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SYNTHETIC DETERGENT BAR

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My invention relates to the production of novel synthetic detergents by the sulfitation of ethylene homopolymers, the detergents thus obtained having particular utility in the making of synthetic detergent bars.

While synthetic detergents have found widespread use in powdered and liquid form, they have had little commercial success in displacing, in bar form, the familiar bars of household toilet soaps. This inability of presently available synthetic detergent bars to make any substantial inroads into the soap bar market is attributable to a number of factors. From an economic standpoint, synthetic detergents which are sufficiently inexpensive to be considered for making bars and which have the requisite lathering and cleansing power are, generally speaking, more soluble than the soaps utilized in the making of conventional soap bars. Furthermore, most synthetic detergents do not become plastic, and the machinery for fabricating satisfactory bars from such substances must be specially designed. Still further, conventional synthetic detergent bars tend to develop a slimy surface upon standing in contact with a wet surface, and they do not possess the "feel" of ordinary toilet soaps. Numerous efforts have been made to meet these and other problems including the incorporation of considerable quantities of fillers such as bentonite, starch, and the use of waxes for various purposes including that of attempting to impart a soap-like feel to the bars.

Another problem with certain synthetic detergents, particularly the alkylaryl sulfonates which now constitute the principal component of many of the widely used detergents, and which is becoming increasingly serious, centers around problems of sewage disposal. Very small quantities of such detergents cause the formation of highly stable foams in the aerators of sewage systems and greatly decrease the rate of settling of solid suspended matter. Such conditions hamper and add to the costs of the sewage treating processes. These effects are believed to be due to the resistance of such detergents to breakdown by conventional biochemical sewage-treating processes. For these and other reasons, it is important that detergents be biologically degradable by conventionally used sewage disposal techniques so that they may be removed from water undergoing sewage treatment.

In accordance with the present invention, I have discovered that synthetic detergents capable of being formed into a bar, particularly without the incorporation of inactive fillers or additives or appreciable proportions thereof, and which are biologically degradable, can be produced by the sulfitation of ethylene homopolymers, particularly those having from 12 to 14 carbon atoms. Such detergents are sufficiently plastic in character to permit them to be formed into bars with conventional machinery, and the bars themselves have substantially all of the characteristics of fatty acid derived soap bars not only from the standpoint of surface feel but also with respect to their lather producing and cleansing properties.

The ethylene homopolymers having utility for the purposes of my invention are those which contain predominately 1-alkenes having from 8 to 22 carbon atoms, with especially desirable sulfitation detergent products being obtainable from such ethylene homopolymers, and mixtures thereof, having from 10 to 16, and, better still, from 12 to 14, carbon atoms in the molecule. They are essentially linear in structure but may contain a few percent, say 2 to 5% of branched chain materials. Such

branched chain materials serve to increase resistance to water hardness of the finished detergent products of this invention. The production of the ethylene homopolymer starting materials may be accomplished by any method known in the art. One such method, by way of illustration, is the Ziegler procedure wherein ethylene is passed into contact with triethylaluminum at elevated temperatures. Particularly effective results have been achieved in accordance with the practice of my invention with commercial sources of such polymerized ethylene comprising about 90%, or more, for instance, 92 to 97%, of said ethylene homopolymers consisting essentially of 1-alkenes, said commercial sources containing minor amounts of other materials which apparently have no observable adverse effects on the properties of the ultimate synthetic detergent products. The term "ethylene homopolymers," as used herein and in the claims, will, accordingly, be understood to mean such ethylene homopolymers as contain predominately 1-alkenes and which are mainly of linear character.

In my prior U.S. Patent 2,653,970, there is described a process for producing detergents by the addition of water-soluble bisulfites to olefins containing from about 10 to 22 carbon atoms. The olefins disclosed and utilized in the practice of the process of that patent were derived from cuts obtained by cracking aliphatic higher waxy petroleum fractions such as petrolatum, and also from cuts of olefins obtained by the Fischer-Tropsch synthesis. While the detergents produced in accordance with the teachings of my prior patent were obtained in reasonably good yields, prolonged reaction times, for example, of the order of 16 to 40 hours, or more, were required. Moreover, the detergents produced in accordance with said patent, while possessing good detergent properties, as well as good color, low hygroscopicity, and good alkaline and acid stability, were not adequately satisfactory for fabrication into synthetic detergent bars, particularly essentially all-synthetic detergent bars.

I have made the surprising discovery that, if ethylene homopolymers of the type described above are reacted with water-soluble bisulfites, synthetic detergents are produced having markedly improved properties for the production of synthetic detergent bars, especially from the standpoint of their ability to be formed into bars of substantially 100% active synthetic detergent having the appearance and surface feel of a conventional soap bar. I have also discovered, that, by employing the aforesaid ethylene homopolymers in the reaction with the water-soluble bisulfites, the reaction proceeds at rates at least twice as fast as with such olefins as are disclosed in my said prior patent, and, in many instances, up to 5 or more times faster than was possible utilizing such olefins as are disclosed in my prior patent. Moreover, essentially quantitative yields of detergent are obtained based on input homopolymer, a matter of major economic importance, not only because it minimizes cost of raw material but also because it avoids the problem of non-detergent impurity which besets the customary routes to sulfonate detergents. Hydrocarbon impurities contaminate the sulfonates from bisulfite addition to olefins made from carbon monoxide and hydrogen or by cracking higher hydrocarbons. Hydrocarbons and sulfones contaminate sulfonates made by reacting alkylaromatics with sulfur trioxide or other sulfonating agent. Unless removed, these impurities impair detergency, odor and other properties, yet their removal requires the significant added expense of such separate steps as adsorption, solvent extraction or prolonged steam distillation. Accordingly, a synthesis which avoids these impurities, as does the present one, represents a marked advance.

The procedural steps per se, for the production of the

novel and useful synthetic detergents of my present invention, may, generally speaking, follow those disclosed in my aforesaid prior patent. Thus, the reaction mixture may comprise water; the ethylene homopolymer (or mixtures thereof) having from 8 to 22 carbon atoms; a water-soluble bisulfite; an alkaline agent, especially an alkali metal sulfite, to maintain the aqueous phase of the mixture at the desired pH level; a polar organic solvent; and, advantageously, a water-soluble synthetic detergent or organic surface active agent. The reaction is induced by dispersing a gas containing molecular oxygen, particularly desirably air, through the reaction mixture.

The water-soluble bisulfite employed as the sulfitating agent in the practice of my present invention may be an alkali metal bisulfite such as and especially sodium bisulfite, but other water-soluble bisulfites exemplified by ammonium bisulfite or aliphatic amine or pyridine bisulfites may be used. Furthermore, compounds which, in solution, are converted to bisulfites can be used as, for example, sodium metabisulfite ($Na_2S_2O_5$) which, in the presence of water, is converted to sodium bisulfite ($NaHSO_3$).

While control of pH may be effected by various alkalies or alkaline reagents, it is especially desirable to use alkali metal sulfites, such as sodium sulfite. The pH of the aqueous phase of the starting reaction mixture is advantageously between about 6 or 6.5 and about 7.5, as measured with a glass electrode at 30° C. During the reaction proper, the pH is maintained above 6 and below 9 as measured with a glass electrode at 30° C.

The polar organic solvent is advantageously a water-soluble volatile alcohol containing at least 3 carbon atoms or any other water-soluble volatile liquid can be used such as ethanol; propanol; isopropanol; butanol; isobutanol; pentanols; hexanol; dioxane; methyl, ethyl, and butyl mono-ethers of ethylene glycol; and aliphatic amines such as ethylamine, propyl amine and isopropyl amine. The polar organic solvent used should be essentially non-reactive under the process conditions employed. Convenience of recovery of the polar organic solvent is an important practical consideration. If air is used, as distinguished from pure oxygen in the reaction, excessive solvent loss will occur during the reaction period if the solvent has a normal boiling point below about 60° C. While this loss can be avoided by putting the reaction system under pressure or by passing the effluent air through an adsorbent system, it is preferred to avoid such procedures. Generally speaking, the solvent desirably should not have a boiling point in a range that requires the use of excessive quantities of heat and/or negative pressure to accomplish removal thereof of distillation. Hence, from the standpoint of these practical considerations, the normal boiling point of the solvent should not exceed about 150° C. and is advantageously in the range of 70 to 100° C.

The quantity of polar organic solvent employed in the process of my present invention may vary within wide limits. Generally speaking, excesses should be avoided to reduce distillation times to a minimum. Desirably the quantities of solvent utilized in my present process will range from 1 to 8 mols, usually from 4 to 6 mols, per 100 mols of water used in forming the reaction mixture.

The use of a water-soluble surface active agent or synthetic detergent in the practice of my present invention, while not essential, is highly desirable as will be made clear hereinafter. The surface active agent used may be obtained from previous runs, or may be any of a number of commercially available products. I have found that effective results can be attained by adding a small quantity of a liquid detergent product, for instance, an alkylaryl sulfonate, such as that sold under the trade name "Vel" (Colgate-Palmolive Company). Alkylaryl sulfonates, such as dodecyl benzene sodium sulfonate, tridecyl benzene sodium sulfonate, and pentadecyl benzene sodium sulfonate; alcohol sulfates such as lauryl sodium sulfate and myristyl sodium sulfate; lauric acid amide of taurine (sodium salt); and lauric acid ester of sodium isethionate are illustrative of numerous other surface active agents which can be used with good results. The amount of the water-soluble surface active agent employed is generally in the range of from 40 to 200 grams, usually about 100 grams of the surface active agent, based on its content of active material, per mol of the ethylene homopolymer in the reaction mixture.

Generally speaking, the reaction mixtures of my present invention, at the start of the reaction, may be present in (a) systems of three liquid phases wherein, so far as ascertained, the top phase comprises an ethylene homopolymer-rich phase, the intermediate phase is one containing all of the components of the reaction mixture with the polar organic solvent predominating, and the lower phase is rich in water and inorganic salts; or (b) systems of two liquid phases. Good yields of the novel detergents of my present invention are obtained in systems of three liquid phases regardless of whether a surface-active agent is initially present, but with systems of two liquid phases good yields have been obtained only when such an agent has been added at the start of the reaction period. A system of three liquid phases is obtained by mixing the ethylene homopolymer and a concentrated aqueous solution of the water-soluble bisulfite and sulfite and gradually adding, with stirring, the volatile polar organic solvent, periodically allowing settling to verify that three liquid phases are present. Three-phase systems may also be present where surface active agents or synthetic detergents are utilized in the reaction mixtures. As reaction proceeds, in batch operation, the top layer in a system of three liquid phases disappears.

Upon completion of reaction, sulfitations of ethylene homopolymers contain either one or two liquid phases. Solid, which may be either sodium sulfite or sodium sulfate if sodium salts and small amounts of water are used, or alkane sulfonates if ethylene homopolymers of comparatively high C_n are used, may also be present. The high C_n sulfonates may be brought into solution by warming.

If a product containing the salts of inorganic anions is wanted, the reaction mixture is adjusted to a pH of about 8, heated to distill off the volatile, polar organic solvent for reuse, and the remaining detergent solution is then either used as is or dried to a white solid.

For some purposes, as in production of bars for household use, a product free of salts of inorganic anions is preferable. This may be prepared by adjusting the content of volatile organic solvent in the final reaction mixture until two liquid phases are obtained with most of the detergent in the upper layer and most of the salts of inorganic anions in the lower. To achieve the desired disposition between the two layers, in some cases more solvent should be added at the end of a sulfitation; in others some of the solvent already present should be distilled off. Simple testing on small portions of the final reaction mixture is usually indicated to determine which should be done. After separation of the liquid layers, the volatile organic solvent is distilled from each and recovered for reuse. The upper layer may then be dried, either completely or with only partial removal of water, to provide solid organic sulfonate essentially free of salts of inorganic anions. This material may be converted into bars by methods conventional in the soap industry. The lower layer may be dried to afford valuable by-product salts.

It is highly desirable, at least in certain cases, in the recovery of the novel synthetic detergents of my present invention, after the sulfitation reaction has been completed, to remove the upper ethylene homopolymer-bisulfite reaction product-rich phase by, for example, decantation, and subject this phase to a conventional distillation operation to remove solvent. The solvent, as is the case in all of the distillation operations utilized in my present

invention, is circulated through the system for reuse. Some sodium sulfate is obtained in the reactions and can be utilized as a valuable by-product.

Whether the initial reaction medium exists as a three-phase or two-phase system is not critical to the properties of the novel synthetic detergents obtained in accordance with the practice of this invention. The polar organic solvent, and the initially present surface active agent or synthetic detergent where used, are utilized in the formation within the reaction mixture of a liquid phase in which two reactants, that is, the ethylene homopolymer and the water-soluble bisulfite, are significantly soluble. The provision of such a liquid phase for the reactants is directly connected to the extent of completion of the addition reaction between the water-soluble bisulfite and the ethylene homopolymer. Unless such a liquid phase is present, the oxygen required to induce the addition will oxidize the bisulfite and the sulfite ions present to the corresponding sulfate (and to a small amount of dithionate), with the result that practically none, or at least very little, of the desired synthetic detergent will be formed.

The molecular oxygen-containing gas employed as an inducing agent in my present process may be introduced into the reaction mixture in any manner known in the art, and may, as disclosed in my prior patent, be air or relatively pure oxygen.

The temperatures at which the addition reaction takes place may range between about room temperature and the reflux temperature of the reaction mixture. Very satisfactory results have been attained at temperatures ranging from 15° C. to 60° C. Usually, however, temperatures in the range of 20° C. to 30° C. are adequate. Lower temperatures raise cooling costs; and higher temperatures produce increased costs since more organic solvent must be condensed and returned to the reaction mixture.

The reaction may be carried out at either atmospheric or superatmospheric pressure. The quantity of solvent removed from the reaction mixture by a given weight of exit gas is approximately inversely proportional to the absolute pressure on the system and this will in some cases warrant the expense of operation at a pressure at least modestly above atmospheric.

The relative proportions of water, water-soluble bisulfite and water-soluble sulfite or other alkaline material employed in my present process correspond substantially to those of my prior patented process. Thus, the bisulfite is employed in amounts of from about 1 to 2.5 mols, especially desirably from about 1 to 2 mols, per mol of ethylene homopolymer used. Amounts of the order of 3 mols may be used, but such is not particularly practical.

The water-soluble sulfite is desirably employed in a mol ratio to the water-soluble bisulfite in the range of about 1:1 to 3:1. Such mol ratios determine the particular pH of the mixture at the start of the reaction. Where alkaline materials other than water-soluble sulfites are employed, the amounts thereof should be selected so as to produce the desired pH.

The quantity of water used in the reaction mixture advantageously ranges from about 25 to 75 mols per mol of ethylene homopolymer.

In order that those skilled in the art may even more fully understand the nature and advantages of my present invention, I shall describe a few illustrative examples for carrying out my invention. It will be understood, however, that the same are not to be construed in any way as limitative of the true scope of my invention, the latter being pointed out in the claims. It will be understood that variations may be made, among other things, in the nature of the ethylene homopolymers, the polar organic solvents used, and the surface active agents, if any, employed. Those skilled in the art will, in the light of my teachings herein, be able to make various adjustments all of which will fall within the scope of my novel teachings.

Example 1

A mixture was formed of 0.2 gram mol of an ethylene homopolymer containing predominately 16 carbon atoms, 0.15 gram mol of sodium metabisulfite ($Na_2S_2O_5$), 0.5 gram mol of sodium sulfite, 65 grams of tertiary butyl alcohol, 270 grams of water and 10 grams of a detergent sold under the trademark "Vel." Initially three phases were discernible in the mixture together with a small amount of undissolved inorganic salt. The sulfitation reaction was allowed to proceed at room temperature (about 22° C.) for 5 hours. Agitation throughout the reaction period was provided by a kitchen-type electrical mixer. Molecular oxygen to induce the addition of the bisulfite to the ethylene homopolymer came from air beaten into the mixture by the mixer.

Samples were periodically removed from the reaction mixture, warmed, and diluted with water. Unreacted ethylene homopolymer showed up as turbidity. When turbidity was no longer evident, the reaction was allowed to proceed an additional hour to make certain that the ethylene homopolymer had completely reacted. The ethylene homopolymer-bisulfite reaction product appeared in the form of a white, waxy solid suspended through the reaction mixture. The pH of the reaction mixture was adjusted to 8 with sodium bicarbonate and the mixture was evaporated to dryness. The final product was a white, friable solid which produced a foaming solution when a small portion was added to hot water.

Example 2

A mixture was formed as described in Example 1, but, in place of the ethylene homopolymer thereof, an ethylene homopolymer containing predominately 14 carbon atoms was used, and, instead of "Vel," a like quantity of the synthetic detergent obtained in Example 1 was used. Initially three phases were present in the mixture along with a small amount of undissolved inorganic salt. The reaction was allowed to proceed for 4 hours at room temperature. Agitation with the concomitant addition of molecular oxygen was provided as in Example 1. The reaction mixture was a thick, creamy paste. The pH was adjusted to 8 by sodium bicarbonate and water and alcohol removed by evaporation. The final product had properties similar to those of the product obtained in Example 1 but was slightly more soluble in water and foamed more copiously.

Example 3

A mixture was formed as described in Example 1, but using as the ethylene homopolymer one containing predominately 12 carbon atoms, and the detergent obtained from the run of Example 2 was used as the surface active seeding agent. Initially two phases were present in the mixture. The reaction was allowed to proceed at room temperature for a total of 8 hours. The pH was adjusted to 8 by sodium bicarbonate and the water and the alcohol evaporated. A white, friable solid was obtained which dissolved in cool water to give foaming solutions that were opalescent. The solutions became clear upon warming.

Example 4

A run similar to that of Example 3 was made but using as the ethylene homopolymer one containing predominately 10 carbon atoms, and the synthetic detergent obtained from Example 3 was used as the surface active agent. Two phases were present initially. The reaction time was 4 hours. A white, friable solid product resulted, being soluble in cool water to form foaming solutions.

Example 5

A run similar to that of Example 3 was made but using as the ethylene homopolymer one containing predominately 8 carbon atoms, and the synthetic detergent obtained from Example 4 was used as the surface active

agent. Two liquid phases were present initially. The reaction time was 8 hours. During the reaction period the upper liquid layer gradually increased from one third to one half the total volume. The final product was a white, friable solid readily soluble in cool water. Such a solution foamed readily when shaken but the foam broke rapidly.

Example 6

One part of each of the products obtained in Examples 2 and 3 above was mixed together and added to 3 parts of water and 2 parts of tertiary butyl alcohol, said parts being by weight. The mixture was stirred at room temperature and produced two liquid phases with considerable solid suspended in the lower one thereof. The upper liquid phase was drawn off and the solvent evaporated. From this there was obtained slightly less than 1 part of a white, soap-like solid that, when slightly moist, could be molded with the hands into a bar. When dry, the bar had a number of very desirable characteristics. It readily removed dirt from the hands, it gave a stable lather, it felt like a conventional soap bar, and it retained its firmness during the process of wetting and handling to which a conventional soap bar is normally subjected. After use, the bar imbibed the residual water, soon presenting a firm surface.

Example 7

A mixture was formed of 0.1 gram mol of an ethylene homopolymer containing predominately 14 carbon atoms, 0.1 gram mol of an ethylene homopolymer containing predominately 12 carbon atoms, 28.5 grams of sodium metabisulfite ($Na_2S_2O_5$), 63 grams of sodium sulfite, 270 grams of water, and 65 grams of tertiary butyl alcohol. After mixing at room temperature, two liquid phases were present, 25 grams of a synthetic detergent bar made in accordance with Example 6 were added and dissolved by stirring. Two liquid phases were still present, the upper occupying about 40% of the total volume. During a five hour reaction (stirring at room temperature, exposed to air), the volume of the upper phase gradually increased until it was about 75% of the total, holding at this value during the latter part of the run. The lower, salt-rich, phase was discarded. (In commercial operations, this lower phase may be treated to recover the alcohol, the sodium sulfite and sodium sulfate.) The upper phase was evaporated to a thick, white paste which was formed into a bar and cooled. The crude, moist bar, weighing about 200 grams, was redissolved at room temperature in 200 grams tertiary butyl alcohol and 50 grams H_2O. Again two liquid phases were formed along with a little solid that settled to the bottom and appeared to be crystalline, inorganic salt, presumably either sodium sulfate or sodium sulfite. The clear upper layer was drawn off and the solvent evaporated therefrom. While still somewhat moist and warm it was shaped into a bar with a spatula. It was white, firm when cooled and formed a lather when used for washing the hands.

Bar products formed from the synthetic detergents obtained in accordance with my present invention have the smooth surface feel which is referred to in the art as good "slip" or "finish." They manifest quite high resistance to water hardness. Because of their essentially neutural character they do not affect the slight acidity of the skin as do conventional soaps.

It will be understood that various changes and modifications may be made without departing from the spirit of this invention.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. A synthetic detergent bar containing as the essential synthetic detergent agent thereof a solid reaction product of a water-soluble bisulfite with an ethylene homopolymer containing predominately 1-alkenes which are mainly linear in character and have a few percent of branched chain materials and containing from 10 to 16 carbon atoms, said synthetic detergent agent being prepared by a process comprising forming a reaction mixture comprising an ethylene homopolymer containing predominately 1-alkenes which are mainly linear in character and have a few percent of branched chain materials and containing from 10 to 16 carbon atoms, water, a water-soluble volatile polar organic solvent, a water-soluble bisulfite, and an alkaline material, the aqueous phase of said reaction mixture having a pH between about 6 and about 7.5, the mol ratio of said bisulfite to said ethylene homopolymer being in the range of 1:1 to 3:1, and dispersing a gas containing molecular oxygen through said reaction mixture, the reaction mixture being maintained at a temperature between about room temperature and the reflux temperature of the reaction mixture, the pH in the aqueous phase being maintained above about 6 and below about 9.

2. An all synthetic detergent bar containing as the essential synthetic detergent agent thereof a reaction product of sodium bisulfite with an ethylene homopolymer containing predominately 1-alkenes which are mainly linear in character and have a few percent of branched chain materials and containing from 12 to 14 carbon atoms, said synthetic detergent agent being prepared by a process comprising forming a reaction mixture comprising an ethylene homopolymer containing predominately 1-alkenes which are mainly linear in character and have a few percent of branched chain materials and containing from 12 to 14 carbon atoms, water, a water-soluble volatile polar organic solvent, a water-soluble bisulfite, and an alkaline material, the aqueous phase of said reaction mixture having a pH between about 6 and about 7.5, the mol ratio of said bisulfite to said ethylene homoploymer being in the range of 1:1 to 3:1, and dispersing a gas containing molecular oxygen through said reaction mixture, the reaction mixture being maintained at a temperature between about room temperature and the reflux temperature of the reaction mixture, the pH in the aqueous phase being maintained above about 6 and below about 9.

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