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Surface-Chemical Studies on Graphite Suspensions using Inorganic Dispersants

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Abstract

Electrokinetic and dispersion characteristics of graphite suspensions were studied in the absence and presence of varying concentrations of different inorganic dispersants, namely sodium silicate, sodium hexametaphosphate and sodium tripolyphosphate. The isoelectric point of graphite was found to be located at pH 2.3. From the zeta potential data obtained as a function of pH in the presence of varying concentrations of the dispersants, it was observed that the phosphate based inorganic dispersants were more efficient in enhancing the electronegative character of zeta potential. Thus, better stability of the graphite suspension could be obtained using the phosphate based dispersants. The results of the dispersion tests corroborated the zeta potential data. The electron microscopic studies indicated that the graphite particles obtained from the supernatant were finer than those in the settled portion.

Keywords: *graphite; zeta potential; dispersion tests.*

INTRODUCTION

Colloidal graphite is a specially manufactured compound of pure finest grade graphite powder dispersed in mineral oil with suitable additives, where graphite content is 25%. Colloidal graphite is recommended for use mainly in ferrous forging plants working at high temperatures and pressures. It is an ideal lubricant and release agent for dies, moulds, tools, die-casting, glass moldings, etc. It is used as an additive for the manufacture of extreme pressure lubricants, wire and tube drawing compounds, as an anti-wear for machining and cutting fluids, greases, etc.

Colloidal graphite also finds use in the production of conducting composite materials, liquid electro photographic toners, pigments in inks and paints, rubber reinforcing and fillers, electrodes and conducting films, preparation of special purpose electrodes by applying a coating on non-conducting material to avoid eddy current losses. Colloidal graphite is highly concentrated and therefore may be diluted with good quality, light mineral oil in the proportion of 1:3 to 8 parts depending upon the job in view.

Until now whatever colloidal graphite is available is mainly oil based, due to which it is very expensive. Efforts are being made to develop water based colloidal graphite. The main problem in this technique is the hydrophobic nature of graphite, which renders it almost unwettable by water. This problem can be solved by a proper study of the surface chemical properties of graphite in aqueous media using different dispersants. In recent years, appreciable work has been done on the agglomeration characteristics of carbon blacks [1- 4], however there is a paucity of literature on the synthesis of colloidal graphite.

In the present investigation, with the above objectives in mind, various inorganic dispersants have been assessed for their ability to stabilize graphite suspensions in aqueous medium.

EXPERIMENTAL

Materials

Graphite powder was obtained from the Graphite India Limited, Bangalore. The proximate analysis of this sample was as follows: Moisture content – 0.2%; Volatile matter – 2.1%; Ash – 5.1%; Fixed Carbon – 92.6%. The d_{50} size of this powder sample was determined as 19.2µm by Malvern mastersizer. The density of the graphite powder sample was found to be 2.12 gm/cc.

Potassium nitrate was used as an indifferent electrolyte. Sodium silicate (SS), sodium tri poly phosphate (STPP) and sodium hexametaphosphate (SHMP) were used as dispersing agents. Deionized, double distilled water was used for all the experiments.

Methods

Zeta Potential Measurements

20 mg graphite was added to 50 ml of deionized, double distilled water. This was followed by the addition of dispersants of desired concentration such that the total volume was 100ml. The pH was adjusted in the range of 2-12. The ionic strength was kept at 10^{-3} M by using KNO_3 as an indifferent electrolyte. The suspension was allowed to equilibrate for 1h by agitation in a Remi orbital shaking incubator at 250 rpm at $30^0C \pm 0.4^0C$. The sample was ultrasonicated for 30 seconds in a Imeco model ultrasonicator bath. The zeta potentials were measured using a Malvern zeta sizer (model 3000).

Dispersion Tests

1gram sample of graphite was added to 100 ml of deionized, double distilled water. The pH was adjusted between 3-12. This sample was allowed to equilibrate for 1 hour by agitating in a Remi orbital shaking incubator at 200 rpm at $30^0C \pm 0.4^0C$. The sample was transferred to a 100 ml measuring jar and ultrasonicated for 30 seconds in a Imeco model ultrasonicator bath, and allowed to stand for 3 hours. After this, 30 ml of the supernatant was siphoned out, filtered and dried. The weight of the graphite thus obtained was determined.

To study the effect of the dispersants on the stability of graphite suspension in water, the dispersion procedure was standardized as follows: 1 gram of graphite sample was pulped to a volume of 50 ml and pH was adjusted between 10.8 - 11.1. This was followed by the addition of the chosen dispersant of desired concentration and pre-adjusted pH equivalent to that of the suspension pH, such that the total volume was 100 ml. The suspension was allowed to equilibrate for 1 hour by agitating in a Remi orbital shaking incubator at 250 rpm at $30^0C \pm 0.4^0C$. The sample was transferred into a 100 ml measuring jar and ultrasonicated for 30 seconds in a Imeco model ultrasonicator bath and allowed to stand. Exactly 30 ml of the supernatant was siphoned out into a clean beaker after time intervals of 2h, 4h, 6h, 8h, 10h, and 12h. The suspension was filtered and the solids dried and weighed.

Electron Microscopic Study

Scanning electron micrographs of the graphite powder, obtained from the above dispersion test, were taken in a Jeol JSM 840A scanning electron microscope. Separate micrographs were taken for the graphite sample obtained from the supernatant and that from the sink.

RESULTS AND DISCUSSION

Zeta Potential Studies

In order to study the surface charge characteristics of graphite, both in the absence and presence of the dispersants, zeta potential measurements have been carried out. The effects of pH and dispersant concentration on the zeta potentials of the graphite dispersion have been examined. The influence of pH on zeta potential of graphite in the absence of dispersants and at different ionic strengths is depicted in Figure 1. It is evident that the isoelectric point of graphite is located at pH 2.3, which is in good agreement with the earlier reported values [5]. The zeta potential values of graphite become increasingly electronegative as the pH is increased from 2 to 12. Zeta potential values are about –55 to –60mV at pH 10, attesting to the good stability of the graphite suspension. When the electrolyte concentration is increased from 10^{-3} M to 10^{-2} M KNO_3, zeta potential values of graphite become less negative. This may be attributed to the adsorption of K^+ ions of the indifferent electrolyte, due to double layer compression. Figure 2 shows the zeta potential values of graphite as a function pH in the presence of 100 ppm concentration of various dispersants. The zeta potential values become more electronegative with increase in pH for all the cases. The maximum zeta potential value is about –63 mV around pH 12 in the presence of sodium silicate. With respect to SHMP and STPP, the maximum zeta potential values are in the vicinity of –75mV around pH 12. Based on the results of zeta potential studies carried out, the beneficial effect of the addition of the inorganic dispersants particularly in the pH range of 6 to 12 is clearly borne out, when compared to the stability of graphite suspension in the absence of the dispersants. It is noteworthy that the electronegative character of the graphite suspension is enhanced by 20mV in the pH range of 10-12 in the presence of the dispersants. The efficiency of the various dispersants with respect to increasing the stability of graphite dispersion can be arranged in the following order: STPP ≅ SHMP > SS

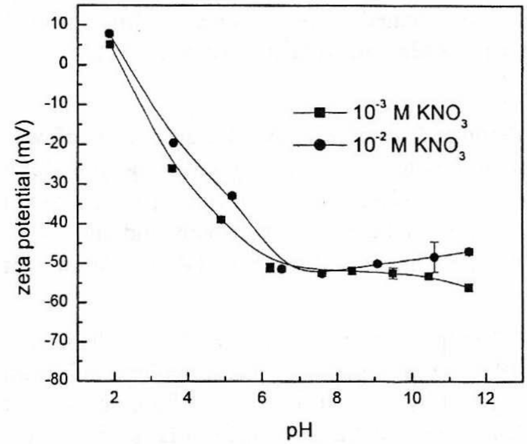


Fig. 1: Zeta Potential of Graphite as a Function of Ph and Ionic Strength in the Absence of Dispersants

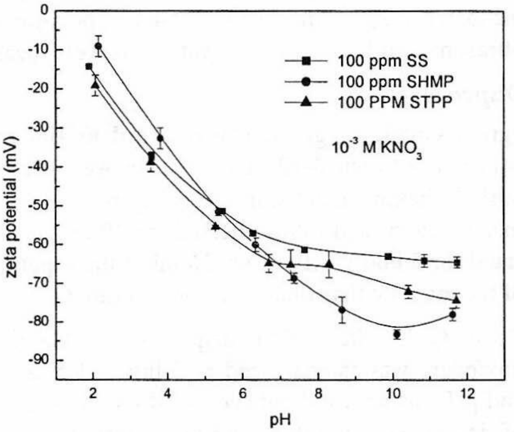


Fig. 2: Zeta Potential of Graphite as a Function of Ph in the Presence of 100 ppm Concentration of Different Dispersants

Dispersion Studies

Initially, dispersion tests were carried out in the pH range of 3-12 to assess the stability of graphite suspension. The results shown in Figure 3 reveal that the percentage dispersion of graphite steadily increases with increase in pH from 3 to 12. These results corroborate the zeta potential data wherein the stability of suspension was found to be higher in the alkaline pH range (Figures 1 and 3). In the next set of experiments, dispersion tests were carried out as a function of time keeping the pH in the range of 10.8-11.1 (Figure 4). In the absence of dispersants the percentage dispersion decreases from 47% at 2 hours to 40% at 12 hours. The addition of sodium silicate improved the percentage dispersion to 65% after 2 hours and to 58% after 12 hours. The percentage dispersion values further improved to 85% after 2 hours and to 76% after 12 hours by the addition of 100 ppm of SHMP and STPP. Thus almost a twofold increase in the percentage dispersion values of graphite is achieved consequent to the addition of SHMP and STPP, compared to that of obtained in the absence of dispersants.

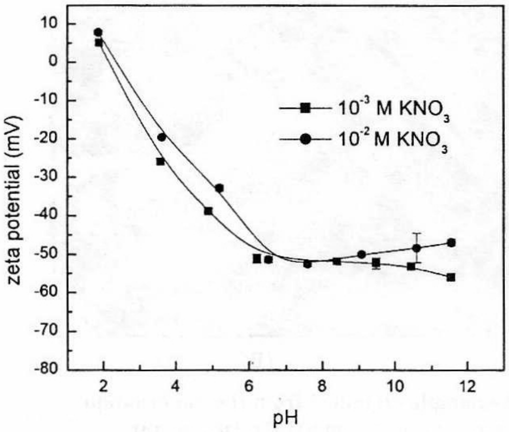


Fig. 3: Percent Dispersion of Graphite as a Function Ph

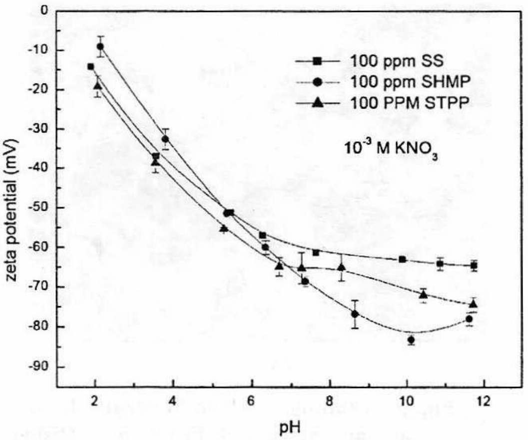


Fig. 4: Percent Dispersion of Graphite as a Function of Time in the Presence of 100 ppm Concentration of Different Dispersants

Figure 5 portrays the percentage dispersion of graphite as a function of the concentration of the chosen dispersants. In these experiments the pH was maintained between 10.8-11.1 and the dispersion values were measured after six hours. The trend observed in Figure 4 is maintained namely, that the phosphate based dispersants (SHMP and STPP) are more efficient compared to sodium silicate. From Figure 5 it is also evident that there is an optimum concentration of the dispersant namely 100 ppm beyond which a decrease in the percentage dispersion values are obtained. From the above results the efficiency of the dispersants can be arranged in the following order: STPP > SHMP > SS

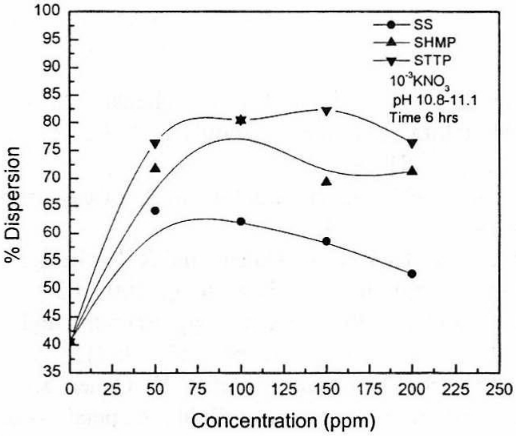
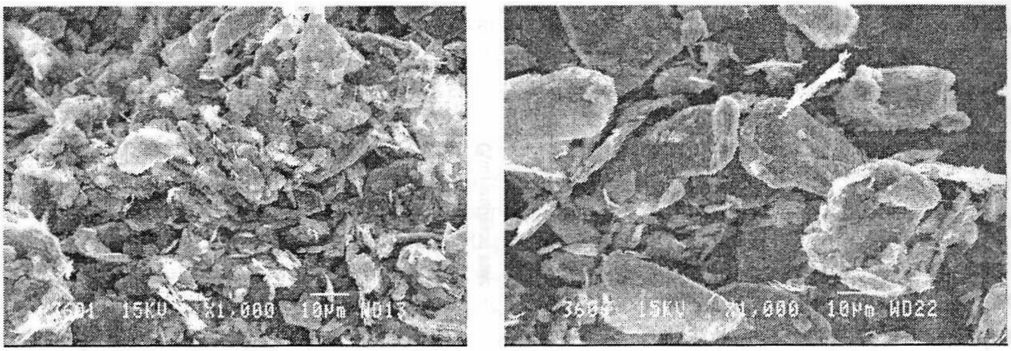


Fig. 5: Percent Dispersion of Graphite as a Function of Concentration of Different Dispersants

Thus there is good correlation between the results of the dispersion and zeta potential tests.

Electron Microscopic Study

Scanning electron micrographs of the graphite powder obtained from the supernatant and settled fractions of the dispersion tests carried out using 100 ppm of SHMP dispersant are shown in Figures 6a and 6b respectively. It is apparent that the finer particles remain in the suspension while the coarser particles are found in the settled fraction. It can be expected that better dispersion of graphite particles can be achieved by minimizing the coarser size fraction adopting fine grinding techniques.



(A) (B)

Fig. 6: Scanning Electron Micrographs of Graphite Sample Obtained from the Supernatant (A) and Settled (B) Fractions of Dispersion Test using 100 ppm SHMP Dispersant

CONCLUSIONS

The following major conclusions can be arrived at based on the studies carried out:

1. The zeta potential studies indicate that the isoelectric point of the graphite sample is located at pH 2.3. The electronegative charge of graphite is significantly enhanced by the addition of the dispersants, especially in the alkaline pH range.
2. The percentage dispersion values are found to continuously increase with the increase of pH from 3 to 12. A twofold increase in the percentage dispersion of graphite is observed consequent to the addition SHMP or STPP dispersant.
3. Based on the zeta potential and dispersion tests, the efficiency of dispersants can be arranged as: STPP≅SHMP>SS

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