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Preparation of Acrylic Emulsions for Use in Waterborne Coatings

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Abstract:

Acrylic emulsions are formed by co-polymerizing diol amide derived from methyl soyate with maleic anhydride and phthalic anhydride through an emulsion polymerization reaction. The anionic surfactants used are sodium dodecyl sulfate and sodium lauryl sulfate. Two different initiators can be used: potassium persulfate and sodium bisulfite. Molecular weight of the polymer can be increased by using the initiator in smaller quantities. The anionic surfactant is used in excess to ensure the maximum amounts of micelles to be present, in which polymerization takes place. The emulsion polymerization reaction is conducted between 50⁰C and 85⁰C in distilled water. The acrylic emulsions are then stabilized with ammonium hydroxide to a pH range of 8-12.

Introduction:

The goal of this project is to design a coatings system for traffic paint while abiding by several factors. While synthesizing this coatings system, cost was kept to a minimum, renewable resources were used, and an environmentally friendly process was utilized.

In order to keep cost at a minimum, two strategies were employed. The first strategy was to design a “one pot” synthesis. In this sort of synthesis, all of the reagents that are initially used are present in the final product. This means that no waste is created which can be costly to dispose of. It also means that the process is simple and does not require transferring chemicals between many stages of the synthesis. Another strategy to keep cost at a minimum was to use water as the solvent. Water is inexpensive and easily attainable.

Perhaps the biggest goal of this project was to incorporate methyl soyate, which is a soy bean oil derivative, into a coatings system. It is beneficial to use methyl soyate as a binding component, because it is derived from soy beans, which is a renewable resource. Once the synthesis of this paint is perfected, it can be reproduced without any concern of running out of materials.

The United Soybean Board recently published an initiative to increase soy bean usage in America. In this initiative, they claim that the need for paints and coating systems are expanding with the growing economy. Once this coatings system is produced, the demand will be fulfilled. [1]

Results and Discussion:

Emulsion Polymerizations:

An emulsion polymerization was chosen for this process, as it is a common way to make coatings in the paint industry. The main ingredients of an emulsion are the solvent, stabilizer, initiator, monomer, comonomer, and surfactant. [2]

The solvent that was always used was water. Water was chosen as it is readily available, inexpensive, and not harmful to the environment. The amount of water used was varied from about 25 ml to 100ml.

The stabilizer works to keep the emulsion in a homogeneous state. The stabilizer that was used in all of the experiments was sodium dodecyl sulfate (SDS). It is readily available and inexpensive, which are two important attributes for the goals of this coating. [2]

The initiator starts the reaction. It works to produce a free radical which then reacts with other molecules in order to produce a polymer. The amount of initiator used had a direct impact on the percent solids produced in the reaction; if more initiator was used, more polymer chains started, producing a polymer with lower percent solids. If less initiator was used, fewer polymer chains were formed, which allowed the polymer chains to grow longer and created a product with greater percent solids. In the reactions, the initiator was varied between potassium persulfate ($K_2S_2O_8$) and sodium bisulfite ($NaHSO_3$). These are both common initiators used in coatings applications. [3]

The monomer used in all of the reactions was diol amide (the detailed synthesis of diol amide is described on p 5). This is made from methyl soyate, which comes from soybeans. Once this monomer is incorporated into a coatings system, the demand for soybeans will increase. The use of soybean oil derivatives in paints is beneficial because soybeans are a renewable resource and are not harmful to the environment. [1]

The comonomers used were varied in this reaction. The role of the comonomer is to act as a binding agent for the monomer in the polymer chains. The comonomer can be varied in order to change the properties of the polymer chain. Some experiments were done in which a mixture of equal parts of phthalic anhydride and maleic anhydride were used. Other reactions were performed in which only phthalic anhydride was used, and some in which only maleic anhydride was used.

The surfactant was used in some experiments and not used in others. Its role is to provide micelles, or reactive sites for the polymer to form. The surfactant that was used in some experiments was fatty acid soap (Ivory© brand). [3]

Main experimental setup:

In all of the experiments conducted, a 100 ml flask was filled with a varying amount of distilled water. The prescribed amount of comonomer and selected amount of SDS was added. The solution was allowed to heat to approximately 70°C and stir until all components were dissolved. Then, the selected amount of diol amide was added via pipet and shortly after that several grains of initiator were added. The reactions were then all allowed to heat and stir for approximately an hour. If the reaction proved to be unstable, a small amount of base was added to stabilize the emulsion. They were then allowed to cool and a cold-roll steel test substrate (Q-Panel) was cast from the product. If the Q-panel had desirable qualities, it was put through a series of tests such as the flexibility test in which the plate is bent in both inwards and outwards in order to test for film adhesion and cracking/crazing properties of the coating. The product was then tested for percent solids by drying a small measured volume of the product and comparing the initial weight to the dried weight. Also, the product was kept in a beaker and observed frequently to determine if the emulsion remained stable.

Variance in Surfactant:

Simple dishwashing soap (Ivory® brand), was used as the surfactant in this experiment. Each time it was used as a surfactant, it produced emulsions that contained air bubbles. With no way to remove these bubbles, the reaction was continued without use of the surfactant. It was clear after several reactions were conducted without the use of surfactant, that reaction sites were still forming and polymers were being produced. The sodium lauryl sulfate (SDS) that was always added as the stabilizer is known to act as a surfactant as well. The SDS most likely formed the micelles in the absence of the dishwashing soap and created a film with fewer bubbles. Eliminating the soap might have caused the reaction to continue at a slower rate. [4]

Variance in Initiator:

The initiator most commonly used in the reactions was potassium persulfate ($K_2S_2O_8$). It was found that the best emulsion was produced when only a few crystals of potassium persulfate were added to the reaction. When films with potassium persulfate as an initiator were cast on metal Q-panel, the film became a golden color and it appeared that the Q-panel rusted. When the same film were cast on plastic sheets, they did not turn the same golden color. This feature is unacceptable because when the paint is used for traffic coatings, it should not rust the metal machines used to apply it or the cars that will drive on it. The initiator was then changed to sodium bisulfite ($NaHSO_3$). This produced an emulsion that was not uniform and created crystals in the bottom of the beaker. When the reaction with sodium bisulfite was reproduced with more stabilizer, the emulsion was still not uniform and contained chunky, waxy components in the bottom of the beaker.

Variance in amount of solvent:

The amount of water used varied from 25-100 ml. This was found to have a direct effect on the percent solids formed. When more water was used in the emulsion, the percent solids decreased, and when less was used, the percent solids increased as would be expected. The percent solids are very important when producing coatings applications for traffic paints, because the paint industry has strict guidelines concerning the percent solids needed to make a useable traffic paint.

Variance in proportions of monomer and comonomer:

It was found that the ratio between the monomer and comonomer directly affected the properties of the polymers that were produced. The reaction that seemed to produce the best results was made from 67 percent comonomer and 33 percent monomer. The only problem with this reaction was that the film cast from it had a waxy component to it.

In order to eliminate the waxy component, a reaction with less diol amide was performed. When 5% diol amide and 95% comonomer were used, after the reaction was complete, a white powdery substance remained at the bottom of the flask. The film that was cast from this reaction was not desirable. The white powdery substance is assumed to be unreacted comonomer.

Stabilizing the emulsion:

Many emulsions formed were only stable for about 24 hours. After this time, waxy chunks settled to the bottom of the flask. It was found that the unstable emulsions were all very acidic (pH of about 2-3). This problem was combated by adding a strong base to the emulsion after it was cooled. The base was added until the pH was changed to about a 9, and this made the reaction much more stable and created emulsions that remained homogeneous for months. It is important to have a stable emulsion as the emulsions used for coatings applications may need to sit for months before being put to use and need to still be homogeneous when they are used.

Synthesis of diol amide:

Equimolar amounts of methyl soyate (9.72 mmol, 14.514 g) and diethanolamide (9.72 mmol, 5.365 g) as well as a stir bar were added to a 100ml 3-neck flask. 5 mol percent of NaOH (0.486 mol, 0.038 g) was then added. The 3 neck flask was heated using a heating mantle and was allowed to heat at approximately 70°C and stir for 23 hours. A viscous golden yellow product was produced.

Changes in diol amide:

The diol amide that was used in the experiments had an unsaturated component. This came from the part of the methyl soyate that is unsaturated. It is believed that this unsaturated portion caused many of the coatings to be waxy in nature. This waxy property is undesirable for a coating. There was an attempt to remove

the unsaturated component through a "winterization" process as described below. A similar process is used in the food industry to separate oils for salad dressings. [5]

The winterization process of the methyl soyate was conducted as follows: the methyl soyate was frozen for several days. It was then removed from the freezer and centrifuged. The frozen and unfrozen portions were separated from each other. The unfrozen portion was disposed of and the remaining portion, the saturated portion, was again frozen and the entire process was repeated to ensure all of the saturated component was discarded. This "winterized" methyl soyate was then used in place of regular methyl soyate to produce diol amide. An IR was run on both the winterized and unwinterized components of the methyl soyate. The comparison of these IRs was not very useful, because it was expected that the IR of each of these samples would be similar. There was not enough difference in either IR to draw any conclusions. These IRs can be found on pages 10 and 11.

The new diol amide was employed in reactions that had been run with "unwinterized" diol amide. The coatings that were created still contained a waxy property.

It is thought that the winterization process failed because the methyl soyate was frozen very quickly. Most winterization procedures call for the oil to be frozen slowly while being lightly shaken so that the saturated and unsaturated components can separate from each other. [5] The methyl soyate was frozen at one temperature, which most likely froze it in a homogeneous state inhibiting separation of the saturated and unsaturated components.

Concern with production of Crystals:

Many of the procedures led to a production of white crystals which settled at the end of the reaction to the bottom of the container. It is thought that in the cases where these crystals were formed, the crystals did not polymerize, but were simply recrystallized and settled to the bottom of the container. This hypothesis is supported by the fact that the comonomers used (maleic anhydride and phthalic anhydride) are both white crystals. An IR was run on a sample of crystals from the bottom of one of these beakers and compared to an IR run on a mixture of maleic anhydride and phthalic anhydride. It was clear from this comparison, that the white powdery substance was not simply a mixture of recrystallized maleic anhydride and phthalic anhydride, because the IRs were very different. The results of these IRs can be found on pages 12 and 13.

Specific Reactions with Results:

- The reaction that produced the crystals which were analyzed by IR (page 12) was performed in the following manner: 50 ml water and 0.730g SDS were heated and stirred to 60°C. 0.5g maleic anhydride and 0.5g phthalic

anhydride were added and then heated until they dissolved. Then, 0.5 g diol amide was added followed by a few flakes of sodium bisulfite. This heated at 78°C for one hour. It was then allowed to cool. The crystals that formed had a melting point of 182-187°C

- The reaction that seemed to work best was performed in the following manner: 50 ml water was added to a 100ml round bottom flask. 1.0g SDS and a stir bar were added and the reaction was allowed to heat at 60°C for about 5 minutes. Then, 0.5g maleic anhydride and 0.5g phthalic anhydride were added to the reaction flask. After these two substances were dissolved, 2.637 g diol amide was added via pipet. The reaction turned a dark yellow color after about ten minutes. A few grains of potassium persulfate were then added which caused the solution to become dark orange. Upon further heating and stirring, the reaction evolved into a cream color. At this point, the heat was removed. Ammonium hydroxide was added drop-wise to the mixture until it reached a pH of 9. The only undesirable property of this film was that it rusted the Q-panel.
- A reaction without diol amide: 50 ml water and 1.0g SDS was heated to 60°C. 0.5g maleic anhydride and 0.5g phthalic anhydride were added to the mixture. After they were dissolved, a small amount of potassium persulfate was added and the mixture was stirred and heated for 90 minutes. The solution changed from pink to creamy peach and back to pink in this time. After the coating cooled, a few drops were placed in an aluminum pan. It was clear that the coating was not waxy, but it was very sticky. This property shows that polymer was likely not formed. From this reaction it was concluded that, diol amide plays an integral role in the formation of polymer.

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Reflection on the Learning Experience:**1. Describe your foundational understanding of how research is conducted in your discipline.**

Research in chemistry is conducted in a several step process. The first step is to figure out the problem and then to find all information of related science that has been conducted. The next step consists of finding information from this data that is relevant to the experiment that will be conducted. This is followed by planning an experimental design and then conducting the experiment based on that design. Once the experiment is analyzed, the researcher must attempt to interpret the chemistry that occurred and then create more experiments that will alter this chemistry to produce a desirable effect.

2. How have you expanded your understanding of the informational resources available and how to best use these resources?

I have greatly developed my knowledge of the uses of SciFinder. This program was very useful to me when I first started with my project so that I could understand ways in which scientists addressed similar problems to mine. I also learned how to use certain internet sites to my advantage and was able to find information in polymer text books that benefited me.

Perhaps the greatest resource that I was able to use was other scientists. I was able to talk with both professors and students to increase my understanding of the science being conducted in my research project.

3. Describe the knowledge you have gained regarding the fundamentals of experimental design

I now believe more in the scientific approach as it was taught in school. Through my experiments, I learned that changing one variable at a time is extremely important in order to isolate the variable that is causing a change.

4. Describe how you have learned to interpret the results of your research project.

By making one change at a time on my experiments, I was able to determine the roles of the various chemicals used in my experiments. Isolating each of these changes allowed me to interpret the exact effect of each factor in my experiment.

I was upset at first that nothing seemed to work that would benefit companies, but then realized that even though the things we produced

were not useful to industry; we still gained valuable information on chemicals such as methyl soyate, which may be used in future applications.







