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3,010,849

FABRIC CONDITIONERS

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This invention relates to the use of high molecular weight, branched chain, monohydric, primary alcohols as conditioners for textile fabrics.

In particular, the invention relates to the use of aqueous emulsions of such alcohols having 13 to 32, particularly 13 to 26, and preferably 16 to 20 carbon atoms per molecule to impart softness, loftiness and anti-static properties to the treated fabrics.

More particularly, the invention relates to the use of such emulsions in laundering to impart the aforesaid properties to such fabrics.

In another embodiment of the invention the aforesaid alcohols are applied as a finishing process in the preparation of the textile fabric.

Softness, as a characteristic of textile fabrics, is highly desirable except for certain special uses. The application of softening finishes is therefore extensively used in the textile industry not only to improve the handle of a material but also to facilitate mechanical finishing operations, to reduce the harshness and coarseness imparted to textiles by certain film-forming sizes and corrective finishes, and to increase the life and utility of a fabric.

Another problem always present where textiles are used or handled is that of static electricity. The presence of such static charges causes the material to cling to the body of the user, attract dirt and dust, and by crackling or by creating a spark when rubbed or moved. Certain finishes which have been applied have demonstrated an initial anti-static effect. However, they are, for the most part, removed during laundering.

The high molecular weight monohydric, primary alcohols which are a liquid at room temperatures have not been available in large quantities in the past. Other alcohols have found some use in the textile industry. For instance, the lower water soluble alcohols have found use as solvents and higher polyhydric alcohols have been used as chemical intermediates in the synthesis of various surface active agents.

It has now been found that the C_{13} to C_{32} , branched chain, monohydric, primary alcohols make excellent textile softeners and anti-static agents. Such alcohols are particularly suitable for use in laundering textile products such as towels, terry cloth, pile fabrics and knit goods from cellulosic fibers. The term "cellulosic fibers" as used herein shall be understood to include fibers of cotton, organic derivatives of cellulose, and other fibers having wettability characteristics equivalent to such fibers. Examples of other organic derivatives of cellulose materials which may be lubricated and conditioned with the composition of the invention are cellulose esters such as cellulose propionate, cellulose butyrate, cellulose acetate propionate, cellulose acetate butyrate, and cellulose ethers, such as ethyl cellulose and benzyl cellulose.

The term "branched chain, monohydric, primary alcohol" as used herein shall be construed to include both monohydric, primary alcohols which aside from the hydroxyl group are composed exclusively of carbon and hydrogen atoms and monohydric, primary alcohols which aside from the hydroxyl group are composed of carbon atoms, hydrogen atoms and a single oxygen atom forming an ether linkage with two of such carbon atoms.

Such alcohols are also suitable for conditioning fabrics

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made from other natural and synthetic fibers such as wool, silk, polyamide, polyester and acrylic fibers. Depending on the type of fabric and properties desired the alcohol may be employed in amounts in the range of about 0.25 to 2.0, preferably about 0.25 to 0.5, wt. percent based on the weight of the fabric to be treated per each application.

The alcohol may be added to the laundering process in the form of a water and alcohol emulsion or the emulsifying agent and the alcohol may be added to the water in the washer and emulsified therein by the agitation of the washing process.

Alcohols of the type herein described are not emulsifiable with water without the aid of an emulsifying agent. For this purpose nonionic, cationic and anionic surface active agents may be employed to effect the desired emulsions with simple agitation. Particularly suitable for this purpose are the nonionic surface active agents containing an organic hydrophobic group and an alkylene oxide comprising hydrophilic group wherein the hydrophobic group is an alkyl, aryl, or alkylaryl hydrocarbon group or a substituted alkyl, aryl or alkylaryl hydrocarbon group, e.g. ethers and alcohols, and the hydrophilic group contains ethylene oxide and/or propylene oxide. The most preferred of these are the dialkyl phenoxy polyoxyethylene nonionic emulsifiers which contain about 20 to 36 carbon atoms in the hydrophobic group and wherein the ethylene oxide hydrophilic group comprises about 50 to 95, preferably 70 to 95, wt. percent of the compound. The emulsifier may be employed in amounts of 0.05 to 10, preferably 0.075 to 1, wt. percent based on the weight of said alcohol.

Since stability of emulsion is not a factor in this type of treating operation with the agitation of the washer constantly reforming an emulsion from any de-emulsified portions of the same, the ratio of water to alcohol in the washer is not critical. Proper applications of the treating solution can best be calculated on the basis of the fabric material to be treated as hereinbefore set forth. When the emulsion is prepared and then added to the washing operation, the emulsion is preferably formed using about 25 to 35 wt. percent water and 65 to 75 wt. percent of the alcohol. Washing temperatures may be maintained within normal laundering temperatures, e.g. 100° to 200° F. Conventional washing times are suitable for these applications and the application can be successfully made in washing times above about 0.5 minute, e.g. 0.5 to 20, preferably 2-5, minutes.

Suitable alcohols for use in this invention are preferably prepared by the Aldox process, a modification of the well-known Oxo process.

In the Aldox process, a primary alcohol product is prepared from an olefin and a synthesis gas of carbon monoxide and hydrogen. Except for the use of a reaction modifier hereinafter discussed, and the product, the Aldox process is substantially the same as the Oxo process. In the Oxo process, oxygenated organic compounds are synthesized in the presence of a cobalt catalyst from organic compounds containing olefinic linkages by reaction with carbon monoxide and hydrogen. In this reaction predominantly aldehydes and minor proportions of ketones and alcohols are formed. The products from this Oxo step may then be hydrogenated in a second step to convert the organic carbonyl compounds containing one more carbon atom than the olefinic starting material to the corresponding alcohol. The hydrogenation catalyst may comprise any known reduction catalyst such as metallic supported or unsupported nickel, copper chromite, sulfactive catalyst such as oxides and sulfides of tungsten, nickel, molybdenum and the like.

Straight and branched chain olefins such as propylene,

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butylene, pentene, hexene, heptene, styrene, olefin polymers such as di and triisobutylene, hexene and heptene dimers, polypropylenes, olefinic fractions from the hydrocarbon synthesis process, thermal or catalytic cracking operations, and other sources of hydrocarbon fractions containing such olefins may be used as starting materials depending on the nature of the final product desired. The synthesis gas mixture fed to the first stage may be any desired ratio of H_2 to CO, preferably within the limit of 0.5 to 2 volumes hydrogen per volume of carbon monoxide. The conditions for reacting olefins with the synthesis gases vary somewhat in accordance with the nature of the olefin feed, the reaction being generally conducted at pressures in the range of from about 1500 to 4500 p.s.i.g. and the ratio of synthesis gas to olefin may vary widely; in general, about 2500 to 25,000 cubic feet of $H_2 + CO$ per barrel of olefin feed are employed.

The catalyst for the first stage of the process may be employed in the form of an oil-soluble compound of the catalytically active carbonylation metal. Thus, there have been employed the salts of the metals such as cobalt and high molecular weight fatty acid such as stearic, oleic, naphthenic, linoleic and the like. Water-soluble catalyst, such as cobalt acetate, chloride, and the like, may also be used. Catalyst concentrations may vary from about 0.05 to 1.0% by weight of the catalyst calculated as cobalt on olefinic feed. The first stage for carbonylation reaction may be carried out at temperatures in the range of from about 250° to 450° F. depending upon the nature of the olefin and other reaction conditions. In general, the lower olefins will react at lower temperatures and will react to a greater extent than the higher molecular weight olefins.

The Oxo process without modification will produce some alcohols of higher molecular weight, but the yields of such products are relatively low. These alcohols result from several different mechanisms including aldolization, dehydration, dimerization, acetalization, etc. Some of these alcohols contain two more than twice the number of carbons in the olefin feed and are highly branched alkanols. Another type contains three more than twice the number of carbons in the olefin feed but this latter type also contains an additional oxygen atom in the molecule forming an ether linkage with two internal carbon atoms.

For a more accurate description of these ether alcohols see Oxo Ether Alcohols, Bartlett et al., Industrial and Engineering Chemistry, March 1959, pages 257-258.

In the Aldox process the same reactors, catalyst, and reaction conditions may be employed as in the aforesaid Oxo process, and in addition, a reaction modifier is employed which results in the production, in high yields, of a primary alcohol product having $2n+2$ carbon atoms, where an olefin with n carbon atoms is passed to the carbonylation zone. Accompanying this reaction is the normal aldehyde reaction producing aldehydes and alcohols having $n+1$ carbon atoms.

The aforesaid reaction modifiers are preferably zinc compounds. The zinc compounds suitable are salts or fatty acids, oxides, hydroxides, carbonates, and also metallic salts of cobalt hydrocarbonyl. Thus, in the Aldox process there is passed into the first-stage reaction zone along with the olefin, carbon monoxide, hydrogen, and cobalt carbonylation catalyst, a reaction modifier, preferably zinc. Other Aldox modifiers have been suggested in the prior art. The mono-ether, mono-hydroxy alcohols hereinbefore described may also be produced in the Aldox process in somewhat lesser quantities. The C_{13} to C_{32} alcohols of this group may also be used in this invention.

A liquid oxygenated reaction product comprising aldehydes from the carbonylation reaction containing inorganic contaminants, e.g. dissolved cobalt carbonyl and zinc salts, is sent to a catalyst decomposition or decobalting zone, where in the presence of heat and steam,

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water, or dilute organic acid, the inorganic contaminants are removed from the aldehyde product in a manner known in the art. This product, now substantially completely free of inorganic compounds, is hydrogenated under conventional conditions to alcohols and the alcohol product fractionated to produce both the $n+1$ and $2n+2$ alcohols, as described.

The production of such alcohols by the Aldox process is covered by U.S. Patent 2,811,567.

Monohydric, primary alcohols may also be prepared from aldehydes via conventional Aldol condensation. By this process the positive end of a carbonyl group is linked with a carbanion by a typical "Aldol condensation" known to the art. The primary Aldol product may then be dehydrated by means known to the art to yield an unsaturated aldehyde which can be hydrogenated to a primary alcohol.

Another method for preparing monohydric, primary alcohols is by the process known to the art as the Guerbet reaction.

In textile finishing, these alcohols may be used with scours, enzymes and bleaches in removing waxes and pectins from cellulose fiber. This use of the alcohol increases the whiteness of the fabric and reduces the solvent extractable material remaining in cotton after such treatments.

The alcohols suitable for use in this invention are liquids at normal room temperatures, e.g. above 40° F. They are not volatile at temperatures within which textiles can be safely laundered.

Example I

A branched chain C_{16} monohydric alcohol wherein the carbinol group is positioned intermediate to the ends of the longest carbon chain was prepared by the Aldox process. This process and the range of operating conditions within which it may be carried out had previously been discussed herein. The alcohol of this example was prepared by this process employing as the olefin feed a C_7 olefin fraction previously prepared by a U.O.P. type polymerization of a C_3 - C_4 olefin stream, cobalt and zinc catalyst in the form of their oil-soluble fatty acid salts, i.e. oleates, and under the following operating conditions.

Carbonylation reaction C_7	
olefin feed rate-----	510-530 b./d. ¹
Catalyst concentration ----	.08 wt. percent cobalt (on olefin).
	.02 wt. percent zinc (on olefin).
Temperature, ° F-----	350-360.
Pressure, p.s.i.g.-----	3000-3500.
Ratio of H_2 to CO in synthesis gas mixture-----	1:1.4::1.

¹ Barrels per day.

The aldehyde comprising reaction product was subjected to a conventional decobalting treatment to remove inorganic contaminants. The decobalting was carried out at temperatures averaging about 270-380° F., pressures averaging about 155-165 p.s.i.g., in the presence of water employed in a water to feed ratio of about 0.1 to 1.

The aldehyde comprising product now substantially completely free of inorganic compounds was hydrogenated by conventional methods to alcohols, i.e. at an average temperature of about 470° F. and a pressure of about 3000-3500 p.s.i.g., and subsequently fractionated to separate the aforesaid C_{16} alcohol.

Example II

A 25/75 wt. percent water/alcohol emulsion of the C_{16} alcohol of Example I was prepared by conventional mechanical mixing using a commercially available nonionic emulsifying agent comprising a dinonyl phenol alkylene oxide condensate and containing about 85-90 wt. percent ethylene oxide per molecule. The concentration of emul-

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sifying agent used was 0.1 wt. percent based on the weight of said water.

Example III

Cotton bath towels of two colors, green and white, were treated with a C₂₀ branched chain, monohydric alcohol, prepared as the alcohol of Example I except that a C₉ olefin feed was employed, to which was added a non-ionic surfactant, an ethylene oxide condensate of a C₁₃ straight chain alcohol having about 10 ethylene oxide condensation units per molecule. The application was in the amount of about 0.25 wt. percent based on the weight of the towels. The ratio of alcohol to emulsifier was about 9:1.

Prior to application of the alcohol and emulsifier, the towels were subjected to 5 launderings. The aforesaid application was made at each of next 8 launderings and the condition of the towels evaluated after a total of 13 launderings.

The towels were laundered in a home type automatic washer, using a medium washer load at each laundering. Each laundering cycle consisted of 1 wash cycle and 3 rinse cycles. The wash cycles were conducted with a water temperature in the range of 152° to 156° F. At the beginning of each wash cycle ¼ cup of household detergent, All, was added. A water temperature of about 118° F. was employed for the third rinse water. The C₂₀ alcohol and emulsifier were added at the third rinse cycle of each laundry cycle during the course of the treatment.

Another portion of the towels were laundered following exactly the same procedure as above set forth except that the addition of the C₂₀ alcohol and emulsifier was eliminated. These towels were also subjected to a total of thirteen laundering cycles and then compared with the treated towels.

The treated towels were examined after the aforesaid procedure was completed and the following observations were made:

(1) The treated towels exhibited a soft, flexible hand pleasing to the feel and were noticeably softer than the towels of the untreated control.

(2) The treated towels exhibited a marked degree of loftiness or fluffiness and when placed alongside an even number of the comparable untreated towels stood markedly higher than the untreated towels.

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(3) The treated white towels were exceptionally white and bright appearing; the colored towels appeared natural and unclouded.

(4) The treated towels were used for drying water on the human body, and no decrease in absorbency as compared to untreated towels was observed.

Example IV

A 25/75 water/alcohol emulsion is formed with the C₁₆ alcohol of Example I using 0.1 wt. percent of a non-ionic emulsifier containing dinonyl phenol as the hydrophobic group and an ethylene oxide condensate as the hydrophilic group with the latter comprising about 88 wt. percent of the molecule.

This emulsion is added to washing operations as set forth in Example III. The textile fabrics therein laundered are found to have increased softness and loftiness as compared to untreated fabric.

What is claimed is:

1. In the washing of a cotton fabric wherein water is employed in a state of agitation, the improvement which comprises adding to said water an aqueous emulsion consisting essentially of a C₁₃ to C₃₂ branched chain, monohydric, primary alcohol, water and a nonionic emulsifier, said alcohol being a liquid at 40° F.

2. The process of claim 1 wherein said alcohol is a C₂₀ alcohol.

3. In the washing of a cellulose textile fabric wherein water is employed in a state of agitation the improvement which comprises adding to said water from 0.25 to 2.0 wt. percent based on the weight of said fabric of a mixture consisting essentially of a C₁₃ to C₃₂ branched chain, monohydric, primary alcohol and a nonionic emulsifying agent wherein said emulsifying agent comprises from about 0.05 to 10 wt. percent of said mixture, said alcohol being a liquid at 40° F.

References Cited in the file of this patent

UNITED STATES PATENTS

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