Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Rubin, Alan J. and Haberkost, Donald C.(1973) 'Coagulation and Flotation of Colloidal Titanium Dioxide', Separation Science and Technology, 8: 3, 363 — 373
To link to this Article: DOI: 10.1080/00372367308058009
URL: http://dx.doi.org/10.1080/00372367308058009

SEPARATION SCIENCE, 8(3), pp. 363–373, 1973

Coagulation and Flotation of Colloidal Titanium Dioxide

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Abstract

The foam separation of dispersed and coagulated titanium dioxide was investigated using anionic and cationic collector surfactants in a batch flotation system. Aluminum sulfate was used as the coagulating agent, and ethanol served as the frother. Removal was studied as a function of pH with coagulant and collector concentrations as parameters.

INTRODUCTION

Titanium dioxide (TiO_2) is a crystalline material having an extremely small particle size of 0.1 to 0.4 μ that forms a negatively charged sol in aqueous media. Because of its colloidal properties and high refractive index, about 2.55, TiO_2 suspensions are very stable in dilute concentrations and have an intense white to blue color. This material is used as a filler and brightener in high quality paper and as a white pigment for paints (*1*). As a consequence of the manufacturing process, it is commonly present in the waste effluents of these and related industries. The effective and economic recovery of TiO_2 offers both the possibility of savings in process costs and the solving of a significant pollution problem.

Past research on colloid flotation and microflotation has shown these foam separation techniques to be effective for the removal of inorganic as well as organic sols (e.g., Refs. *2–6*). The two processes differ in that the state of dispersion of the particles to be removed are different. In colloid flotation discrete particles are separated and because of their very small size the transport mechanism may appear to be by partition. The partition mechanism is most obvious and strictly applies when soluble components are separated as with foam fractionation. True flotation occurs whenever coarsely suspended materials are removed by foaming. This is the case with microflotation in that the colloidal particles are aggregated before flotation. The aggregation or enmeshment of the sols is accomplished by the addition of a hydrolyzable metal salt or other coagulating agent and pH control. In effect, microflotation is a variation of the foam separation technique of precipitate flotation (*7*).

This investigation was undertaken (a) because of its practical implications and (b) because TiO_2 represents a completely different colloidal system than has previously been studied. The collectors chosen for the study were the strongly ionized surfactants sodium lauryl sulfate (NaLS) and hexadecyltrimethylammonium bromide (CTAB) in aqueous solutions with ethanol frother. Aluminum sulfate was the only metal coagulant used. The flotation experiments were run at a single gas flow rate in a batch system. Several coagulation-settling experiments were also run to examine the effects of metal coagulant and collector on the stability of the sol.

EXPERIMENTAL

The experimental apparatus was a nitrogen gas system designed for the precise control of gas flow rate. A schematic of the apparatus and other details of its construction have been described elsewhere (*2*, *8*). The flotation cell was a 600-ml glass Buchner funnel having a fine sintered-glass frit.

Titanium dioxide suspensions were prepared with Zopaque RG obtained from the Glidden-Durkee Division of SCM Corp. Baltimore, Maryland. This material is a water dispersible powder of the anatase crystal type. Stock suspensions were prepared by adding 4 g to a half-gallon of deionized-distilled water and mixing for several minutes in a Waring blender. This was transferred to a clean 5-gal glass carboy and diluted with five volumes of water to each volume of stock to obtain the working suspension.

Sodium lauryl sulfate, 99.5% (Sipon WD) was supplied by the Alcolac Chemical Corp., Baltimore, Maryland. Technical grade CTAB was purchased from Eastman Organic Chemicals, Rochester, New York. These surfactants were used without further purification and prepared in

50% absolute alcohol–water solutions so that ethanol frother and collector could be added simultaneously to the flotation cell. Solutions of aluminum sulfate (alum) for use with the microflotation studies were prepared from the reagent grade chemical. Dilute working solutions were prepared just prior to experimentation from the concentrated stock solution. Suspension pH was adjusted with nitric acid and sodium hydroxide solutions and measured with a Sargent-Welch model LS pH meter and combination electrode.

The flotation procedure consisted essentially of transferring 400 ml of TiO_2 suspension to the flotation cell followed by adjustment of pH and a period during which the solution was mixed and purged of carbon dioxide. Alum solution was then added if required and the floc allowed to develop. After pH stabilization the gas flow rate was carefully adjusted to 19 ml/min. A sample was withdrawn and, at time zero, 2 ml of collector–frother solution was added near the bottom of the cell with a hypodermic syringe. Samples of 5 ml were withdrawn periodically and the corresponding pH was recorded. Sample turbidities as determined by absorbance measurements with a spectrophotometer at 550 nm were used to estimate TiO_2 concentrations so that percent removals could be calculated. The flotation vessel was carefully washed between each experiment.

Coagulation tests utilized the same reagents as described for the flotation studies. Each sample was prepared in 12-ml batches directly in spectrophotometer cuvettes and sample turbidities were measured at predetermined intervals during quiescent settling. Details of the basic procedure are given elsewhere (*9*).

RESULTS AND DISCUSSION

Several preliminary flotation studies with suspensions of the sol were run in which the effects of pH, frother, coagulant, and collector were observed. As expected, it was found that pH is very important and that the results are greatly affected by the aluminum sulfate concentration. These studies also indicated that collector concentration is a more important variable with TiO_2 than has been observed in other sol flotation studies. It was found that the ethanol frother must be maintained at relatively high concentrations and that below some limiting amount flotation was significantly depressed. The role of frother in producing small bubbles of large specific surface area has been discussed in previous papers (*2*, *3*) and by DeVivo and Karger (*10*). For the subsequent studies described here, the ethanol dose was kept constant at 1.25 ml/l and the effects of aluminum sulfate and collector concentrations were examined in detail as a funtion of pH. The collectors chosen for the study, as opposed to the weak fatty acid and amine surfactants, are highly soluble in water, producing a soluble foam which is stabilized by the presence of colloid.

Typical results showing the removal of TiO_2 as a function of time are given in Fig. 1. These particular experiments were run with and without alum at various pH values using NaLS as the collector. In general, the rate of removal was greatest, with either collector, when using alum over those pH ranges of its maximum insolubility. This is in agreement with earlier findings (*2*, *3*, *5*). In most experiments the maximum or steady-state removals were reached within 20 min. This time was chosen for showing all flotation results in the figures to follow.

The effect of pH on 20-min removals without alum or other aggregating agents (i.e., colloid flotation) using 20 mg/l sodium lauryl sulfate is summarized in Fig. 2. Removals at this collector concentration were excellent in the pH range 2 to 3.3; above pH 4 the anionic collector was incapable of floating TiO_2. Similar experiments were run at several NaLS concentrations to define its interrelationship with pH. The upper and lower pH limits, as estimated by 90% removals from data shown in Fig. 2 and similar results, are plotted in Fig. 3. This figure not only describes the

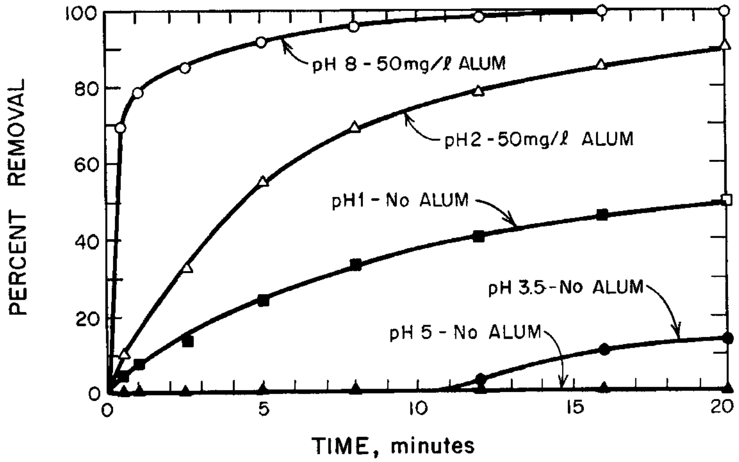

FIG. 1. Typical results showing the removal of TiO_2 as a function of time. Sodium lauryl sulfate concentration 30 mg/l. Ethanol frother dose 1.25 ml/l. Gas flow rate 19 ml/min.

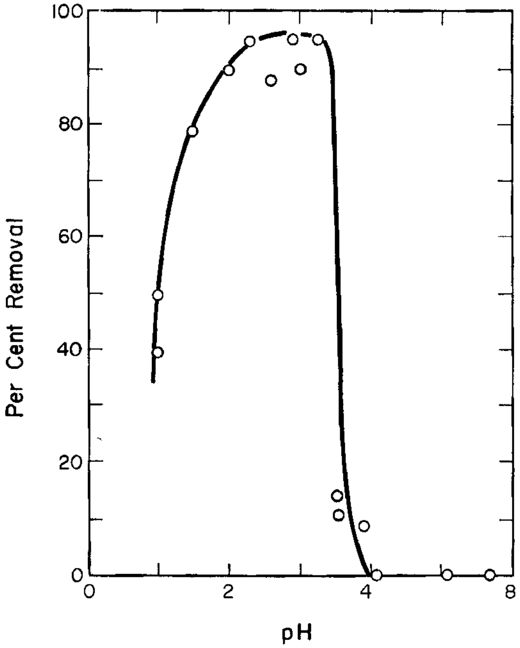

FIG. 2. Effect of pH on the colloid flotation of TiO_2 with 30 mg/l NaLS. Twenty-minute removals at a gas flow rate of 19 ml/min.

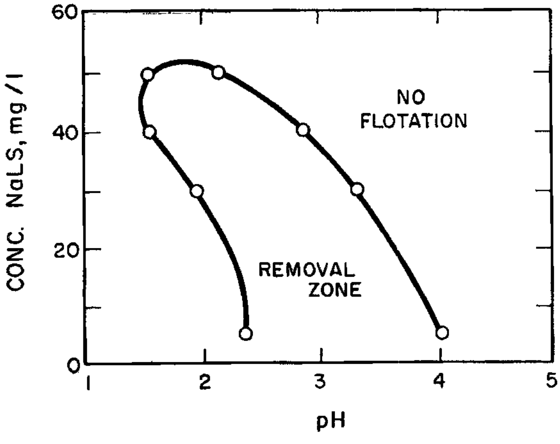

FIG. 3. Effect of NaLS concentration on the pH range of 90% removal of TiO_2 by colloid flotation.

shift of the removal zone toward lower pH as the collector concentration is increased, but also indicates that further increases above 60 mg/l would result in a stably dispersed, presumably hydrophilic sol resistant to removal by colloid flotation. It is interesting that the pH range of removal is increased as the collector dose is decreased, so that the center of the removal zone is just above pH 3 at the lower limiting concentration of NaLS. This value agrees very well with the isoelectric point for TiO_2 as determined by streaming current measurements (Waters Streaming Current Detector) in the absence of surfactant or other chemicals.

Microflotation studies using the same collector were performed at a single alum dose of 50 mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$. The results of this series of experiments are summarized in Fig. 4 which indicates the effect of the coagulant on the extent and rate of removal throughout the pH range of observation. The removals are in general agreement with observations on other sol systems that have been studied. At pH 2, where aluminum is completely soluble and thus has little effect on the system, the rate and extent of removal are very similar to those found in the colloid flotation studies. Increasing the pH beyond pH 4.7 resulted in aluminum hydroxide precipitation, as indicated by the dashed vertical

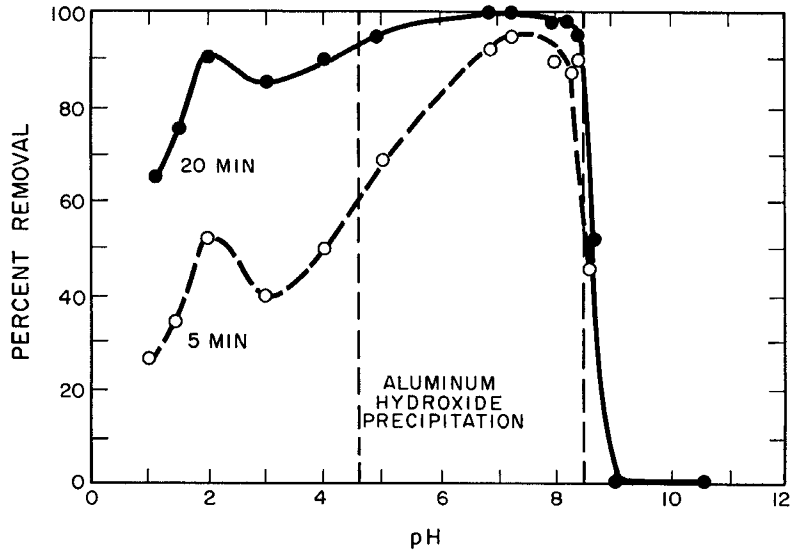

FIG. 4. Effect of pH on microflotation of TiO_2 with 30 mg/l NaLS and 50 mg/l aluminum sulfate.

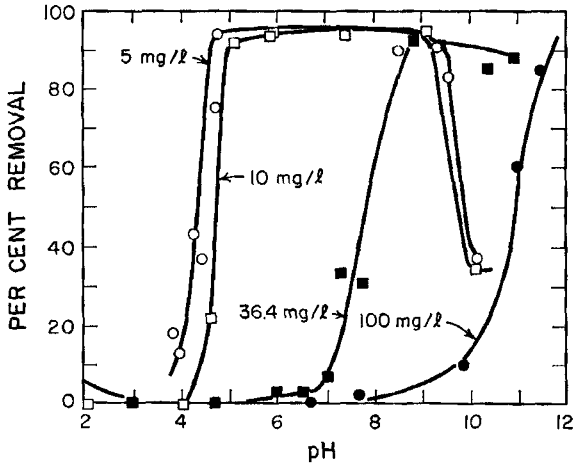

FIG. 5. Effect of pH on the colloid flotation of TiO_2 with various concentrations of CTAB.

lines in Fig. 4, and removals were significantly enhanced. Both the rate of removal and its magnitude were greatest between pH 7 and 8, which corresponds to the range of maximum precipitation of freshly prepared aluminum hydroxide. As expected, removals were sharply decreased at the upper pH limit of precipitation; that is, upon dissolution of aluminum hydroxide to form the soluble aluminate ion.

Results of studies on the colloid flotation of TiO_2 using the cationic collector CTAB are summarized in the next two figures. The effects of several concentrations of this surfactant on 20-min removals are shown as a function of pH in Fig. 5. As with NaLS, there are discrete pH ranges of removal depending on collector dose. At 5 and 10 mg/l flotation efficiency was sharply reduced above pH 9. The foam was very unstable in alkaline solutions with these low collector concentrations, enabling any floated sol to be redispersed into the bulk liquid. In general, the zone of efficient removal by colloid flotation shifted toward higher pH as the CTAB dose was increased. This is in direct contrast to the results just described for the anionic collector which had the opposite effect (Fig. 3). Linear extrapolation of the steep portions of the curves to 100% removal provides a consistent means of determining the limiting pH values needed to define the zone of efficient colloid flotation with CTAB. This data, represented by open circles, is given in Fig. 6. Thus, for example, at pH

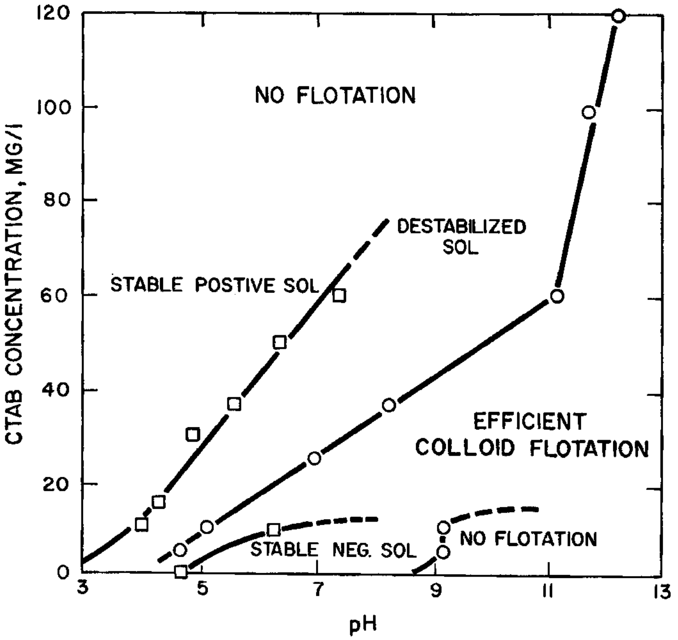

Fig. 6. Effect of CTAB concentration on the settleability and colloid flotation of TiO_2 as a function of pH.

10, colloid flotation occurs at any CTAB dose between about 10 and 50 mg/l. Higher doses are incapable of effectively floating the sol unless the pH is also increased.

It was observed that CTAB had the effect of coagulating or restabilizing ("peptizing") the TiO_2 sol. Consequently, several coagulation-settling experiments were run at several CTAB concentrations to differentiate between the surfactant as a coagulant or as a collector. The results of this study are also summarized in Fig. 6. The open squares form the boundaries of the pH—CTAB concentration zone of destabilization. As indicated by the data, the limiting pH of coagulation increased with increasing concentration of the cationic surfactant. CTAB concentrations greater than those along the line resulted in sol restabilization apparently through charge reversal. This phenomenon is well documented in the literature. At pH 6, for example, 10 mg/l of the collector just coagulates the sol while at 20 mg/l, TiO_2 is still coagulated but no longer floatable. Upon dosing to 40 mg/l the sol, through adsorption of surfactant cations,

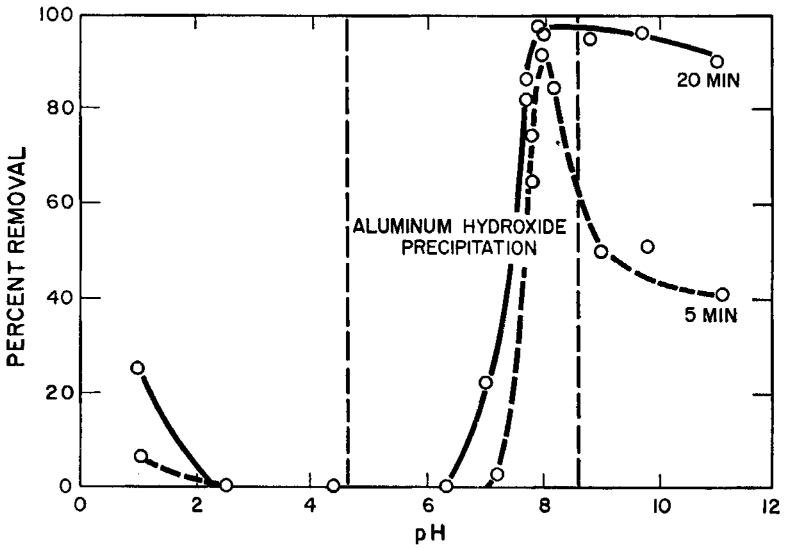

FIG. 7. Effect of pH on the microflotation of TiO_2 with 36.4 mg/l CTAB and 50 mg/l aluminum sulfate. Shown also is the pH range of aluminum hydroxide precipitation.

becomes positively charged and colloidally dispersed once again. In the absence of surfactant the sol is also coagulated, presumably by hydrogen ions, at pH just below pH 5. This is indicated in the figure by the point at zero CTAB to the left of the zone labeled "stable negative sol." From these results it is obvious that surfactant concentration is a significant parameter when attempting to float titanium dioxide.

The microflotation of TiO_2 using CTAB at several coagulant doses was also investigated. As shown in Fig. 7, the addition of 50 mg/l alum did not have a significant effect on the pH range of removal at a collector concentration of 36.9 mg/l (compare with Fig. 5). However, the rate of removal at pH 8 was increased. This pH corresponds to the isoelectric point of freshly prepared aluminum hydroxide as determined by streaming current measurements; at lower pH the insoluble hydroxide is colloidally dispersed, having a positive charge. This effect, the nonfloatability of positively charged sol when using a cationic collector, was observed in similar studies with the clay illite (*5*).

In general, it can be concluded that strongly ionized anionic surfactants such as sodium lauryl sulfate are more effective collectors with microflotation. On the other hand, since most natural sols are negatively charged, it could be concluded that strongly ionized cationics such as CTAB are better suited for use with colloid flotation. With the proper conditions and in the pH range of aluminum hydroxide precipitation, microflotation results in a more rapid and generally more efficient removal process that is less sensitive to surfactant concentration. It is very important that the effect of collector concentration be taken into account when attempting colloid flotation.

CONCLUSION

The results of this work demonstrate the feasibility of removing colloidal titanium dioxide from aqueous dispersion using both the colloid flotation and the microflotation techniques with anionic and cationic collectors. For all systems studied, the removals were dependent upon proper conditions of pH, collector and coagulant concentrations, and other solution and operating parameters.

During colloid flotation, that is, in the absence of hydrolyzing metal coagulant, the cationic collector CTAB removed TiO_2 over a wider range of pH than the anionic sodium lauryl sulfate which was only effective in relatively acid solutions. This is not unexpected since the isoelectric point of the sol occurs at low pH. As the concentration of CTAB was increased, the minimum pH for efficient flotation was also increased. Having reached this minimum, however, effective removals were obtained at all higher values of pH. Increasing the concentration of either collector generally resulted in a decrease in the extent of the pH removal range. The results indicate that both collectors are capable of affecting the magnitude of the charge on the surface of the sol and hence its stability. The presence of aluminum sulfate coagulant during microflotation further affected the pH range of efficient removal with both collectors. Regions of rapid or sweep removal were observed in that removals were essentially complete at the end of just a few minutes of foaming. Increases in the extent of the pH range of efficient removal was most pronounced with sodium lauryl sulfate. Most likely, CTAB was less effective than the anionic collector because the alum floc was positively charged over most of the pH range of its formation.

Acknowledgments

This work was supported in part by a grant from the Office of Water Resources Research, U.S. Department of the Interior, and a traineeship from the U.S. Environmental Protection Agency.

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Received by editor December 18, 1972