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3,190,715

PROCESS OF IMPARTING WASH AND WEAR PROPERTIES TO CELLULOSIC TEXTILES AND FINISHING SOLUTIONS FOR USE IN SUCH PROCESS

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9 Claims. (Cl. 8—116)

This invention relates to textile finishing procedures, and more particularly to processes of treating cellulosic textiles, such as cotton, rayon and viscose fabrics and yarns, to impart thereto wash and wear characteristics, a desirable soft finish or hand, and wrinkle or crease resistance, and this without impairing the tensile strength to an unsatisfactory level.

The treatment of cellulosic textiles with acetals, i.e., derivatives of aldehydes, has been suggested to effect cross-linking of the cellulose, and produce fabrics of good hand, improved crease resistance, and which are non-chlorine retentive.

It is a principal object of the present invention to provide a proces for treating cellulosic textiles, i.e., fabrics or yarns, with acetals to impart to the fabrics improved wash and wear properties, wrinkle resistance and tensile strength.

Another object of this invention is to provide a novel aqueous treating solution for practicing the process of this invention.

Other objects and advantages of the present invention will be apparent from the following detailed description thereof.

In accordance with this invention, cellulosic textiles are treated with an aqueous solution containing the acetal or mixture of acetals hereinafter defined and a synergistic catalyst mixture constituted of (1) an acid salt of a primary aliphatic amine, RNH_2X, in which R is an alkyl group having not more than 6 carbon atoms, and X is a strong acid, and (2) a quaternary ammonium salt having the formula:

$$R—O—CH_2—NR^1R^2R^3\ Hal$$

in which R is alkyl having from 12 to 18 carbon atoms and can be normal or branched, $NR^1R^2R^3$ is an aliphatic tertiary amine or a heterocyclic tertiary amine such as dialkylaniline, trialkylamine, pyridine, piperidine, quinoline, picoline or a homolog of any of these compounds such as the alkyl pyridines, piperidines, quinolines or picolines, and Hal is halogen, preferably chlorine or bromine. The alkyl group can have from 2 to 6 carbon atoms.

The aqueous solution can also contain a third (3) catalyst constituent, namely, a halide, oxyhalide, nitrate or sulfate of a metal of group 2, 3 or 4 of the periodic table or an organic acid which imparts a pH below 7 to the treating solution. Any such water-soluble metallic salt which when added to water produces a solution having a pH below 7 can be used. Examples of such salts are the alkaline earth metal, e.g., calcium or magnesium, chlorides, nitrates, bromides, chlorates and iodides; aluminum chloride or sulfate; boron fluoride; soluble zinc salts including zinc silico-fluoride; and zirconium oxychloride. Instead of, or along with, the metal salt, an organic acid such as citric acid, acetic acid, monochlor acetic acid or formic acid can be used.

The acetal used is the reaction product of formaldehyde

with a glycol or polyglycol containing not more than 6 carbon atoms in the glycol molecule produced by reacting at least one mol of formaldehyde per glycol. Preferably at least 2 mols of formaldehyde are reacted per glycol molecule. In the case of glycols having more than 2 hydroxy groups, it is preferred to employ as many mols of formaldehyde as hydroxy groups in the glycol. Examples of such acetals are pentaerythritol bis acetal and the acetals produced by reacting in each case 2 mols of formaldehyde with one mol of diethylene glycol, ethylene glycol, propylene glycol, trimethylene glycol, dipentaerythritol and tripentaerythritol as well as the acetal produced by reacting 3 mols of formaldehyde with glycerol.

The aqueous treating solution should contain from 2% to 16% by weight of the acetal on a basis of 100% acetal and not more than 10% by weight of the synergistic mixture of catalysts, with the catalyst components in the mixture present in approximately equal amounts. When treating cotton textiles, a solution containing from 2% to 10% by weight of acetal (100%) is used. When treating rayon or viscose textiles, the acetal content should be from 4% to 16% by weight.

Using an aqueous solution containing only catalyst components (1) and (2) above, the amount of the catalyst mixture should not exceed about 7% or 8% by weight based on the total weight of the treating solution. Preferably the solution contains from 0.5% to 2% of each of catalyst component (1) and (2), and if component (3) is also used, as preferred, it is employed in amount of 1.5% to 2.5% by weight of the solution.

The treating solution may also contain additives such as a small amount, e.g., from 0.1% to 5% by weight, of a buffer to minimize degradation of the cellulose due to the acid catalyst. Examples of such buffers are melamine formaldehyde, triazine urea formaldehyde resin (Aerotex 23), dimethylol ethylene urea, dimethylol dihydroxy ethylene urea, dicyandiamide (DCY). The solution can also contain esters of stearyl alcohol and melamine formaldehyde (Permel B sold by American Cyanamide Company), or a mixture of two or more such buffers, and from 0.5% to 4% of glycerin, glucose or sorbitol, which protects the cellulose and acetal in the treating solution during the early stages of the processing while the acetal is chiefly in the liquid phase.

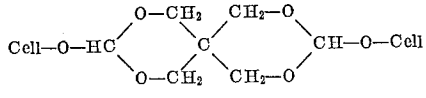
Following application of the treating solution to the cellulosic textiles at any temperature below the boiling point of the solution, preferably at about room temperature (about 70° F.), so that the wet pick-up is from 65% to 85% by weight based on the dry weight of the textile, the textile is dried and thereafter cured at a temperature of from 240° F. to 350° F. for from 1 to 10 minutes, preferably 2 to 5 minutes. For cottons the preferred curing temperature is from 300° F. to 310° F., and for rayons and viscose textiles the preferred curing conditions are at a temperature of about 320° F. for about 4 to 5 minutes.

Treatment of cellulosic textiles, as hereinabove described, results in a finish having a soft, silky, lustrous hand, outstanding wash and wear properties requiring little or no ironing after washing, and exceptionally good tensile properties, particularly as compared with such textiles produced by heretofore known procedures. These improvements are due to the synergistic catalyst system employed in accordance with this invention.

While the explanation for the improvements effected by the synergistic catalyst system is not fully known, the

following explanation, believed to be correct, is given to facilitate a better understanding of this invention. It will be appreciated, however, that this invention is not to be limited to this explanation.

The synergistic catalyst system of this invention provides the most favorable conditions for the reaction between the acetal and cellulose with substantially less deterioration of the physical properties of the cellulose. The components of the catalyst mixture cooperate to promote the reaction with optimum yield and with minimum adverse effect on the cellulose. To trigger the acetal cellulose reactions the pH conditions on the textile must be about 2.5. The reaction between the cellulose molecules and the acetal resin produces acetal cross-linkings; in the case of pentaerythritol acetal, the cross-links are represented as follows:

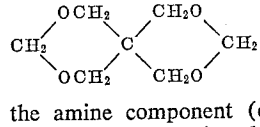


The reaction between the acetal and the cellulose takes place for the most part during the curing; at the curing temperatures the acetal is in its most reactive form. Component (1) of the catalyst system provides the acidic pH at the time when the reaction takes place necessary to promote the reaction. The primary aliphatic amine starts to decompose and provides some H^+ ions at temperatures lower than 200° F.; the major portion, however, does not decompose to form amine vapors and H^+ ions at temperatures above 240° F., i.e., 240° F. to 350° F.

The quaternary compound exercises a desired softening effect on the textile and also aids in promoting, i.e., catalyzing, the reaction between the acetal and the cellulose. The presence of the quaternary compound is particularly important during the early stages of the treatment because the presence of the quaternary ammonium compound assures maximum utilization of the compound. The quaternary compound and the primary aliphatic amine together have a synergistic influence in terms of the overall effect on the cellulosic textiles, particularly from the standpoint of imparting to the textiles improved wash and wear and tensile properties.

The water-soluble metallic salts and/or organic acids promote the formation of inter-molecular cross bonds of the cellulose molecules; the intra-molecular cross bonds are less deteriorative to the cellulose than are the inter-molecular cross bonds. However, both types of cross bonds are necessary to provide good wash and wear performance. Employing a catalyst mixture containing components (1) and (2) above, and not (3), a high dry and wet crease angle can be produced with less deterioration caused by inter-molecular cross bonds; in other words, the tensile strength is greater, and while the wash and wear properties are good they are not as good as is obtained when using a catalyst system containing all three components (1), (2) and (3) above. As indicated, the use of the latter system results in some loss of tensile strength chiefly because of the formation of more inter-molecular cross bonds; component (3) is responsible for more deterioration of the physical properties of the cellulose than is component (1) or (2) of the synergistic catalyst mixture.

Examples of acetals which can be used have been given above. The preferred acetal is pentaerythritol bis acetal having the formula:



Examples of the amine component (component (1) above) are the acid salts of monoethanol amine; butanol amine; ethylamine; 2-amino-1-butanol; 2-amino-2-methyl-1-propanol; 2-amino-2-methyl-1,3-propanediol; 2-amino-2-ethyl-1,3-propanediol; or tris (hydroxy-methyl)-aminomethane, particularly the hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid and citric acid salts. This amine component in combination with the other constituents of the treating solution provides a pH of 2 to 4 on the textile during the curing. Preferred is 2-amino-2-methyl-1-propanol hydrochloride, known commercially as Catalyst AC.

Examples of the quaternary ammonium component (component (2) above) are stearamide methyl pyridinium chloride; octadecyl oxymethyl pryridinium chloride; oleyloxymethylpyridinium chloride; stearamide methyl picolinium chloride; stearamide methyl quinolinium chloride. The preferred quaternary is stearamide methyl pyridinium chloride, sold commercially under the trade name Zelan AP, chiefly because it is readily available.

In preparing the padding bath employed for applying the treating solution, a portion of the water is mixed with the acetal and the other constituents added in solution form to the water-acetal mix. The quaternary ammonium salt is dissolved in hot water (temperature 160° F.). Other constituents, if not soluble in water at room temperature (about 70° F.) are dissolved in water at an elevated temperature below the boiling point. The temperature of the bath will depend on the particular constituents employed and should be such that all constituents remain in solution. Any temperature below the boiling point of water can be used. As a practical matter, temperatures near room temperature or a few degrees above room temperature, e.g., from 70° F. to about 110° F., can be used.

Instead of padding the textiles with the treating solution, the latter may be sprayed or otherwise applied to impregnate the textile with the treating solution. The wet pick-up is from 65% to 85% by weight based on the weight of the dry textile. After application, the treated textile is dried at a temperature of from 200° F. to 260° F. for from about 0.5 to 3 minutes. The dried textiles are then cured at a temperature of from 240° F. to 350° F. for 1 to 10 minutes, the temperature and time of the curing being inversely related.

Thereafter the fabric is washed with water or soap and water; this washing removes unreacted acetal and non-bound reaction products, should such products be formed.

The following examples are given to illustrate the invention. It will be appreciated the invention is not limited to these examples.

In the examples, the indicated fabrics were treated with the solutions of the examples. The solution was at room temperature (70° F.) when the cloth was passed therethrough and passed through the bite of the padding rollers, leaving the latter with a wet pick-up of about 70%. The thus treated cloth was pre-dried at 200° F. to 260° F. and then cured at 310° F. for 3 minutes. The fabric treated in Examples 1 to 3, inclusive, with the formulations given below, was a 128 x 68 broadcloth, 3.11 square yards per pound.

In Examples 1 to 11, inclusive, the acetal was the pentaerythritol bis acetal employed as 56% solution in water. In Examples 12 to 19, inclusive, the acetal was triethylene glycol acetal employed as a 54% solution in water and methanol. The percentage values given below represent percentages by weight of the 56% and 54% solutions, respectively, of the acetal based on the total weight of solution. The Aerotex was used in the form commercially available containing 48% solids in an aqueous or aqueous isopropanol medium. The dimethylol ethylene urea was in the form of a water or water isopropanol solution containing 48% resin solids. The dimethylol dihydroxy ethylene urea was in the form of a 50% aqueous solution containing 50% resin solids. The Zelan was used in a concentration of 50% solids, the rest being water. Component (1) was Catalyst AC but the acid salts of any other primary aliphatic amine having 6 or less carbon atoms, such as the hydrochloric acid, sulfuric

acid, nitric acid, phosphoric acid, or citric acid salts can be used with the same results.

In the formulations below, component (1) of the synergistic catalyst system is referred to as Catalyst AC. Component (2) is referred to as Zelan (the compound used was stearamide methylpyridinium chloride) but any other quaternary ammonium salt, as hereinabove disclosed, can be used with equal results. All percentage values given are by weight, based on the weight of total solution.

EXAMPLE 1

	Percent
Acetal	16
Aerotex	2
Glycerine	1.5
DCY	.25
Catalyst AC	.5
Calcium chloride	2.
Zelan	2
Water	75.75
Total	100

EXAMPLE 2

	Percent
Acetal	16
Aerotex	2
Glycerine	1.5
DCY	.25
Catalyst AC	.5
Calcium chloride	4
Zelan	2
Water	73.75
Total	100

EXAMPLE 3

	Percent
Acetal	16
Aerotex	2
Glycerine	1.5
DCY	.25
Catalyst AC	.5
Zinc silico-fluoride	3
Zelan	2
Water	74.75
Total	100

Examples	4	5	6	7	8	9	10	11
Pentaerythritol acetal	Percent 5	Percent 8	Percent 12	Percent 16	Percent 4	Percent 6	Percent 10	Percent 14
Dimethylol ethylene urea	5				6			
Dimethylol dihydroxy ethylene urea		2	8			6		4
Glycerine	1		1			2		1
DCY	.2		.25	.5				
Catalyst AC	.5	.5	.5	.5	1	1	1	
M. ethanol amine HCl								1
Zelan	2	2	2	2			2	
Magnesium chloride	2	2	2	2				
Zirconium oxychloride							.5	
Mono-magnesium phosphate								3
Bis pyridinium methylene bis oxymethyl chloride					1	1		1.5
Water	84.3	85.5	74.25	79	88	84	86.5	75.5
Total	100	100	100	100	100	100	100	100

Examples	12	13	14	15	16	17	18	19
Triethylene glycol acetal	Percent 5	Percent 8	Percent 12	Percent 16	Percent 4	Percent 6	Percent 10	Percent 14
Dimethylol ethylene urea	5				6			
Dimethylol dihydroxy ethylene urea		2	8			6		4
Glycerine	1		1			2		1
DCY	.2		.25	.5				
Catalyst AC	.5	.5	.5	.5	1	1	1	
M. ethanol amine HCl								1
Zelan	2	2	2	2			2	
Magnesium chloride	2	2	2	2				
Zirconium oxychloride							.5	
Mono-magnesium phosphate								3
Bis pyridinium methylene bis oxymethyl chloride					1	1		1.5
Water	84.3	85.5	74.25	79	86	82	86.5	75.5
Total	100	100	100	100	100	100	100	100

In Examples 20, 21 and 22, a rayon challis (0.24 pound per square yard) was treated as hereinabove described in the case of the treatment of cotton broadcloth with the indicated treating solutions. The pentaerythritol acetal and the dimethylol ethylene urea were used in the same concentration as indicated above in connection with the cotton examples.

Examples	20	21	22
Pentaerythritol acetal	Percent 26	Percent 16	Percent 20
Dimethylol dihydroxy ethylene urea	4	8	6
Catalyst AC	1	1	1.5
Zelan	2	1.5	2
Mono-magnesium phosphate	0	3	0
Water	67	70.5	70.5
Total	100	100	100

The table which follows gives the test results on the fabrics of Examples 1 and 2. In this table the values for tensile strength were obtained by the Scott Tester ASTM Standard D39–49. The Grease Recovery values were obtained by the Monsanto Method, ASTM Standards, D1295–53T American Society for Testing Materials, Philadelphia, Pa. Wash and Wear or No-Iron Rating was determined by AATCC Tentative Test Method, 88–1960, AATCC Technical Manual 1960, volume 36, page 148. According to this test procedure a value of 5 is perfect and a value of 4 is excellent.

Table

Example	Tensile		Crease recovery		No-iron rating spin and drip	No-iron rating spin and tumble	Bound HCHO, percent
	Warp	Fill	Warp	Fill			
1	43	22	120	128	4	4.3	1.02
2	32	18	125	130	4.3	4.5	1.15

These fabrics when tested for shrinkage upon repeated washings showed exceptionally good dimensional stability. They had a pleasing soft hand and showed good wear resistance, rendering them particularly useful for shirtings and other apparel of the better grades.

It will be noted that the present invention provides a process for treating cellulosic textiles, particularly cotton, rayon and viscose fabrics having markedly improved wash and wear properties, good dimensional stability upon washing, a soft pleasing hand and good wear resistance. The finish imparted to the textiles withstands repeated washings and dry cleanings. This invention also provides a treating solution for use in treating cellulosic textiles to

obtain the desirable wash and wear finish requiring no ironing and retaining a non-wrinkled, flat, crisp appearance upon drying.

This invention includes the treatment of textiles containing cellulosic fibers blended with other fibers, such, for example, as polyester and other synthetic fibers; preferably the textile contains at least 50% cellulosic fibers.

It will be appreciated that this invention is not to be limited to the disclosure herein except as indicated by the appended claims.

What is claimed is:

1. The process of finishing cellulosic textiles which comprises applying to the textile an aqueous solution containing from 2% to 16% of an acetal produced by reacting at least one mol of formaldehyde per mol of glycol having not more than 6 carbon atoms in the glycol molecule, and from about 2% to 10% by weight of a synergistic catalyst mixture, the components of said mixture being present in approximately equal amounts and containing an acid salt of a primary aliphatic amine having no more than 6 carbon atoms and a quaternary ammonium salt having the formula

$$R—O—CH_2—NR^1R^2R^3\ Hal$$

in which R is alkyl having from 12 to 18 carbon atoms, $NR^1R^2R^3$ is selected from the group consisting of heterocyclic tertiary amines and aliphatic tertiary amines, the aliphatic chain containing from 2 to 6 carbon atoms, and Hal is halogen, and heating the thus treated textile to a temperature of from 220° F. to 350° F.

2. The process as defined in claim 1, in which the catalyst mixture also contains from 1.5% to 2.5% by weight of a compound selected from the group consisting of the halides, oxyhalides, nitrates, and sulfates of a metal from groups 2, 3 and 4 of the periodic table and an acid from the group consisting of citric acid, acetic acid, monochlor acetic acid and formic acid.

3. The process of finishing cellulosic fabrics which comprises padding the fabrics through a bath containing from 2% to 16% of an acetal from the group consisting of the acetal reaction products produced by reacting at least 2 mols of formaldehyde per mol polyhydric alcohol from the group consisting of ethylene glycol, diethylene glycol, propylene glycol, glycerol, trimethylene glycol, pentaerythritol, dipentaerythritol and tripentaerythritol, from 0.5% to 2% of an acid salt of the primary aliphatic amines containing no more than 6 carbon atoms, from 0.5% to 2% by weight of a quarternary ammonium salt having the formula

$$R—O—CH_2—NR^1R^2R^3\ Hal$$

in which R is alkyl having from 12 to 18 carbon atoms, $NR^1R^2R^3$ is selected from the group consisting of heterocyclic tertiary amines and aliphatic tertiary amines, the aliphatic chain containing from 2 to 6 carbon atoms, and Hal is halogen, and from 1.5% to 2.5% by weight of a compound selected from the group consisting of the halides, oxyhalides, nitrates and sulfates, of a metal from groups 2, 3 and 4 of the periodic table and an acid from the group consisting of citric acid, acetic acid, monochlor acetic acid and formic acid to apply to the fabric from 65% to 85% of said solution based on the dry weight of the fabric, drying the fabric at a temperature of from 200° F. to 260° F., then curing the dried fabric at a temperature within the range of from 220° F to 350° F. for from 1 to 10 minutes and washing the cured fabric to remove unreacted acetal therefrom.

4. The process as defined in claim 3, in which the acetal is pentaerythritol bis acetal, the amino compound is 2 amino, 2 methyl, 1 propanol hydrochloride, and the quaternary ammonium compound is stearamide methyl pyridinium chloride.

5. The process of finishing cellulosic fabrics which comprises padding the fabrics through a bath containing from 2% to 16% of an acetal from the group consisting of the acetal reaction products produced by reacting at least 2 mols of formaldehyde per mol of polyhydric alcohol from the group consisting of ethylene glycol, diethylene glycol, propylene glycol, glycerol, trimethylene glycol, pentaerythritol, dipentaerythritol and tripentaerythritol, from 1% to 5% by weight of a triazine urea formaldehyde resin and from 0.5% to 4% by weight of glycerin, from 0.5% to 2% of an acid salt of a primary aliphatic amine containing no more than 6 carbon atoms, from 0.5% to 2% by weight of a quaternary ammonium salt having the formula

$$R—O—CH_2—NR^1R^2R^3\ Hal$$

in which R is alkyl having from 12 to 18 carbon atoms, $NR^1R^2R^3$ is selected from the group consisting of heterocyclic tertiary amines and aliphatic tertiary amines, the aliphatic chain containing from 2 to 6 carbon atoms, and Hal is halogen, and from 1.5% to 2.5% by weight of a compound selected from the group consisting of the halides, oxyhalides, nitrates and sulfates, of a metal from groups 2, 3 and 4 of the periodic table and an acid from the group consisting of citric acid, acetic acid, monochlor acetic acid and formic acid to apply to the fabric from 65% to 85% of said solution based on the dry weight of the fabric, drying the fabric at a temperature of from 200° F. to 260° F., then curing the dried fabric at a temperature within the range of from 220° F. to 350° F. for from 1 to 10 minutes and washing the cured fabric to remove unreacted acetal therefrom.

6. A finishing solution for the treatment of cellulosic textiles consisting essentially of from 2% to 16% by weight of an acetal produced by reacting at least one mol of formaldehyde per mol of glycol having not more than 6 carbon atoms in the glycol molecule and from about 2% to 10% by weight of a synergistic catalyst mixture, the components of said mixture being present in approximately equal amounts and containing an acid salt of a primary aliphatic amine having no more than 6 carbon atoms, and a quarternary ammonium salt having the formula

$$R—O—CH_2—NR^1R^2R^3\ Hal$$

in which A is alkyl having from 12 to 18 carbon atoms, $NR^1R^2R^3$ is selected from the group consisting of heterocyclic tertiary amines and aliphatic tertiary amines, the aliphatic chain containing from 2 to 6 carbon atoms, and Hal is halogen.

7. A finishing solution for the treatment of cellulosic textiles consisting essentially of from 2% to 16% by weight of an acetal from the group consisting of the acetal reaction products produced by reacting at least 2 mols of formaldehyde per mol of polyhydric alcohol from the group consisting of ethylene glycol, diethylene glycol, propylene glycol, glycerol, trimethylene glycol, pentaerythritol, dipentaerythritol and tripentaerythritol, from 0.5% to 2% of the acid salt of a primary aliphatic amine containing no more than 6 carbon atoms, from 0.5% to 2% by weight of a quaternary ammounium salt having the formula

$$R—O—CH_2—NR^1R^2R^3\ Hal$$

in which R is alkyl having from 12 to 18 carbon atoms, $NR^1R^2R^3$ is selected from the group consisting of heterocyclic tertiary amines and aliphatic tertiary amines, the aliphatic chain containing from 2 to 6 carbon atoms, and Hal is halogen, and from 1.5% to 2.5% by weight of a compound selected from the group consisting of the halides, oxyhalides, nitrates and sulfates of a metal from groups 2, 3 and 4 of the periodic table, and an acid from the group consisting of citric acid, acetic acid, monochlor acetic acid and formic acid.

8. A finishing solution for the treatment of cellulosic textiles consisting essentially of from 2% to 16% by weight of pentaerythritol bis acetal, from 0.5% to 2% of an acid salt of a primary aliphatic amine containing

no more than 6 carbon atoms, from 0.5% to 2% by weight of a quaternary ammonium salt having the formula

$$R—O—CH_2—NR^1R^2R^3\ Hal$$

in which R is alkyl having from 12 to 18 carbon atoms, and $NR^1R^2R^3$ is selected from the group consisting of heterocyclic tertiary amines and aliphatic tertiary amines, the aliphatic chain containing from 2 to 6 carbon atoms and Hal is halogen from the group consisting of chlorine and bromine.

9. A finishing solution for the treatment of cellulosic textiles consisting essentially of from 2% to 16% by weight of pentaerythritol bis acetal, from 0.5% to 2% of an acid salt of a primary aliphatic amine containing no more than 6 carbon atoms, from 0.5% to 2% by weight of a quaternary ammonium salt having the formula

$$R—O—CH_2—NR^1R^2R^3\ Hal$$

in which R is alkyl having from 12 to 18 carbon atoms, and $NR^1R^2R^3$ is selected from the group consisting of

heterocyclic tertiary amines and aliphatic tertiary amines, the aliphatic chain containing from 2 to 6 carbon atoms and Hal is halogen from the group consisting of chlorine and bromine.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,190,715 June 22, 1965

Alex F. Gordon

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 25, for "proces" read -- process --; column 4, line 58, after "as" insert -- a --; column 6, line 44, for "D39-49" read -- D 39-49 --; same line 44, for "Grease" read -- Crease --; line 46, for "D1295-53T" read -- D 1295-53T --; column 7, line 48, and column 8, line 39, for "quarternary", each occurrence, read -- quaternary --; column 8, line 43, for "A" read -- R --.

Signed and sealed this 12th day of April 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

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