions. The circled data have low stable viscosities.

2.66, and 4.00 g of NaOH, respectively, per liter were made. The pH values of these respective solutions were 4.5, 6.15, 6.6, and 7.0. Five suspensions were prepared containing 12.5, 17.5, 25.0, 37.5, and 50.0 mmoles KH$_2$PO$_4$ per 490 g of total pigment from each of the first two solutions. From the other two solutions 5 suspensions each were made containing 6.25, 12.5, 17.5, 25.0, and 50.0 mmoles KH$_2$PO$_4$. All viscosities became minimal after approximately 4 days; those at 46 days are shown in Figure 9. Suspensions having initial viscosities of less than 100 cp remained constant with time, whereas those with higher initial viscosities increased regularly. Equilibrium pH values are shown in Figure 10. Suspensions containing 6.25 mmoles KH$_2$PO$_4$ increased very rapidly in viscosity, and the pH increased from 8.8 to 9.2, which is also the equilibrium value for the interaction between ZnO and TiO$_2$ without additives. Suspensions having
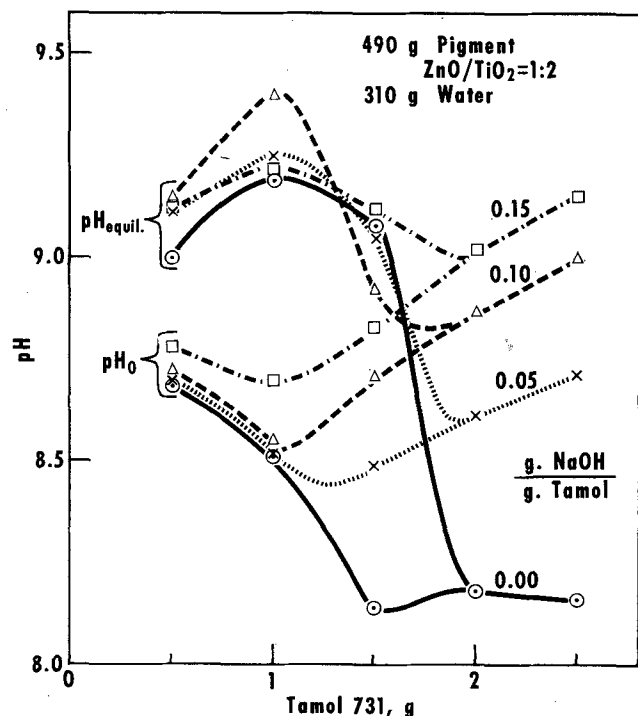

FIG. 11. pH as function of Tamol concentration and varying ratios of NaOH and Tamol for 61% pigment suspensions.

constant viscosities of less than 100 cp are indicated by a circle in Figure 10, and it can be seen that viscosity stability is achieved only if the phosphate concentration and the pH are kept within the rectangular area shown. A small deviation from this pH range (9.25–9.75) is sufficient to increase both the initial viscosity and viscosity instability.

The experiments were repeated at the 61% solids level with Tamol instead of phosphate. Four stock solutions containing 8.07 g of Tamol and 0.0, 0.4, 0.8, and 1.2 g of NaOH, respectively, per liter were prepared. The respective pH values were 10.3, 11.35, 11.8, and 12.0. From each solution 5 suspensions were prepared so that they contained 0.5, 1.0, 1.5, 2.0, and 2.5 g of Tamol, respectively, per 490 g of pigment (Fig. 11). The pH of those suspensions containing less than 2.0 g of Tamol rises rapidly to approximately 9.2 and the viscosities increase to values over 10,000 cp in the same time. Slurries containing 2.0 or 2.5 g of Tamol have constant pH values and viscosities between 30 and 50 cp, independent of NaOH concentration. However, caking of the pigment was again a problem at 2.0 g of Tamol and above. Before each measurement the pigment cake had to be broken up and redispersed. These experiments show that the addition of sodium hydroxide does not improve the qualities of Tamol-dispersed ZnO-containing suspensions.

Discussion

Inorganic phosphates have great advantages over conventional organic dispersing agents in suspensions containing ZnO. Within the pH range of 9.25 and 9.75 the interaction between ZnO and TiO$_2$ can be prevented completely. Foaming of the suspensions is eliminated and although the pigment settles to the bottom of the container, it is easily redispersed by turning the container over gently once or twice.

The behavior of ZnO and TiO$_2$ is entirely different in the presence of phosphate than it is with Tamol and similar dispersing agents. When the pigments are dispersed in a phosphate solution, the pH rises greatly to equilibrium values between 9.25 and 9.75 for viscosity stable suspensions. When dispersed in Tamol solutions, the pH is decreased from very basic to between 8.2 and 9.2. The explanation for this contrasting behavior may be that the adsorption of Tamol is mainly a physical phenomenon and does not prevent the ZnO from dissolving in the alkaline solution, whereas the phosphate is chemisorbed and makes the ZnO particle surface much more inactive. The chemisorption may also account for the lower reactivity with TiO$_2$.

Since the mildewcidal properties of the phosphate-dispersed ZnO may be affected, linseed oil emulsion paint formulations containing these systems have been prepared and are being tested presently in several locations. The results will be published later.

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