United States Patent Office

3,420,703

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PROCESS FOR TREATING A TEXTILE MATERIAL WITH AN AQUEOUS ANTISTATIC AND HANDLE-IMPROVING COMPOSITION AND THE AQUEOUS TREATING COMPOSITION

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Claims priority, application Germany, May 3, 1964, F 43,030
U.S. Cl. 117—139.5 5 Claims
Int. Cl. C08g *41/00;* C10m; D06m

ABSTRACT OF THE DISCLOSURE

A method of improving handle and antistatic properties of fibrous material such as wool, cotton, rayon, cellulose acetate, synthetic polyamides, polyesters, polyacrylonitrile and polypropylene by treating the fibrous material by exhaustion process with a heated aqueous liquor having an acid pH, the active ingredients of the liquor consisting essentially of

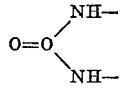
(a) a cationic interface-active compound exemplified by $R—N(CH_2—CH_2—NH—CO—NH_2)_2$, or a cationic polymer thereof wherein R is a long chain alkyl radical, an alkyl-polyoxy-alkylene, or quaternization product thereof;

(b) a lower aliphatic aldehyde exemplified by formaldehyde and

(c) an anionic interface-active or anionic polymeric compound exemplified by the ammonium salts of alkylaryl sulfonic acids.

The present invention relates to a process for treating fibrous materials; more particularly it concerns a process wherein fibrous materials are treated by the exhaustion process, while heating, with an acidic aqueous liquor containing

(a) cationic interface-active or cationic polymeric compounds which contain, in addition to a grouping



at least one further grouping of this type or at least one amino group which possesses at least one hydrogen atom bound to the nitrogen atom;

(b) lower aliphatic aldehydes or compounds yielding lower aliphatic aldehydes; and/or alkylol compounds formed from (a) and (b) or their ethers with lower alcohols; and

(c) anionic interface-active or anionic polymeric compounds;

whereupon the materials are squeezed or centrifuged and dried in the usual manner, a rinsing operation being inserted before drying, if desired.

Examples of cationic interface-active compounds are compounds of the general formula

$$R—N(CH_2—CH_2—NH—CO—NH_2)_2$$

in which R stands for a long-chain alkyl radical, such as $CH_3(CH_2)_{16}CH_2—$, or for an alkyl-polyoxy, alkylene radical, such as

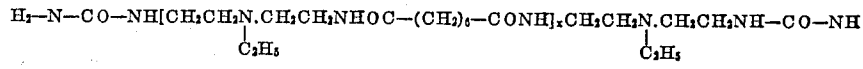
$$CH_3(CH_2)_{14}CH_2—O—(CH_2—CH_2O)_{10}—CH_2—CH_2—CH_2—$$

or their quaternisation products, and compounds of the general formula

$$R—CONH—CH_2CH_2NH—CH_2CH_2NH—CO—NH_2$$

in which R stands for a long chain alkyl radical, e.g. for the radical $CH_3—(CH_2)_{15}—CH_2—$.

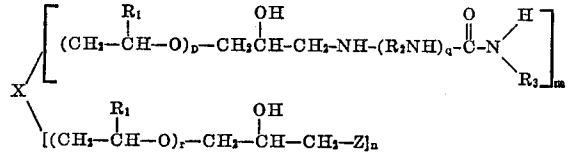
As cationic polymeric compounds there may be used, for example, compounds of the formula



in wich x stands for a number of 3 to 100, preferably 5 to 15, or their quaternisation products, as well as compounds of the formula

$$H_2N—CO—NH[CH_2CH_2NH.CH_2CH_2NH.OC—(CH_2)_6—CONH]_x—CH_2—(CH_2)_{16}CH_3$$

in which x stands for a number of 3 to 100, preferably a number of 5 to 15, or their quaternisation products which still contain at least one NH group. Especially suitable are cationic interface-active compounds of the formula



in which X stands for the radical of a compound which contains at least two hydrogen atoms capable of reacting with alkylene oxides, for example, for radicals of polyhydroxy compounds, such as glycerol, trimethylol-propane, pentaerythritol and sorbitol, R_1 denotes hydrogen or an alkyl radical, R_2 means an aliphatic, cycloaliphatic or aromatic radical, and R_3 denotes hydrogen, an alkyl radical, an alkoxy radical, an alkoxyalkyl radical or an aryl radical, and Z stands for an aliphatic, cycloaliphatic or aromatic radical containing at least 10 carbon atoms, preferably for the radical of stearyl alcohol, stearic acid, stearic acid amide, stearylamine, N-methyl-stearylamine or distearylamine, while m is a number of 2 to 6, n is a number of 1 to 4, p is a number of 1 to 100, q is a number of 0 to 4, and r is a number of 1 to 100, or the quaternisation products thereof. Relevant compounds are described in Belgian patent specifications Nos. 639,105 and 638,860.

As lower aliphatic aldehydes or of compounds capable of yielding lower aliphatic aldehydes there may be mentioned, for example, formaldehyde, polyoxymethylene dihydrate, acetaldehyde and glyoxal or hexamethylene-tetramine, dimethylol-urea, dimethylol-N,N'-ethylene-urea, methylol compounds of melamine as well as the ethers of these methylol compounds with lower alcohols, especially with methyl alcohol, furthermore the methylol compounds of carboxylic acid amides, e.g. of formamide and acetamide.

The alkylol compounds formed from the compounds (a) and (b) include, for example, the reaction products of the cationic compounds mentioned above with formaldehyde, or the ethers obtained from these reaction

products with lower aliphatic alcohols, such as methanol or ethanol.

Examples of anionic interface-active compounds are the alkali metal or ammonium salts of alkylaryl-sulphonic acids, e.g. of dodecylbenzene-sulphonic acid, dibutylnaphthalene-sulphonic acid, and dinaphthyl-methane-disulphonic acid, furthermore the alkali metal or ammonium salts of alkyl-sulphonic acids, e.g. of hexadecyl-sulphonic acid, and also the alkali metal or ammonium salts of higher fatty acids, such as stearic acid or oleic acid, of dioctyl-sulphosuccinic acid ester, monofatty alcohol-sulphuric acid or -phosphoric acid esters fatty acid sarcosides or taurides, alkyl-polyoxyalkylene- or alkylaryl-polyoxyalkylene-carboxylic acids and -sulphonic acids. Suitable anionic polymeric compounds are, for example, the alkali metal or ammonium salts of glycollic acid etherified with cellulose, of polyvinyl-sulphonic acid and polyacrylic acid; the molecular weight of these polymeric compounds is advantageously about 1000 to 10,000.

The amounts or proportions of the components contained in the aqueous liquor may vary within wide limits; expedient amounts or proportions which ensure the optimum absorption can easily be determined by preliminary experiments. For example, the quantity of cationic compounds depends upon the desired amount to be applied; in general, it will amount to about 0.5–10%, referred to the weight of the fibrous material. The quantity of lower aliphatic aldehydes or of aldehyde-yielding compounds is advantageously so chosen that more than 1 mol aldehyde, generally about 2–5 mol aldehyde, are present per one mol of cationic compound. The anionic compounds are normally used in such a quantity that the equivalent ratio between the anionic and cationic compounds lies within the range of 0.5–3:1; it is expedient to choose the equivalent ratio at which a dilute aqueous acidic solution of the components, when heated to 30–55° C., shows the strongest cloudiness, since the power of the cationic compounds to draw on the fibrous materials, possibly together with anionic compounds, is then greatest. Organic acids, such as formic acid and oxalic acid, are advantageously used for acidifying the aqueous liquor.

The treatment of the fibrous materials according to the invention is expediently carried out by initially moving the fibres for 30 to 40 minutes in an aqueous bath having a liquor-to-goods ratio of 20:1 to 50:1 containing the components concerned and having a pH value of, advantageously, 2 to 4, and raising the temperature during this period to about 60° C.; following the resulting absorption of the cationic compounds, which can be recognised from the fact that the cloudy liquor has become clear, the temperature of the bath is raised to 65–70° C. and maintained at this level for about 15–30 minutes, while adjusting the pH value to a value below 3 in order to complete the reaction of the cationic compounds with the aldehydes on the fibrous materials.

Instead of adding the aldehydes to the liquor from the start, it is also possible to add them to the liquor only during the treatment. If desired, the temperature of the liquor may also be raised above 70° C. to 90 to 100° C. and the duration of the treatment thus shortened, provided this is tolerated by the fibrous material.

By means of the process according to the invention valuable effects, for example, softening and hydrophobing effects, crease-proof and anti-static effects can

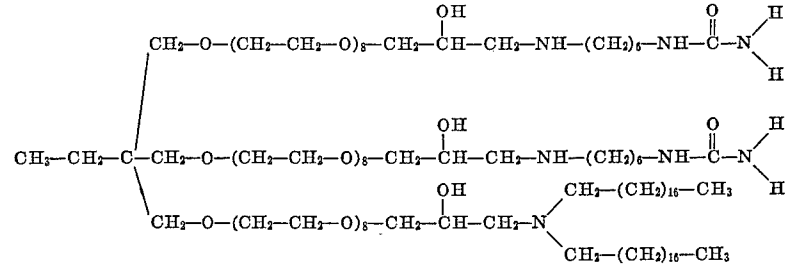
be achieved by the exhaustion process and at comparatively low temperatures, depending upon the type of cationic compounds employed, on a great variety of fibrous materials, e.g. on fibres, threads, yarns, fabrics or knitted fabrics of natural and especially of synthetic origin, such as wool, cotton, rayon, cellulose acetate, synthetic polyamides, polyesters, polyacrylonitrile and polypropylene. It is noteworthy that the effects achieved are largely resistant to washing, and this already before the treated fibrous materials have been dried, so that the materials can be freed before the drying operation from any excess of liquor by rinsing.

If desired, other agents suitable for the finish of fibrous materials, for example, plasticisers, anti-slip agents and stiffening agents may also be used when carrying out the process according to the invention.

The following examples serve to illustrate the invention without, however, limiting its scope.

Example 1

Yarns of fibres of polyacrylonitrile, polyester, polyamide or cotton, or of rayon are treated in an open or closed apparatus which permits a mechanical circulation of the goods or the liquor, in a liquor-to-goods ratio of 40:1 with an aqueous liquor which contains, per litre, 0.5 g. of the cationic compound



1.25 g. of 40% formaldehyde and 0.4 g. of a 42% commercial sodium salt of monolauryl alcohol-sulphuric acid ester, and which has been adjusted with oxalic acid to a pH value of 2.6; the liquor also contains a defoaming agent based on silicone in a quantity of 0.025 g. per litre. The liquor which is initially clear at room temperature, is heated to about 55° C. in the course of 15 minutes whereby a marked cloudiness appears. The temperature is then raised to 60° C. within 15 to 20 minutes and the bath is kept at this temperature for a few minutes until the liquor has again become clear. The temperature of the bath is then raised to 65–70° C., the pH value adjusted to 2.6 to 2.8 by the addition of oxalic acid, and the bath is kept at the same temperature for a further 30 minutes. The liquor is then cooled to 30° C. by the addition of cold water, the yarns are rinsed with water at 30° C. for about 5 minutes, then centrifuged and dried in the usual manner in a drying cabinet at 50 to 60° C. The yarns thus treated have a pleasant soft feel which is substantially resistant to washing. Yarns of synthetic fibrous materials exhibit moreover an antistatic effect which is also substantially resistant to washing.

The ratio of cationic to anionic compound stated above, which is advantageous for achieving the optimum absorption, was established by a simple preliminary experiment in the following manner: six aqueous solutions each of which contained, per litre, 0.5 g. of the cationic compound and 1.25 g. of 40% formaldehyde and was adjusted with oxalic acid to a pH value of about 3, were mixed at 20° C. with different amounts of the anionic compound, viz. with 0.1 g., 0.2 g., 0.3 g., 0.4 g., 0.5 g. and 0.6 g., respectively, and the almost clear solutions thus prepared were then heated to 45–55° C.; the solution containing 0.4 g. of the anionic compounds per litre thereby exhibited the strongest cloudiness, whereas the solutions which contained 0.3 g. and 0.5 g. of the anionic compound showed only a slight cloudiness, and the solutions

containing 0.1 g., 0.2 g. and 0.6 g. of the anionic compound exhibited practically no cloudiness at all.

Example 2

The process described in Example 1 is modified in that the suitable amount of 40% formaldehyde is not added to the liquor from the start, but only in the course of the treatment at 50 to 65° C. The finishing effects thus achieved are the same as those obtained by the method according to Example 1.

Example 3

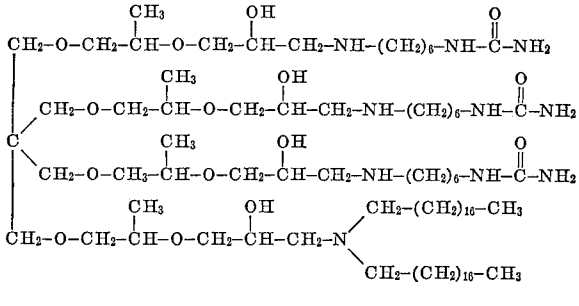
The process described in Example 1 is modified in that the liquor contains, instead of 0.4 g. of a 42% commercial sodium salt of monolauryl alcohol-sulphuric acid ester, per litre 0.4 g. of a 66% commercial sodium salt of oleic acid methyl tauride or 0.4 g. of a 70% commercial sodium salt of dibutyl-naphthalene-sulphonic acid. The finishing effects thus achieved are the same as those obtained by the method according to Example 1.

Example 4

Yarns of fibres of polyacrylonitrile, polyester, polyamide or cotton, or of rayon are treated in a cheese dyeing apparatus, after a conventional dyeing and after careful rinsing, in a liquor-to-goods ratio of 20:1 with an aqueous liquor which contains, per liter, 1 g. of the cationic compound of Example 1, 2.5 g. of the 40% formaldehyde, .05 g. of the defoaming agent based on silicone, and corresponding to commercial sodium salt of monolauryl alcohol-sulfuric acid ester as generally described in Examples 1 and 5, the liquor having been adjusted by means of oxalic acid to an initial pH value of 2.6. The liquor which is almost clear at room temperature is then heated to about 55° C. within 15 minutes, while changing the direction of the circulating liquor as frequently as possible, whereby a marked cloudiness of the liquor becomes apparent. The temperature of the liquor is then raised to 60° C. within 15–20 minutes, while, starting after about 10 minutes, the pH value is gradually adjusted to 2.2 by slowly adding a dilute aqueous oxalic acid solution in order to ensure a uniform and slow absorption. When using cheese apparatus with a particularly vigorous liquor circulation, the liquor is advantageously adjusted at the beginning to a pH value of 2.8–3, instead of to 2.6, and then gradually adjusted to a pH value of 2.2 in the course of the treatment. After the stated time, the liquor which has become completely clear, is maintained at pH 2.2 and at 65–70° C. for a further 30 minutes. The liquor is then cooled to about 30° C. by the addition of cold water. The yarns are then rinsed for 2–3 minutes and dried at 50–60° C. in the usual manner. The fibrous material thus treated has a pleasant soft feel which is substantially resistant to washing; yarns of synthetic origin moreover exhibit an antistatic effect which is also substantially resistant to washing.

Example 5

Yarns of fibres of polyacrylonitrile, polyester, polyamide or cotton, or of rayon are treated in an open or closed apparatus which permits a mechanical circulation of the goods or the liquor, in a liquor-to-goods ratio of 40:1 with an aqueous liquor which contains at the start of the treatment, per litre, 0.5 g. of the cationic compound



and 0.4 g. of a 42% commercial sodium salt of monolauryl alcohol-sulphuric acid ester, and has been adjusted with oxalic acid to a pH value of 4; the liquor also contains 0.2 g./litre of a defoaming agent based on silicone. The slightly cloudy liquor is heated to about 55° C. in the course of 15 minutes, whereby the cloudiness increases. A further 0.17 g. of a 42% commercial sodium salt of monolauryl alcohol-sulphuric acid ester are then added to the bath; the liquor is subsequently heated to 60° C. in the course of 15–20 minutes and kept at this temperature for a few minutes until it has become clear. 1 gram of a 50% commercial dimethylol-N,N'-ethyleneurea is then added per litre of liquor, the pH value is adjusted to 2.6 by means of oxalic acid, and the liquor is kept at 65–70° C. for about 30 minutes. The liquor is then cooled to 30° C. by the addition of cold water and the fibre material is rinsed for 2–5 minutes, then centrifuged and dried at 50–60° C. in a drying cabinet in the usual manner. The yarns thus treated have a soft feel which is substantially resistant to washing, and exhibit to some extent also a hydrophobic effect.

Example 6

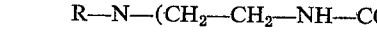
The process described in Example 1 is modified in that the liquor contains, per litre, 0.5 g. of 100% pentamethylol-melamine or 1 g. of a 50% commercial dimethylol-N,N'-ethylene-urea, instead of 1.25 g. of 40% formaldehyde. The finishing effects thus achieved are the same as those obtained by the method according to Example 1.

We claim:

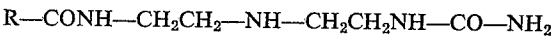
1. A method for improving the handle of and imparting antistatic properties to fibrous materials inclusive of one or more of wool, cotton, rayon, cellulose acetate, synthetic polyamides, polyesters, polyacrylonitrile and polypropylene, comprising treating the fibrous material by exhaustion process with a heated aqueous liquor having an acid pH, the active ingredients of said liquor consisting essentially of

(a) a cationic component comprising one of

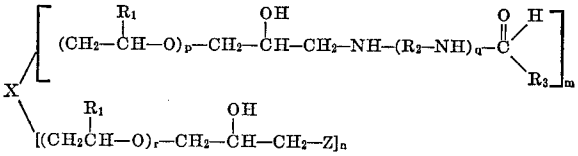
(1) the cationic interface-active compound selected from the group consisting of



the corresponding quaternization product thereof wherein R is a long-chain alkyl or an alkyl-polyoxy-alkylene radical; a compound of the formula



wherein R is a long-chain alkyl radical; and a compound of the formula

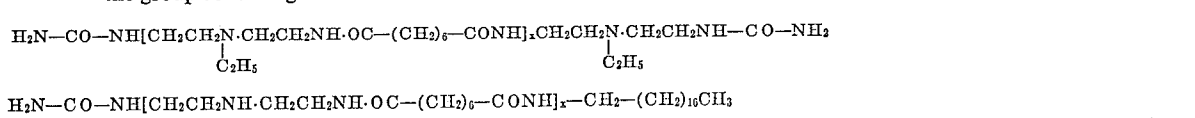


wherein X is an organic radical containing at least two hydrogen atoms reactive with alkylene oxides; *m* is 2–6; *n* is 1–4; *p* is 1–100; *q* is 0–4; *r* is 1–100; R_1 is a member selected from the group consisting of hydrogen and alkyl; R_2 is a member selected from the group consisting of aliphatic, cycloaliphatic and aromatic radicals; R_3 is a member selected from the group consisting of hydrogen, alkyl, alkoxy, alkoxy-

alkyl, and aryl; and Z is a member selected from the group consisting of aliphatic and aromatic radicals containing at least 10 carbon atoms;

or

(2) a cationic polymeric component selected from the group consisting of



and the corresponding quaternization product thereof wherein x is an integer of 3–100.

(b) a component selected from the group consisting of

(1) one of lower aliphatic aldehyde and a component capable of yielding a lower aliphatic aldehyde, and

(2) an alkylol formed from (a) and (b) (1); and

(3) the corresponding ether of (2) with a lower alcohol; and

(c) an anionic component consisting of one of

(1) an anionic interface-active compound selected from the group consisting of dialkyl-sulphosuccinic acid ester, monofatty alcohol-sulphuric acid ester, monofatty alcohol-phosphoric acid ester, fatty acid sarcoside, fatty acid tauride, alkyl-polyoxy alkylene-carboxylic acid, alkyl-aryl-polyoxy alkylene-sulphonic acid, and the alkali metal or ammonium salts of alkylaryl sulphonic acids, of alkyl sulphonic acids, and of higher fatty acids; and

(2) an anionic polymeric component inclusive of one of an alkali metal and an ammonium salt of glycollic acid etherified with cellulose, of polyvinyl sulphonic acid, and polyacrylic acid; the molecular weight of these polymeric components being about 1000–10,000;

the ratio in molar equivalents of (a), (b) and (c) being about 1:2–5:3.

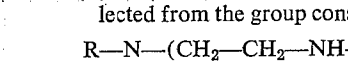
2. The method of claim **1** wherein the aqueous liquor contains about .5–10% by weight of fibrous material of the (a) cationic component and about 2–5 mol of the (b) alhehyde component per mol of cationic component; the equivalent ratio of anionic to cationic components being about .5–3:1, and the pH of the aqueous liquor is about 2–4.

3. The method of claim **1** wherein the fibrous material is treated for about 30–40 minutes in the aqueous bath having a liquor-to-goods ratio of about 20–50:1 and a pH of 2–4, maintaining a temperature of liquor and material at about 60° C. to effect absorption of the cationic compounds, and thereafter raising the temperature to about 65–70° C. at a pH below 3.

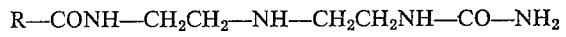
4. A fabric-treating composition consisting of an aqueous liquor having an acid pH, the active ingredients of said liquor consisting essentially of

(a) a cation component comprising one of

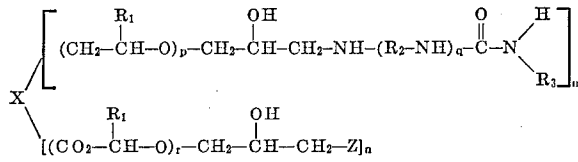
(1) the cationic interface-active compound selected from the group consisting of



the corresponding quaternization product thereof, wherein R is a long-chain alkyl or an alkyl-polyoxy-alkylene radical; a compound of the formula



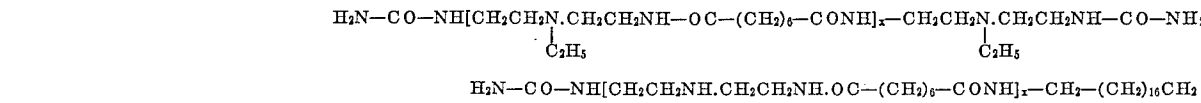
wherein R is a long-chain alkyl radical; and a compound of the formula



wherein X is an organic radical containing at least two hydrogen atoms reactive with alkylene oxides; m is 2–6; n is 1–4; p is 1–100; q is 0–4; r is 1–100; R_1 is a member selected from the group consisting of hydrogen and alkyl; R_2 is a member selected from the group consisting of aliphatic, cycloaliphatic and aromatic radicals; R_3 is a member selected from the group consisting of hydrogen, alkyl, alkoxy, alkoxyalkyl, and aryl; and Z is a member selected from the group consisting of aliphatic and aromatic radicals containing at least 10 carbon atoms;

or

(2) a cationic polymeric component selected from group consisting of



and the corresponding quaternization product thereof wherein x is an integer of 3–100.

5. The composition of claim **4** wherein the aqueous liquor contains a ratio of anionic to cationic components of about .5–3:1 and is maintained at a pH of about 2–4.

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WILLIAM D. MARTIN, *Primary Examiner.*

T. G. DAVIS, *Assistant Examiner.*

U.S. Cl X.R.

117—138.8, 139.4, 141, 143, 145; 260—29.4, 29.6

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

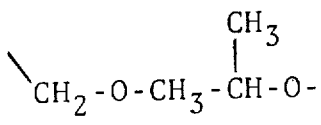
Patent No. 3,420,703 January 7, 1969

Helmut Kirschnek et al.

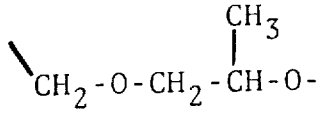
It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Columns 1 and 2, lines 18 to 23, the right-hand portion of the formula reading "NH-CO-NH" should read -- $NH\text{-}CO\text{-}NH_2$ --.

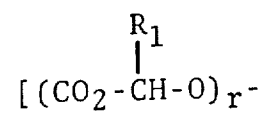
Column 5, lines 64 to 75, that portion of the formula reading



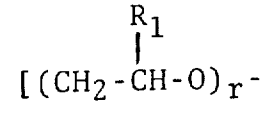
should read



Column 7, line 52, "alhehyde" should read -- aldehyde --. Column 8, lines 21 to 27, that portion of the formula reading



should read



Column 8, line 46, that portion of the formula reading "$-CH_2-(CH_2)_{16}CH_2$" should read -- $-CH_2-(CH_2)_{16}CH_3$ --.

Signed and sealed this 24th day of March 1970.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents