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SURFACE CHARGE OF TITANIUM DIOXIDE AND ITS EFFECT ON DYE ADSORPTION AND AQUEOUS SUSPENSION STABILITY

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ABSTRACT

The point of zero charge (PZC) of pigmentary food grade and fumed titanium dioxide was investigated and observed to be variable, possibly due to the presence of impurities in the samples. The adsorption of FD&C yellow #5 and methylene blue USP from aqueous solution by the titanium dioxide samples was studied as was the relative stability of aqueous suspensions of the titanium dioxide samples. Both the dye

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adsorption and the suspension stability were found to be dependent on the pH of the oxide suspension and the PZC of the titanium dioxide.

INTRODUCTION

Titanium dioxide is widely used as an opacifier in sugar and film coatings. For this purpose, it is often included in aqueous coating suspensions with other ingredients, including water soluble dyes. In aqueous suspension, titanium dioxide possesses a pH-dependent surface charge. This charge is due to hydroxyl groups at the surface of the oxide and may be represented by the following equilibria (1).

$$\mathrm{Ti - OH_2^{+}} \;\underline{\qquad\qquad}\; \mathrm{Ti - OH} \;\underline{\qquad\qquad}\; \mathrm{Ti - O^{-} + H^{+}}$$

$$\longleftarrow\!\!\!-\!\!\!-\!\!\!- \; \text{Decreasing pH} \qquad \text{Increasing pH} \; -\!\!\!-\!\!\!-\!\!\!\longrightarrow$$

The presence of a surface charge on colloidal particles in aqueous suspension may influence the interaction of the particles with other charged species, including water soluble dyes, present in the system as well as influence the dispersion of the suspension.

An important parameter in defining the charge characteristics of surfaces is the Point of Zero Charge (PZC), which is the pH at which the net surface charge is zero. The PZC of various titanium dioxide samples has been studied (2-4), and reported PZC values are highly variable and may be dependent on the presence of impurities (2,3). Published studies are generally concerned with the rutile polymorph of titanium dioxide which is widely used as a pigment, particularly in the paint industry. Considerably less information is available on the surface charge characteristics of titanium dioxide samples with respect to pharmaceutical formulations, in which the anatase polymorph finds use.

The purpose of this study was to examine the PZC and the surface charge of selected anatase titanium dioxide samples. It was further intended to study the effect of such surface charge on the adsorption of water soluble dyes which exist as charged species in aqueous solution, and on the dispersion of titanium dioxide in aqueous suspension.

MATERIALS AND METHODS

Materials

Two samples of titanium dioxide, food grade titanium dioxide (H. Kohnstamm & Co., Inc., New York, N.Y.), and Cab-O-Ti, fumed titanium dioxide (Cabot Corp., Boston, MA) were studied. FD&C yellow #5 (H. Kohnstamm & Co., Inc., Camden, N.J.) and methylene blue USP (Fisher Scientific Co., Fair Lawn, N.J.) were used as obtained from the suppliers without further purification. All other chemicals were reagent or analytical reagent grade. All water was distilled following deionization.

Point of Zero Charge Determination

The PZC of the titanium dioxide samples was determined by titration using the technique employed by Feldkamp, et. al. (5), for aluminum hydroxide gels with slight modification for the titanium dioxide samples. In the procedure, 5 grams of titanium dioxide, or 2 grams of the fumed oxide, were dispersed in 125 mls of distilled, deionized water. The ionic strength was adjusted using potassium nitrate which has been shown to be an indifferent electrolyte to titanium dioxide (6). Three sample suspensions, each at a different ionic strength were prepared and titrated for each sample of titanium dioxide. Following preparation, all sample suspensions were stirred for 1 hour and allowed to equilibrate overnight. The following day, the sample suspensions were placed on a pH meter with continuous stirring and titrated with either 0.025 or 0.1 N nitric acid or 0.025 N potassium hydroxide, depending on the particular sample. Titrant was added in small increments by means of a 50 microliter syringe, and the samples were allowed to equilibrate approximately 1-2 minutes before recording the pH and performing the following titrant addition. The micromoles of titrant added were plotted versus the pH, and the PZC of each titanium dioxide sample was determined from the intersection of the three titration curves for each sample.

Zeta Potential Measurement

The zeta potential of the titanium dioxide samples was determined by electrophoresis using an Electrophoretic Mass-Transport Analyzer (Model M1C-1201, Numec Instruments and Controls Corp., Apollo, PA). Sample suspensions were prepared containing 5 grams of titanium dioxide per 100 milliliters of 10^{-4}M potassium nitrate solution prepared with distilled, deionized water. The pH of these samples was adjusted using either nitric acid or potassium hydroxide.

Polymorphic Form, Particle Size and Shape

The polymorphic composition of the titanium dioxide samples was determined by powder X-ray diffraction. Scanning electron microscopy was used to determine the size and shape of the titanium dioxide particles.

Analysis of Impurities

Selected titanium dioxide samples were treated for the removal of impurities. The samples were washed with 0.1 N HNO_3 at 80°C for 15 minutes, filtered, and rinsed with distilled, deionized water. The acid washed samples were then washed with 0.1 N KOH at 80°C for 15 minutes, filtered, and rinsed with distilled, deionized water. Finally, the samples were dried at 150°C. X-ray spectrometry was used to analyze the samples for the presence of impurities both before and after treatment. In addition, washings recovered from the treatment of the titanium dioxide samples with 0.1 N KOH were analyzed for the presence of phosphate and sulfate. The presence of phosphate was determined colorimetrically by the Heteropoly Blue Method (7) and the presence of sulfate was determined turbidimetrically after precipitation as barium sulfate (8).

Adsorption of Dyes Versus pH

The adsorption of two water soluble dyes, FD&C yellow #5, an anionic dye, and methylene blue USP, a cationic dye, by the titanium dioxide samples was studied. Samples were prepared by placing an accurately weighed 3 gram sample of titanium dioxide, or a 2 gram sample of fumed titanium dioxide, into a

250 ml Erlenmeyer flask. To the sample, a total of 100 mls of dye stock solution and distilled, deionized water were added to produce a final concentration of 70 mg/100 mls of either FD&C yellow #5 or methylene blue USP. Necessary pH adjustments were made during the addition of the dye solution using either HNO_3 or KOH. Each sample was sealed with a rubber stopper lined with Parafilm to prevent any adsorption of the dye by the stopper, and each sample was sonicated for 5 minutes to insure adequate dispersion. The samples were then placed in a mechanical shaker bath at a temperature of 23 ±1°C. Blank samples containing dye solution but no titanium dioxide were also prepared and tested.

Preliminary experiments indicated that adsorption equilibrium of the two dyes with the titanium dioxide samples was reached in 2-4 hours with the greatest extent of adsorption occurring in less than 1 hour. An exception to this, however, was the adsorption of FD&C yellow #5 by the fumed titanium dioxide, for which equilibrium required approximately 5 days. An equilibrium period of 24 hours was considered sufficient and was used for all adsorption studies except those involving FD&C yellow #5 and fumed titanium dioxide for which an equilibrium period of 7 days was used.

At the appropriate sampling times, 30 mls of each sample suspension were placed in a 40 ml glass centrifuge tube and centrifuged at 4000 rpm, equivalent to a relative centrifugal force (RCF) of 2202 G, for 10 minutes. Also, the pH of each sample suspension and blank was measured on a standard pH meter equipped with a combination electrode. Following centrifugation, the supernatant liquid from each sample was decanted into a second 40 ml glass centrifuge tube and recentrifuged at 4000 rpm for 10 minutes.

The resulting supernatant solutions and blanks were diluted with distilled, deionized water to a suitable concentration and assayed spectrophotometrically taking an average of 3 individual readings. Previous studies indicated that a change in the absorbance at 426 nm for aqueous solutions of FD&C yellow #5 occurred at a pH of 8.0 and above. Therefore, samples containing FD&C yellow #5 at pH 7.0 and above were buffered to pH 5.0 using a neutralized phthalate buffer before spectrophotometric measurements were made. FD&C yellow #5 solutions were assayed at 426 nm and methylene blue solutions at 664 nm. The amount of free, unadsorbed dye remaining in the titanium dioxide suspensions was calculated from the spectrophotometric data and compared to that for the blank solutions in order to determine the amount of dye adsorbed by the titanium dioxide samples.

Relative Stability of Titanium Dioxide Dispersions

Sample suspensions were prepared containing 5 grams titanium dioxide/100 mls with distilled, deionized water. Nine suspensions, covering a pH range of approximately 2-8 were prepared for each titanium dioxide sample studied. The pH of the suspensions was adjusted during preparation using either 0.025 N HNO_3, 1.4 N HNO_3, or 0.025 N KOH. The suspensions were placed in 100 ml graduated cylinders, dispersed by shaking, and allowed to settle undisturbed for 24 hours. During this time, the general settling behavior and the volume of any sediment which formed were noted. Also, the pH of each sample suspension was recorded after 24 hours.

RESULTS AND DISCUSSION

Initial attempts to determine the PZC of the food grade titanium dioxide samples by titration proved unsuccessful. At a pH of 3.0, the addition of KNO_3 to the suspensions resulted in a decrease in the pH of the samples indicating a PZC of less than 3.0 for the samples. At such acidic pH values, the titration procedure may no longer be used for PZC determination. Since such a low PZC value for titanium dioxide had not been encountered in published reports, it was suspected that some impurity may have been responsible for the observed behavior. Therefore, the sample of titanium dioxide was washed with 0.1 N HNO_3 followed by washing with 0.1 N KOH. X-ray powder diffraction of the untreated and treated samples indicated that no conversion of the crystalline form of the titanium dioxide, which was determined to be anatase, had occurred as a result of the treatment. Also, scanning electron photomicrographs of the two samples revealed no significant changes in the particle size and shape of the samples, which were composed of aggregates of smaller primary particles ranging from 0.1 - 0.3 microns in diameter and of roughly spherical shape. Titration of the treated sample indicated a PZC of 4.65 for the sample as shown in Figure 1 which illustrates the PZC plot. Titration of a sample of the oxide which was only subjected to the acid wash with 0.1 N HNO_3 proved unsuccessful, showing little difference from the untreated sample and indicating

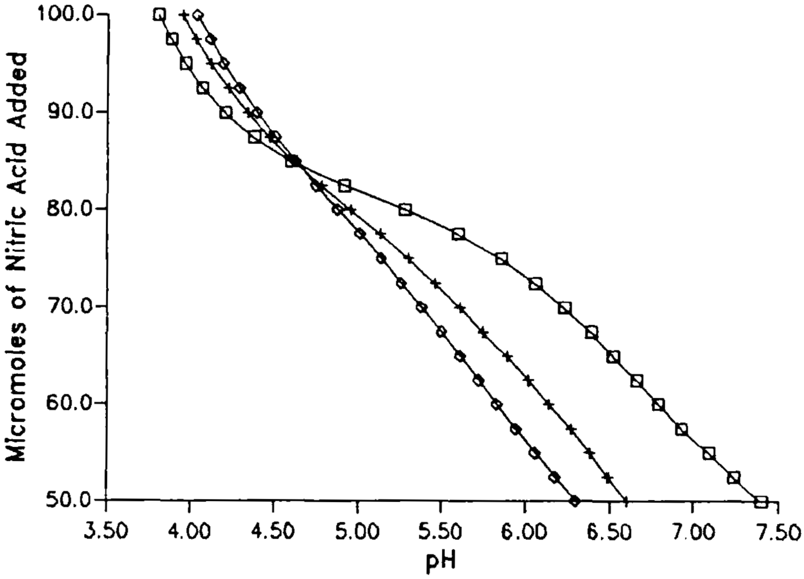

Figure 1. Titration plot for treated titanium dioxide indicating a PZC of 4.65 for the sample. (Key: - no adjustment of ionic strength; - added ionic strength 0.04; - added ionic strength 0.20).

the importance of the basic wash with 0.1 N KOH in bringing about the observed increase in PZC.

Pure samples of titanium dioxide are reported to have a PZC in the range of 5.5 - 6.0 (3, 4). The PZC of 4.65 for the treated sample as compared to the lower PZC originally indicated for the untreated sample is thought to correspond to the removal of impurities from the sample during treatment. Titration of the fumed titanium dioxide yielded a PZC of 6.83 indicating that sample to be relatively pure as received from the supplier with respect to impurities which influence the PZC. The fumed titanium dioxide studied possesses a very small particle size, averaging 0.03 microns, and is composed of 85-90 percent anatase with the remainder rutile (1). The presence of a small percentage of rutile in the sample was confirmed by powder X-ray diffraction.

The zeta potential in 10^{-4}M KNO_3 solution was determined to be -40.0 mV at a pH of 7.59 for the untreated food grade titanium dioxide and -12.0 mV at a pH of 7.56 for the sample washed with acid and base (Table 1). The recorded zeta potentials are indicative of a substantial negative charge present at the surface of both the untreated and treated samples at these pH values. The surface charge on the samples may be expected to be negative at pH values above the PZC, and these results are consistent with the PZC values indicated for the samples in previous studies.

The untreated and treated samples of the oxide were analyzed by X-ray spectrometry for the presence of impurities. The results (Table 2) indicate the purity of the samples for the elements listed. The presence of impurities which form oxides such as aluminum, iron, and silicon may result in the formation of a mixed oxide system. The PZC of such

Table 1. Properties of Titanium Dioxide Samples

Sample	PZC	Zeta Potential (mV)	Particle Size (microns)	Polymorphic Form
Untreated	<3.0	-40.0 (pH = 7.59)	0.1-0.3	Anatase
Treated	4.65	-12.0 (pH = 7.56)	0.1-0.3	Anatase
Fumed	6.83	-	0.03	Anatase/ Rutile

Table 2. Results of X-ray Analysis of Titanium Dioxide Samples

Sample	Impurity (percent by weight)	
Untreated Titanium Dioxide	Aluminum	0.26
	Chlorine	0.00
	Copper	0.66
	Iron	0.00
	Silicon	0.02
Treated Titanium Dioxide	Aluminum	0.51
	Chlorine	0.00
	Copper	0.20
	Iron	0.00
	Silicon	0.26

mixed oxides lies at a pH between the PZC values of the pure oxides which comprise the mixed oxide (10). The PZC of silicon dioxide is generally in the range of 1-3 (2); however, at the levels detected in this study, it is not believed that the formation of a mixed oxide system is responsible for the observed PZC values of the titanium dioxide samples.

The solution recovered following washing of the titanium dioxide with 0.1 N KOH, a step which has been shown to be critical in producing an increase in the PZC of the titanium dioxide, was analyzed for phosphate and sulfate. The results indicated no detectable presence of sulfate in the solution. However, a significant amount of phosphate, equivalent to 0.3% of the weight of the titanium dioxide, was detected as being removed from the sample during the washing procedure. Phosphate has been found to specifically adsorb to oxides including aluminum hydroxide to which it is thought to be specifically adsorbed by a ligand-exchange reaction independent of surface potential (11, 12). In general, the specific adsorption of anions increases the negative charge on the surface and shifts the PZC to more acidic values (10). Liu, et al. (12), recorded a decrease in the PZC of aluminum hydroxide gels from 9.8 to 4.1 corresponding to the specific adsorption of phosphate. It appears that the very acidic PZC indicated for the untreated titanium dioxide may be due to the presence of phosphate which is specifically adsorbed and that the increase in PZC determined following washing of the sample may be due to the removal of some portion of that phosphate.

The adsorption of both FD&C yellow #5 and methylene blue USP by the titanium dioxide samples was studied and found to be variable between samples. The untreated titanium dioxide did not adsorb the anionic dye, FD&C yellow #5, over the entire pH range of 2 to 7. However, the treated titanium dioxide (PZC 4.65) and fumed titanium dioxide (PZC 6.83) adsorbed significant amounts of this dye at pH values below the PZC of the samples, and the amount of dye adsorbed increased with decreasing pH (Fig. 2 and Fig. 3). In contrast to these results, adsorption of the cationic dye, methylene blue USP, was found to occur over the entire pH range of 2 to 7 for the untreated titanium dioxide (Fig. 4) and at pH values above the PZC for the treated sample (Fig. 5). In both cases, the amount of methylene blue USP adsorbed was observed to increase with increasing pH.

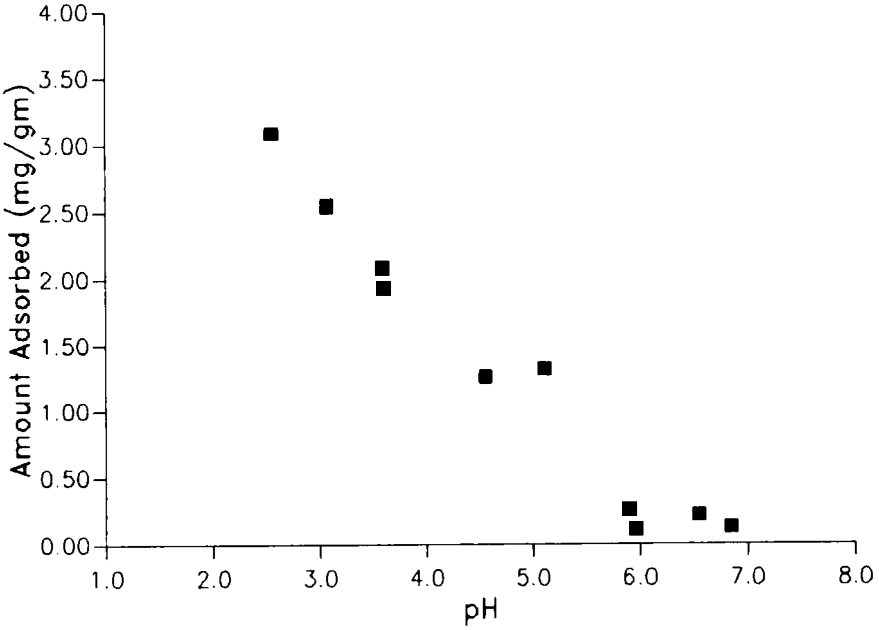

Figure 2. Adsorption of FD&C yellow #5 by treated titanium dioxide versus pH.

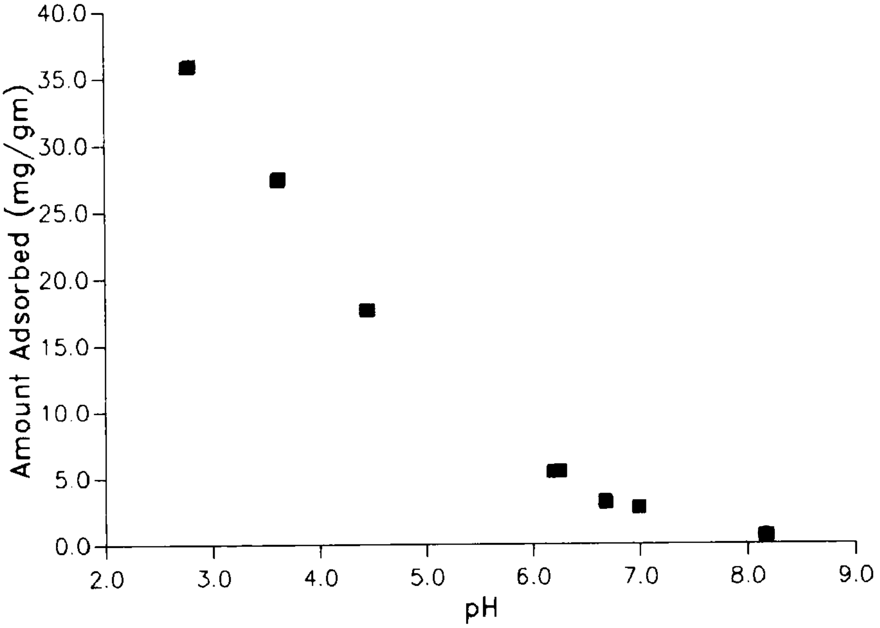

Figure 3. Adsorption of FD&C yellow #5 by fumed titanium dioxide versus pH.

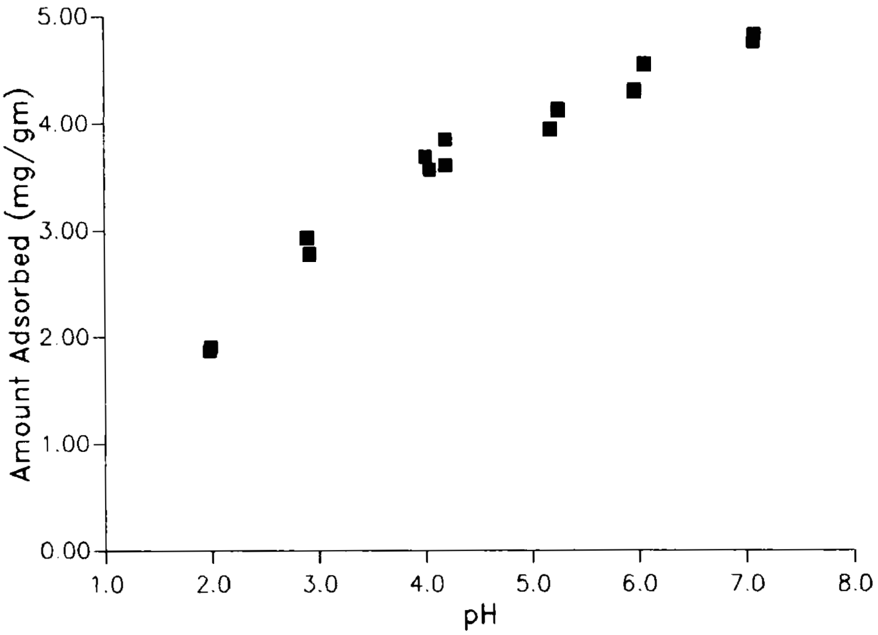

Figure 4. Adsorption of methylene blue USP by untreated titanium dioxide versus pH.

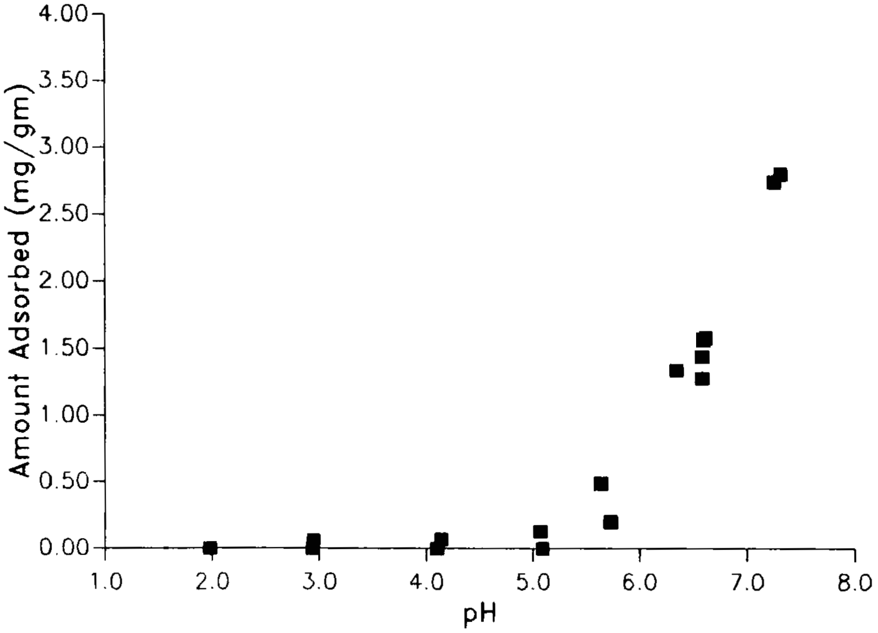

Figure 5. Adsorption of methylene blue USP by treated titanium dioxide versus pH.

These results show the adsorption of the two dyes to be dependent on the surface charge of the titanium dioxide samples. Adsorption of anionic FD&C yellow #5 occurs at pH values below the PZC where the net surface charge on the oxide is positive. Similarly, adsorption of cationic methylene blue USP occurs at pH values above the PZC where the net surface charge is negative. This suggests that the adsorption is due to electrostatic attraction and is non-specific in nature. Such adsorption will not affect the PZC of the samples. The results for the untreated titanium dioxide (Fig. 4) also appear to indicate a negative surface charge exists on the sample at a pH of approximately 2.0. This is in support of previous results suggesting a very acidic PZC value for this sample. It should also be noted that the amount of FD&C yellow #5 adsorbed was, in general, much greater for the fumed titanium dioxide than the treated food grade titanium dioxide. This is believed to be due to a difference in surface area for the two samples as related to particle size.

The relative stability of aqueous dispersions of the untreated and the treated titanium dioxide samples was dependent on the pH of the suspensions over the pH range from approximately 2 to 8. The results listed in Table 3 show that for the untreated titanium dioxide only the suspensions at pH 2.24 and 2.97 settled during the test period. The settling observed in these samples occurred rapidly and immediately upon preparation of the suspensions. The suspensions at pH 3.73 and above, however, remained suspended with no settling observed after 24 hours. For the treated titanium dioxide, rapid settling occurred in the suspensions at and between pH 3.81 and 6.93, while the suspensions at pH values outside this range remained stable and well dispersed for 24 hours.

These results demonstrate the importance of surface charge, as influenced by pH, in determining the stability of aqueous titanium dioxide suspensions. At pH values furthest from the PZC of the titanium dioxide samples, a significant surface charge, positive or negative, is present on the titanium dioxide particles. This surface charge gives rise to repulsive forces which are of a magnitude and which operate over a sufficient distance from the surface to counteract attractive forces between the particles. Thus, suspensions at these pH values will remain dispersed for extended time periods. As the pH approaches the PZC, the repulsive forces will be diminished until at some pH the attractive forces

Table 3. Sediment Volumes of Titanium Dioxide Suspensions After 24 Hours

Sample	pH	Sediment Volume (milliliters)
Untreated Titanium Dioxide	2.24	23.0
	2.97	21.5
	3.73	N
	4.16	N
	4.80	N
	5.80	N
	6.79	N
	7.50	N
	7.94	N
Treated Titanium Dioxide	2.15	N
	3.02	N
	3.81	12.0
	4.19	15.0
	4.55	21.0
	5.71	21.0
	6.93	13.0
	7.60	N
	8.44	N

N: denotes no significant sedimentation occurred

between the particles will predominate and cause flocculation to occur.

The results given in Table 3 show that suspensions at the pH values furthest from the PZC of the titanium dioxide samples remain dispersed after 24 hours. As the pH of the suspensions approaches the PZC, settling begins to take place. The untreated sample at pH 2.24 and the treated sample at pH 5.71

exhibited marked flocculation accompanied by rapid settling and the formation of a sediment which could be easily resuspended by shaking. This result for the suspension containing untreated titanium dioxide is consistent with previous results which suggest a very acidic PZC for that sample of titanium dioxide.

CONCLUSION

The PZC of the titanium dioxide samples studied was variable. Deviations in the PZC from that normally reported for pure titanium dioxide samples appeared to be due to the presence of impurities. Treatment of the oxide samples to remove such impurities resulted in a shift in the PZC to values nearer to those reported for pure samples. The adsorption of both FD&C yellow #5 and methylene blue USP from aqueous solution by the titanium dioxide samples was dependent on pH and the PZC of the samples. This suggested a non-specific adsorption based on electrostatic attraction. The amount of dye adsorbed was inversely related to the particle size of the titanium dioxide. The relative stability of aqueous suspensions of the titanium dioxide samples was observed to depend on the pH of the suspensions and its relation to the PZC of the samples.

Flocculation and rapid settling was observed in suspensions at pH values near to the PZC of the samples.

Due to its surface charge, titanium dioxide has a significant potential to interact with other components of aqueous suspensions and to influence the physical properties of these suspensions. Titanium dioxide is often included in aqueous coating suspensions with numerous other components, including water soluble polymers. It is conceivable that interactions with other components may also occur and lead to marked effects on the properties of both the coating suspensions as well as the coatings prepared from them.

REFERENCES

1. G. D. Parfitt, Croat. Chem. Acta, 45 (1973) 189-194.

2. G. A. Parks, Chem. Rev., 65 (1965) 177-198.

3. R. M. Cornell, A. M. Posner and J. P. Quirk, J. Colloid Interface Sci., 53 (1975) 6-13.

4. Y. G. Berube and P. L. DeBruyn, J. Colloid Interface Sci., 27 (1968) 305-318.

5. J. R. Feldkamp, D. N. Shah, S. L. Meyer, J. L. White and S. L. Hem, J. Pharm. Sci., 70 (1981) 638-640.

6. G. D. Parfitt, J. Ramsbotham and C. H. Rochester, J. Colloid Interface Sci., 41 (1972) 437-444.

7. M. Halmann, "Analytical Chemistry of Phosphorous Compounds," Wiley-Interscience, New York, 1972.

8. "The United States Pharmacopeia," 22nd revision, Mack Publishing Co., Easton, Pennsylvania, 1990.

9. "Technical Bulletin," Cabot Corporation, Boston, Massachusetts, 1968.

10. G. A. Parks, "Aqueous Surface Chemistry of Oxides and Complex Oxide Minerals" in Equilibrium Concepts in Natural Water Systems, R. F. Gould, editor, Am. Chem. Soc., Washington, D.C. (1967) 121-160.

11. F. J. Hingston, R. J. Atkinson, A. M. Posner and J. P. Quirk, Nature (London), 215 (1967) 1459-1461.

12. J. Liu, J. R. Feldkamp, J. L. White and S. L. Hem, J. Pharm. Sci., 73 (1984) 1355-1358.