Factors to Consider in Selecting a Dispersant for Treating Industrial Water Systems

by

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Carbosperse™ K-700
Water Treatment Polymers*

Introduction

In virtually all processes in which untreated water is heated, fouling of equipment surfaces is the single most serious problem encountered. Affected application areas include cooling, boiler, geothermal, power generation, and many other production processes. The problems associated with fouling include:

- Reduced heat transfer by formation of an insulated layer of mineral scales,
- Corrosion, and
- Flow restrictions including blocked pipes, heat exchangers, and nozzles.

For example, the fouling of reverse osmosis membranes adversely degrades product quality, reduces product quantity, increases energy consumption, increases membrane cleaning frequency and cost, and reduces membrane life.[1] Over the years, environmental restrictions and water conservation measures[2,3] have combined to make these problems increasingly challenging to solve. Accordingly, deposit control treatment has become an essential to the operation of industrial water systems.

Commonly encountered foulants in industrial water systems include corrosion products, particulate matter, microbiological mass, and sparingly soluble salts of alkaline earth metals. Various approaches have been developed to control these problems. However, the control of iron-based foulants (e.g., Fe_2O_3, Fe_3O_4, $Fe(OH)_3$, $FePO_4$) is generally considered to be one of the most challenging problems. This paper focuses on the control of iron foulants, particularly iron oxide.

Deposit prevention and removal of iron foulants can be achieved by either of two methods as follows:

- Mechanical: Control of cycles of concentration, reduced recovery, side stream filtering), or
- Chemical: Use of corrosion inhibitors or dispersants.

However, mechanical approaches to control iron-based foulants are typically not economical and ineffective if not used in combination with chemical treatment. Treating industrial water systems involves using a wide variety of chemicals to prevent the build-up of deposits on equipment surfaces. Water treatment programs typically include the following components:

- Scale control agents: Polyphosphates, phosphonates, poly(acrylic acid), poly(maleic acid),
- Corrosion inhibitors: Molybdate, orthophosphate, polyphosphate, phosphonate, benzotriazole, tolyltriazole,
- Dispersants: Acrylic or maleic-acid based polymers, and
- Biocides: Oxidizing and non-oxidizing chemicals.

Historically, many of deposit control chemicals were natural products (e.g., modified corn starches, tannins, lignins, alginates). However, natural dispersants are not used today because they provide marginal performance, temperature stability problem, and nutrients for biological growth (especially in the case of starch).

Since the development of synthetic polymers in the 1950s, essentially all effective water treatment formulations have incorporated deposit control polymers (DCPs) to improve system efficiency and reduce operating costs. The DCPs in these formulations are used as scale control agents and/or dispersants. DCPs inhibit the precipitation of scale forming salts such as calcium carbonate, calcium sulfate, and calcium phosphate. DCPs are also invaluable in industrial water systems for dispersing or suspending a wide variety of solids that would otherwise settling out to form scale or deposits.

Environmental concerns and rising operational costs, are among the drivers for industries to continuously investigating new approaches to conserve (use and reuse) water. Water conservation efforts have led operators to minimize cooling tower blow down resulting in increases in the cycles of concentration thereby increasing the concentration of dissolved ions (e.g., calcium, magnesium, iron, sulfate, and suspended matter) and thus increasing fouling potential.

The selection of DCP(s) for a particular application can be a very challenging and time consuming process. Water treatment formulators must consider a myriad of factors and have a great variety of DCPs available from several manufacturers. DCPs are characterized in many ways including composition, molecular weight, ionic charge, charge density, and product form (liquid or solid). Criteria for selecting DCPs should include:

- Dispersion of suspended matter (e.g., iron oxide, clay, and calcium phosphate)
- Retention of activity in the presence of high calcium and magnesium hardness
- Retention of activity in the presence of iron (III)
- Tolerance to cationic flocculant
- Scale inhibition
- Compatibility with biocide
- Hydrolytic stability
- Environmental acceptability

In our previous contributions,[4,5,6] we have shown that the performance of water treatment formulations is affected by various factors including pH, temperature, suspended solids, and flocculating agents. We have continued our investigations of the role of process water variables on the performance of DCPs toward the goal of expanding and improving the criteria use by water treatment technologists to select dispersants that ensure optimum system performance. The work presented herein addresses the effect of system variable including dispersant dosage, water hardness, pH, total dissolved solids, and flocculating agent on the performance of commercially available dispersants. Table 1 lists the dispersants evaluated in this study. The dispersancy power of the polymers was evaluated according to the method described in our previous publication.[7]

Effect of Dispersant Dosage

Dispersancy as a function of active product dosage was evaluated using standard test conditions. Reference to these conditions will be found throughout the text, with exceptions clearly noted.

- 100 mg/L Ca
- 30 mg/L Mg
- 610 mg/L SO_4
- 61 mg/L HCO_3

Figure 1 shows the '% Dispersancy' vs. 'Inhibitor Dosage' profiles for several products and illustrates that low polymer dosages have a marked effect. Other noteworthy observations include:

- An increase in dispersant concentration results in increased dispersancy.

- Poly-C (AA:SA:SS terpolymer) exhibits better performance than Poly-E (competitive terpolymer) and superior performance compared to Poly-A (polyacrylic acid) and Poly-B (polymaleic acid).

- PBTC (a well-known calcium carbonate inhibitor) shows the poorest performance in terms of dispersing iron oxide in aqueous solution.

- The presence of additional carboxyl groups in a homopolymer (i.e., Poly-B vs. Poly-A) does not significantly improve the dispersancy power of the dispersant.

Although PBTC and Poly-C are both strong acids, the performance of the Poly-C is far superior to PBTC. This suggests that the ionic charge, size, and adsorption power of the functional group play important roles in imparting more negative charge on iron oxide particles. It is well known that the higher the negative charge imparted on the particles, the stronger the repulsive forces between the charged particles, hence better dispersancy.

The dispersancy data presented in Figure 1 also suggest that the substitution of carboxyl group with stronger acidic and bulkier groups (i.e., SA and SS) in an acrylic acid polymer markedly improves the dispersancy power of the polymer. It is also noteworthy that increasing the dispersant concentration from 0.25 to 0.50 ppm results in ~50% increase for the Poly-C compared to ~35% increases in the case of Poly-A and Poly-B. Figure 1 illustrates that further increasing the dispersant concentration from 0.5 to 1.0 ppm only shows marginal improvement. Therefore, a thorough evaluation is necessary in selecting a dispersant for developing a formulated product to achieve optimum performance. From a practical point of view, the ability of a dispersant such as Poly-C to provide superior performance at low dosage is a desirable characteristic.

Effect of Divalent Cations

Calcium and Magnesium Ions
Water hardness affects iron oxide dispersancy by decreasing the amount of negative charge from polymer on the agglomerating particles, hence decreasing charge repulsion. Additionally, the hardness ions shield the initial charge on the particles, allowing increased agglomeration. The influence of water hardness (calcium and magnesium) on the performance of two commercially available dispersants was evaluated by conducting a series of dispersancy experiments.

Figure 2 presents iron oxide dispersancy data for Poly-A and Poly-C (1 ppm) in the presence of varying concentrations of calcium ions (0 to 400 mg/L total Ca, no Mg, 610 mg/L SO_4, 61 mg/L HCO_3). The graphs in Figure 2 clearly show that calcium ions have a marked influence on the performance of two commonly used commercial dispersants. In zero hardness water (i.e., distilled water) both Poly-A and Poly-C show excellent dispersancy activity (i.e., >95%). However, increasing the calcium ion concentration to 50 mg/L results in dispersancy reductions (~50% and 5% decreases, respectively) for both Poly-A and Poly-C. These dispersancy data indicate show that Poly-C retains its dispersancy activity far better than Poly-A in the presence of high calcium hardness (especially at 400 mg/L).

Iron oxide dispersancy data for several polymers were collected in the presence of 400 mg/L Ca or 240 mg/L Mg total cation concentration plus 610 mg/L SO_4, 61 mg/L HCO_3). Figure 3 illustrates the same performance profile in presence of either Ca or Mg ions versus the control for the five (5) polymers tested and the rank order (highest to lowest) of ion iron dispersancy performance is a follows:

$$Poly\text{-}C \; > \; Poly\text{-}D \; \approx \; Poly\text{-}E \; > Poly\text{-}B \; \approx \; Poly\text{-}A$$

Poly-D (copolymer) displays better performance than either homopolymer (i.e., Poly-A or Poly-B). The performance increase observed for Poly-D vs. Poly-A may be attributed to the presence of additional strong acidic sulfonic acid group.

Poly-C (AA:SA:SS terpolymer) is the best polymer in terms of dispersant effectiveness. In contrast to Poly-A, Poly-C has a lower acrylic acid content but includes two different sulfonic acid monomer groups. The competitive terpolymer (Poly-E) under these stressed high hardness experimental conditions shows significantly less ion oxide dispersancy. Overall, the dispersant performance trend observed (terpolymer > copolymer > homopolymer) is similar to the ranking order reported for inhibiting the precipitation of calcium phosphate and calcium phosphonates.[5,6,8]

Iron (II), Manganese, and Zinc Ions
The influence of divalent cations [e.g., Fe(II), Mn(II), Zn (II)] on the performance of various dispersants was also investigated. Figure 4 shows the dispersancy data collected under standard conditions and in the presence of 10 mg/L of each metal ion. The presence of Fe(II) and Mn(II) at low concentrations does not significantly affect the dispersancy power of the polymers. However, zinc ions appear to have an antagonistic affect on the performance of dispersants. The observed decrease in dispersancy

activity may be attributed to the precipitation of zinc hydroxide thus providing additional surface area for the adsorption of dispersant molecules. The adsorption of dispersant on freshly precipitated zinc hydroxide decreases the effective concentration of dispersant in solution thereby resulting in overall poor performance. The data presented in Figures 3 and 4 clearly show that both type and concentration of cations present in the recirculating water can influence the performance of a dispersant.

Influence of Trivalent Cation

Figure 5 shows the dispersancy data collected in the presence of 1 ppm of iron (III) and varying concentrations of two terpolymers (Poly-C and Poly-E) under standard conditions. As is evident, ~16% and 35% additional amounts of Poly-C and Poly-E, respectively, are needed to achieve performance similar to that obtained in the absence of iron (III). In cooling water applications where low concentrations of iron (III) are encountered, the incorporation of a DCP in the formulation that exhibits more tolerance to iron (III) and other metal ions (e.g., Ca, Mg, Zn) is beneficial.

Figure 6 presents the influence of iron (III), a commonly encountered trivalent cation in industrial water systems, on dispersancy of various polymers. As shown, the presence of low concentration (i.e., 1 ppm) of iron (III) exhibits a marked antagonistic effect on the dispersancy power of polymers. For example, '% Dispersancy' values obtained in the presence of 0 and 1 ppm of iron (III) are 82% and 58%, respectively for Poly-C compared to 72% and 40%, respectively for Poly-D. It is interesting to note that sodium lignosulfonate (Poly-G) which is a natural dispersant containing sulfonate groups, shows better dispersancy power in the absence of iron (III) than either homopolymer (Poly-A or Poly-B). However, the performance of Poly-G in the presence of 1 ppm iron (III) is markedly reduced and comparable to the homopolymers.

The data presented in Figures 4 and 6 indicate that ~400 times more divalent cations (i.e., Ca, Mg) are required to obtain a similar decrease in dispersant performance as is obtained from 1 ppm of a trivalent metal ion. The observed change in dispersant performance caused by divalent and trivalent cations may be attributed to the difference in charge density between calcium and iron (III) ions. It is interesting to note that a similar negative effect on polymer performance caused by low levels of iron (III) has been observed for calcium phosphate precipitation.[5]

Effect of Solution pH

The influence of pH on the performance of several polymeric and non-polymeric inhibitors for controlling the precipitation of various scale forming salts has been reported.[7,8] Based on the studies involving the effect of various phosphonates as crystal growth inhibitors, it has been suggested that in the pH 5 to 9 range the performance of the phosphonate increases with increasing pH of the solution.[9] For polymeric inhibitors, such as poly(acrylic acid) and acrylic-based copolymers, the degree of deprotonation has been suggested to explain the observed improvement in polymer performance as the solution pH is increased from 4.5 to 9.0.[10]

Figure 7 shows the effect of pH in the range 5.5 to 9.0 on dispersant performances for Poly-A, Poly-C, and Poly-E under standard conditions. The data indicate that solution pH exhibits slight positive influence on the dispersant performance. The observed influence may be due to several factors including (a) ionization of polymer functional groups, (b) coiling/uncoiling of polymer, and (c) iron oxide particle charge. Although uncoiling of polymer at high pH may play a role in improving dispersancy activity, the concentration of polymer used is so low (i.e., 1 ppm), that this factor may not play significant role. Because the polymers evaluated contain COOH and SO_3H groups, it is expected that ionization of these acidic groups increases with increasing pH thus, increasing the potential for adsorption of polymers onto iron oxide particles, hence improving dispersancy.

Effect of Cationic Polymer

The type and extent of upstream pretreatment processing may play a role on the performance of cooling water treatment programs containing anionic polymers. Certain feed waters (especially surface waters) normally require far more extensive pretreatment than deep well water. Changes in water composition may occur due to alternating supply sources or seasonal variations. Waters containing suspended matter are typically treated with coagulating or flocculating agents before entering the cooling water system. The effectiveness of surface water treatment to reduce suspended solids is dependent upon the proper selection and feed rate of coagulants, pH, mixing, and residence time, etc. One of the chemicals commonly used as coagulant or flocculant is high molecular weight cationic polymer diallyldimethylammonium chloride or DADMAC (Poly-F). DADMAC has been known to "carryover" and could potentially interfere with the performance of anionic polymers used in treating industrial water systems.

The effect DADMAC (Poly-F) on the performance of iron oxide dispersants was investigated under standard test conditions. Figure 8 shows iron oxide dispersancy data for Poly-A, Poly-C, and Poly-D, in the presence of 0.1 ppm Poly-F. The presence of low concentrations of Poly-F has a marked antagonistic effect on the performance of various dispersants.

Effect of Polyphosphates, Phosphonates, and Surfactants

Polyphosphates and phosphonates are a family of compounds widely used in industrial water treatment programs to control mild steel corrosion and calcium carbonate scale formation. Phosphonates are key compounds in most cooling water treatment programs. A number of experiments were conducted under standard synthetic water conditions containing 1 ppm product in order to understand the role of several formulation ingredients (i.e., polyphosphates, phosphonates, and surfactants) on the iron oxide dispersancy. The data presented in Figure 9 clearly demonstrate that phosphorous-containing compounds that are effective in preventing the precipitation of calcium carbonate, barium sulfate, calcium sulfate, etc., exhibit poor iron oxide dispersancy power compared to Poly-C (terpolymer). It is also evident from Figure 9 that the surfactant does not show any significant activity in terms of dispersing iron oxide.

Miscellaneous

Many water treatment programs frequently incorporate chlorination for controlling microbiological fouling. Our testing on Poly-C and Poly-D show that under simulated field conditions these polymers do not lose any activity in the presence of chlorine. In addition, testing of both Poly-C and Poly-D after storage for 1 year at room temperature shows no significant decrease in performance both for iron oxide dispersancy and calcium phosphate inhibition.

Conclusions

In summary, it has been shown that iron oxide dispersant performance can be adversely impacted by a variety of conditions commonly encountered in industrial water systems. The results presented in this study suggest that the following factors be considered when selecting a dispersant for developing a water treatment program to ensure optimum performance.

1. Polymers are the most effective class of chemicals for dispersing particulate iron oxide. Polyphosphates and phosphonates exhibit poor dispersancy power.

2. Polymer dosage is critical to dispersant performance. The ability of a dispersant to perform at low dosages is an important selection criterion.

3. Polymer performance as a dispersant strongly depends upon ionic charge, monomer type, functional group, and molecular weight. Based on the dispersancy data, the ranking of the dispersant is:

    Terpolymer > Copolymer > Homopolymer

4. Cation charge and concentration are the two most important water quality factors that impact the performance of a dispersant.

5. Cationic polymer exhibits adverse influence on dispersant performance.

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Table 1 - Dispersants Evaluated

Description	Composition
Poly-A	Poly(acrylic acid)
Poly-B	Poly(maleic acid)
Poly-C	Poly(acrylic acid: 2-acrylamido-2-methyl propane sulfonic acid: sulfonated styrene) or Poly(AA:SA:SS)
Poly-D	Poly(acrylic acid: 2-acrylamido-2-methyl propane sulfonic acid) or Poly(AA:SA)
Poly-E	Competitive terpolymer
Poly-F	Poly(diallyldimethyl ammonium chloride)
Poly-G	Sodium lignosulfonate
HEDP	Hydroxyethylidine 1,1 diphosphonic acid
SHMP	Sodium hexametaphosphate
AMP	Aminotris (methylene phosphonic acid)
PBTC	2-phosphonobutane-1,2,4-tricarboxylic acid
Surfactant	Block polymer of ethylene oxide and propylene oxide

Note: Poly-A, Poly-C, and Poly-D are Carbosperse™ (formerly Good-Rite) K-7028, K-798, and K-775 polymers, respectively supplied by The Lubrizol Corporation (formerly BFGoodrich Performance Materials).
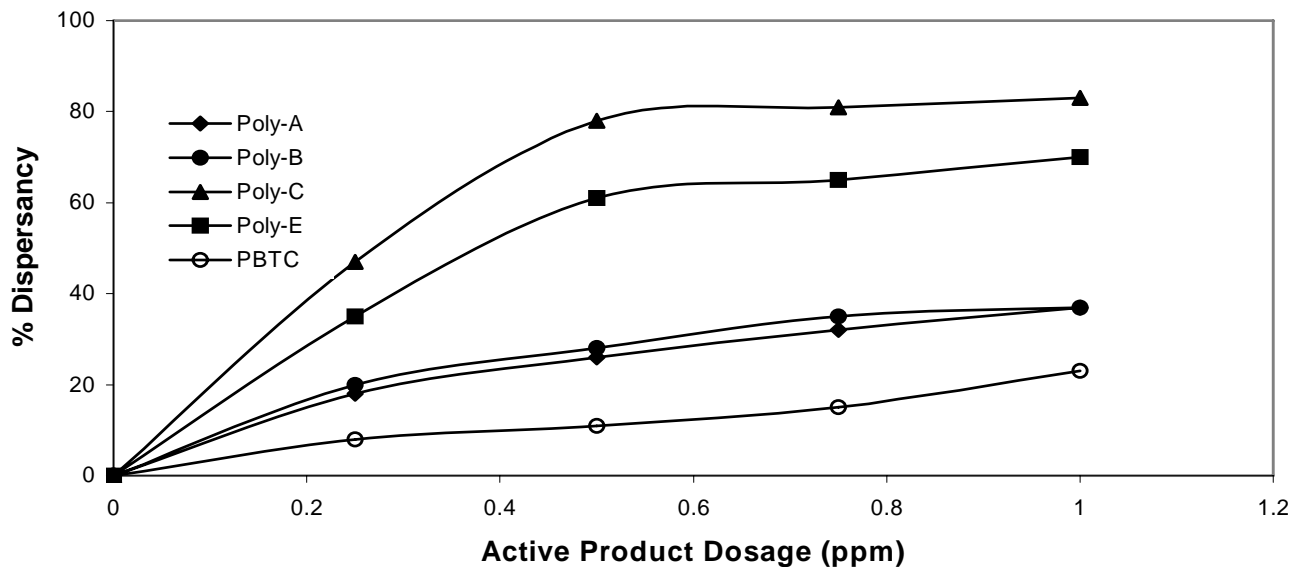
Figure 1 - Iron Oxide Dispersion as Function of Product Dosage
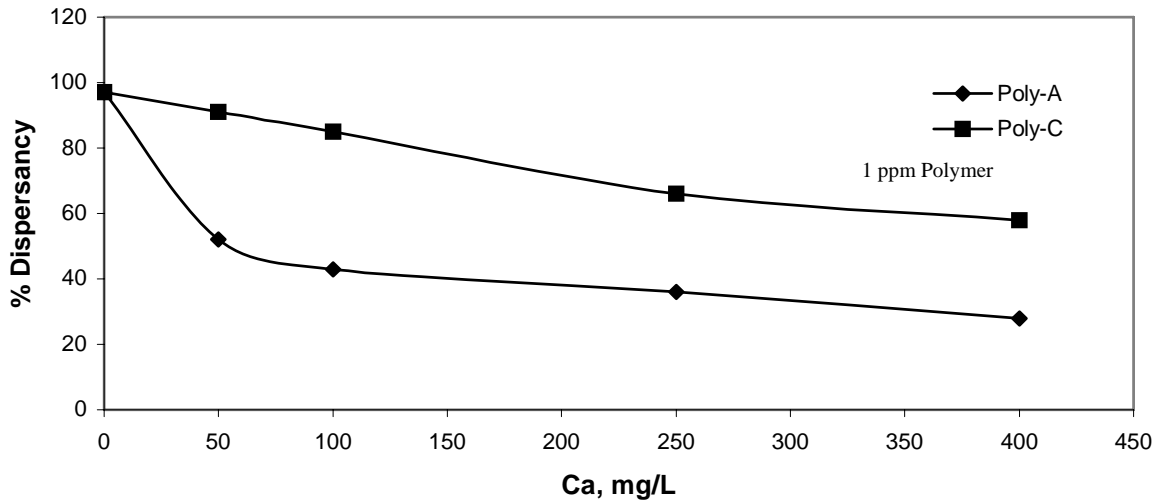
**Figure 2 - Iron Oxide Dispersion for Poly-A and Poly-C
as a Function of Varying Calcium Ion Concentrations**
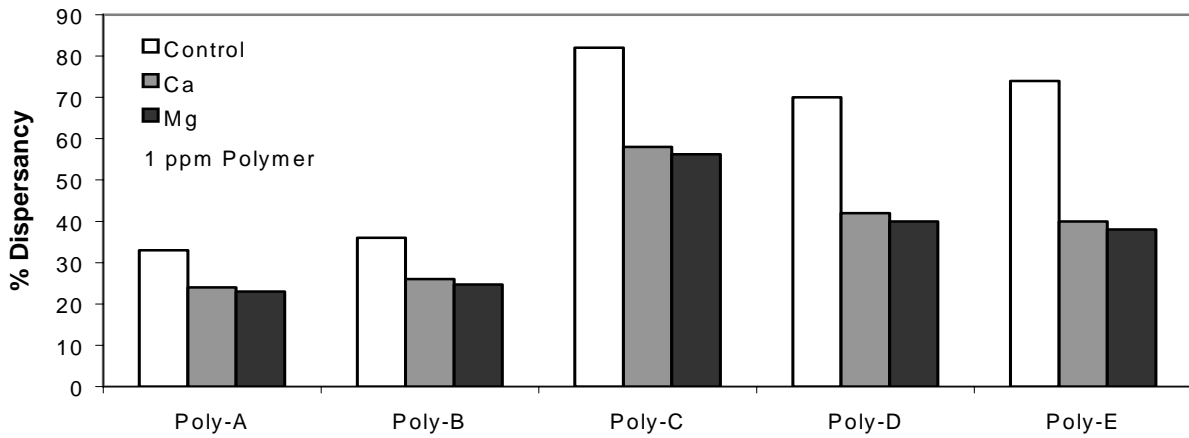
**Figure 3 - Iron Oxide Dispersion for Various Polymers
in the Presence of 400 mg/L Ca or 240 mg/L Mg**
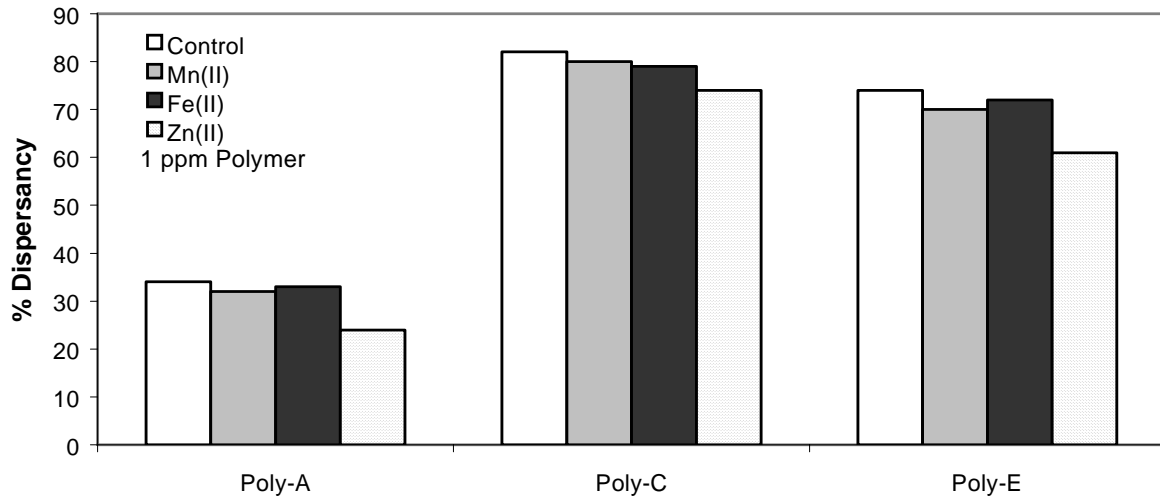
**Figure 4 - Iron Oxide Dispersion for Various Polymers
in the Absence and Presence of 10 ppm Mn(II), Fe(II), or Zn(II) Ions**
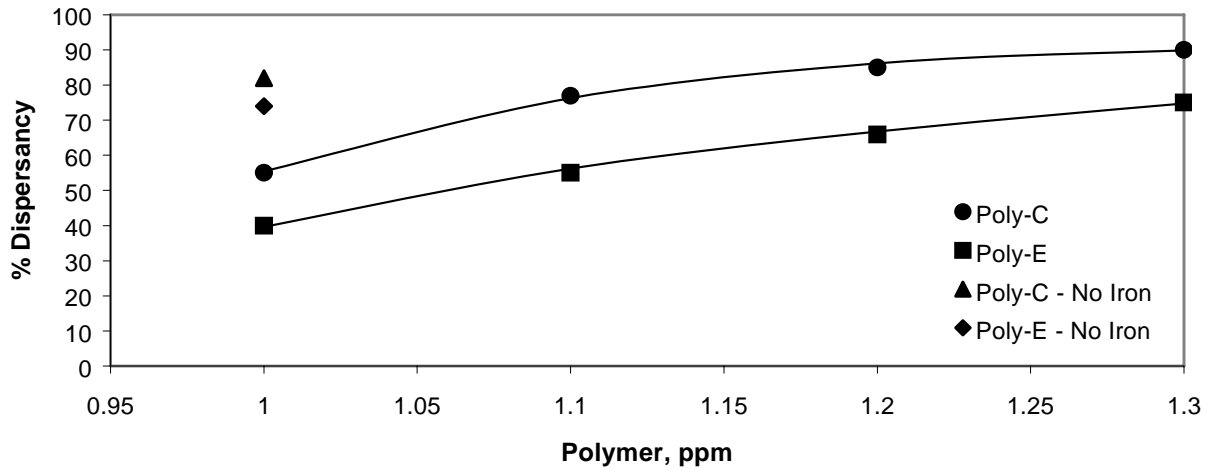
**Figure 5 - Iron Oxide Dispersion for Poly-C and Poly-E
in the Presence of 1 ppm Fe(III)**
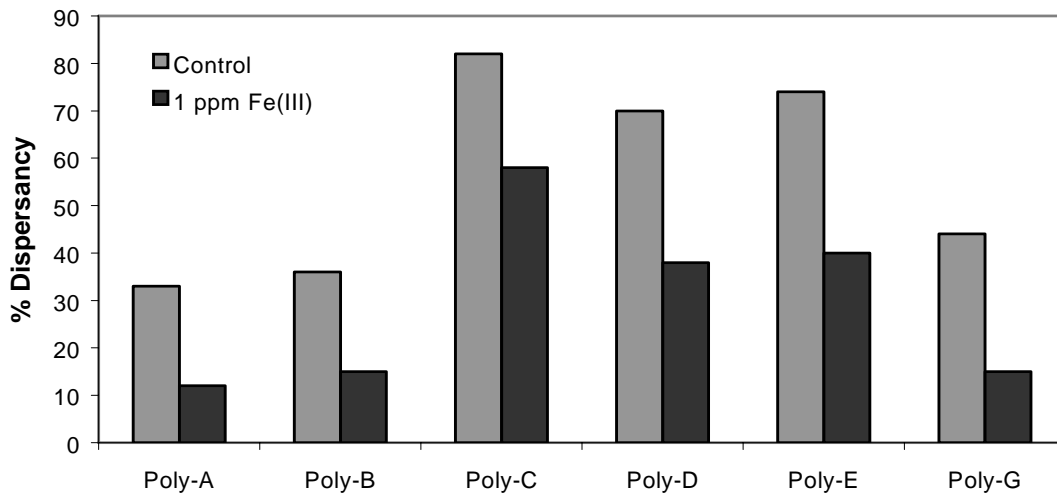
Figure 6 - Iron Oxide Dispersion for Various Polymers (at 1 ppm Active Solids Dosages) in the Absence and Presence of I ppm Fe(III)
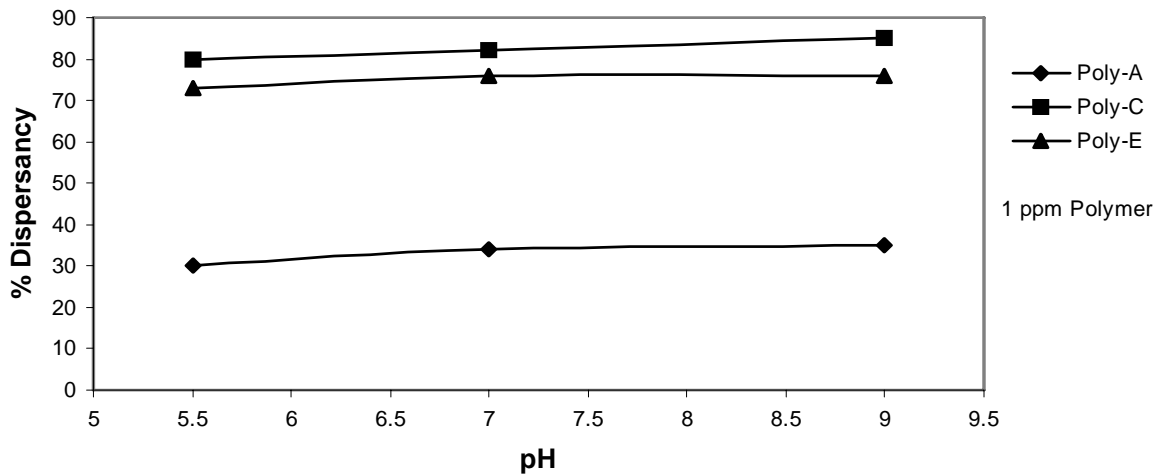
Figure 7 - Iron Oxide Dispersion for Poly-A, Poly-C, and Poly-E as a Function of varying pH
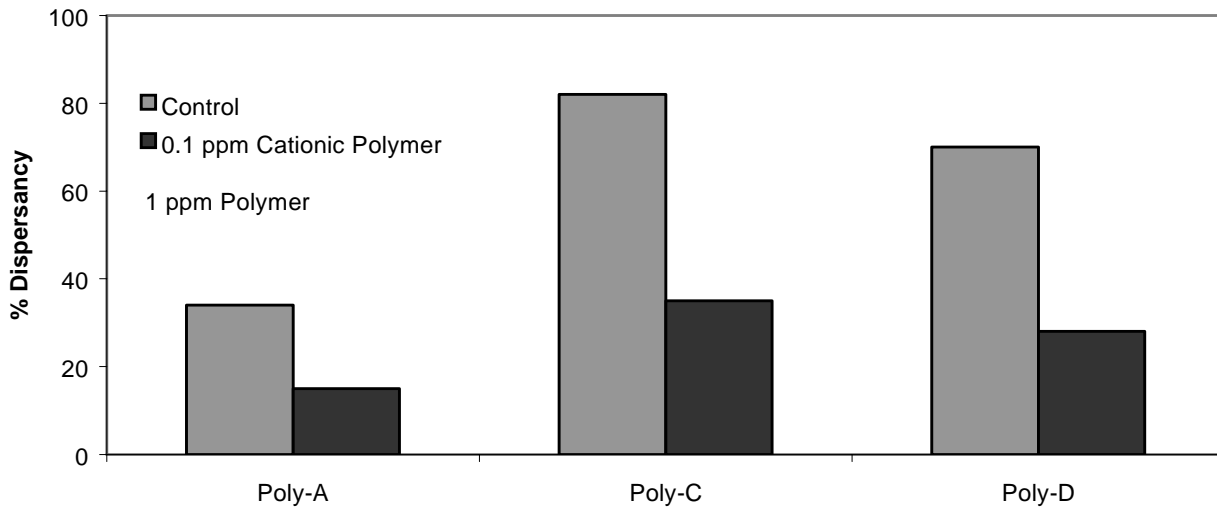
**Figure 8 - Iron Oxide Dispersion for Poly-A, Poly-C, and Poly-D
in the Presence of 0.1 ppm cationic polymer Poly-F**
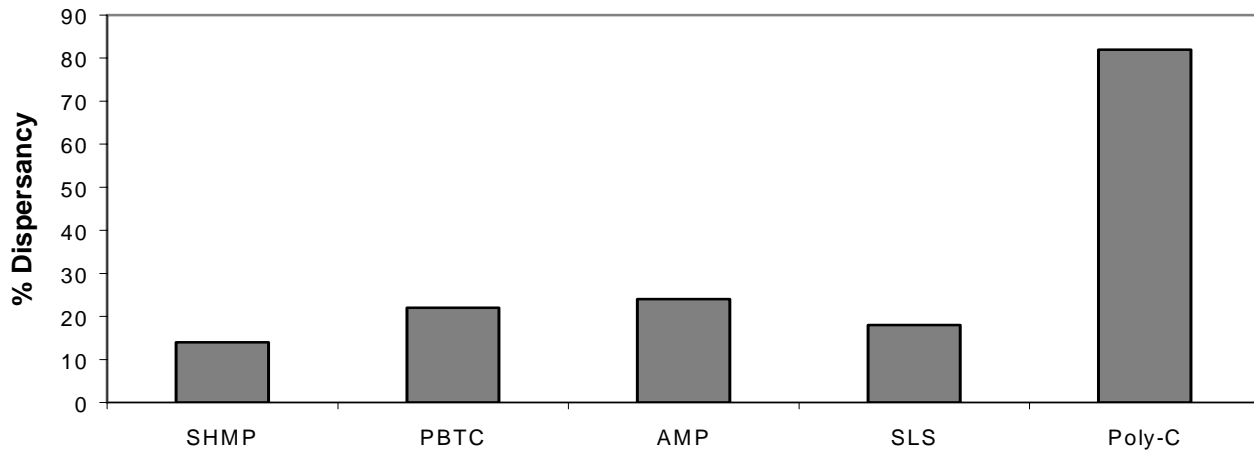
**Figure 9 - Iron Oxide Dispersion in the Presence
of 1 ppm Phosphorous Containing Compounds, Surfactant, or Poly-C**

For additional technical information pertaining to Lubrizol's Carbosperse™ (formerly Good-Rite) K-700 Polymers, please contact us as follows:

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