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3,715,186

DRYCLEANING METHOD AND DETERGENTS THEREFOR

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6 Claims

ABSTRACT OF THE DISCLOSURE

The present invention relates to a method of drycleaning fabrics, such as garments and other dry-cleanable materials, which provides improved detergency and reduced soil redeposition. The invention also relates to particular cationic surface-active agents for use in the improved method as the primary detergent and to specific combinations of such surfactants in a drycleaning system utilizing a moisturized solvent. In addition, the invention also relates to a process for the synthesis of a preferred type of surface-active agent for use in the process.

This application is a continuation of Ser. No. 539,675 filed Apr. 4, 1966 now abandoned.

In the process of drycleaning as practiced commercially and also in coin-operated units, the soiled garments are agitated in an organic solvent in a perforated cylinder (referred to as a "wheel") to remove oil and grease stains and particles of soil. The solvent is repeatedly recirculated through a filter to remove the soil particles suspended in the solvent. The cleaning phase of the process usually takes from about ten to thirty minutes, depending upon load conditions, after which the solvent is drained from the wheel, and the garments are then extracted (spun) to remove the bulk of the solvent from the wet load. Residual solvent and moisture deposited in the clothes are then removed by drying, usually in a current of hot air, by tumbling, or in a drying cabinet.

The solvent is used over and over with periodic make-up for the solvent retained by the clothes. Periodic or continuous partial distillation to maintain a low concentration of dissolved impurities is recommended as a good drycleaning practice but is not necessarily an integral part of the process.

It has become established practice at least in commercial drycleaning with hydrocarbon and chlorinated hydrocarbon solvents, e.g. Stoddard solvent and perchloroethylene, to add small quantities of a drycleaning detergent to remove and suspend particulate soil. Small quantities of water are also usually added to remove water-soluble soil from the fabrics and the detergent functions as an absorbefacient to solubilize the water in the solvent and thus avoid shrinkage or other deleterious effects on the fabric. The water in the solvent is progressively depleted by exhaustion onto the fabrics being cleaned, and it is usual practice to replenish the water in the solvent with each load of clothes charged to the solvent, or in response to certain indicia of moisture content in the solvent, such as relative humidity of a vapor space above the solvent or electrical conductivity of the moisture-containing solvent.

The oil-soluble surfactants or detergents most commonly used in drycleaning are those of the anionic and non-ionic types used alone or in various combinations. Cationic surface-active agents have been also proposed for use, but this latter category has not found application because of their substantivity to textile fibers resulting in excessive losses from the solvent, and consequent in-

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ability to achieve consistently high and efficient soil removal (detergency) and low soil redeposition (graying or dulling of the fabrics with suspended soil deposited back on the cleaned fabric). Opposed to this, the oil-soluble anionic and non-ionic detergents generally utilized in drycleaning tend to remain in the solvent and require make-up additions only in proportional relation to solvent mechanically removed by the fabrics. The term "cationic" as used herein means those surfactants possessing a hydrophobic cation and a hydrophilic acidic anion, e.g. quaternary nitrogen compounds, and also those ampholytic compounds, such as betaines, which form zwitterions.

It has been discovered, according to the present invention, that by proper selection of the type of cationic surfactant and by particular conditions of use, there is provided a drycleaning method exhibiting superior detergency and soil suspension and marked reduction in soil redeposition. At the same time, the cationic detergent contributes unique results in terms of the soft hand and feel of the drycleaned fabric and absence of lint on the garment through the antistatic function it exerts. The foregoing improved results in drycleaning and condition of the cleaned fabric are obtained by the method of the present invention at a substantially consistent and uniform level throughout the processing of repeated loads in the drycleaning solvent and without loss of the detergent.

Accordingly, it is a principal object of the invention to provide an improved drycleaning method utilizing a novel detergent combination and procedure in a solvent-water system in which a quantity of selected cationic surfactant together with a non-ionic compound functions as the principal oil-soluble detergent, and additional cationic surfactant is introduced in specific quantities in aqueous solution for each successive load of clothes processed in the solvent-water system. Surprisingly, it was found that the latter quantity of cationic agent introduced to maintain the desired concentration level for optimum results is substantially less than the rate of depletion of the cationic portion of the primary detergent when used without replenishment.

A further object of the invention is to provide novel ampholytic betaine quaternary compounds and a method for synthesis of this preferred class of cationic detergent for use in the drycleaning method. These and other objects of the invention will become apparent from the following detailed description thereof.

The problems attendant with previous attempts to use cationic surfactants as drycleaning detergents in moisturized drycleaning solvent systems are overcome in a relatively simple but unobvious manner by the present invention. In spite of the substantivity of cationics to textile fibers, the foregoing objects and advantages are obtained by the method of the invention when certain essential steps and conditions defined below are observed.

First of all, the surfactant utilized as the primary drycleaning detergent must not be strongly cationic. The drycleaning detergent of the invention is selected from the group of cation-active agents consisting of (1) betaines either as internal salts or acidified to cationic form, and (2) quaternary ammonium salts whose anion is derived from an acid having a pK greater than 2 (pK is the reciprocal log of the dissociation constant-K of the acid), which cationic agents contain in the quaternized nitrogen cation at least one but not more than two hydrophobic chains having eight or more carbon atoms to provide sufficient surfactant activity. Any betaines or other mildly cationic quaternary ammonium compounds are suitable for use in the invention, provided they meet the foregoing requirements. This includes those derived from aliphatic, aromatic or heterocyclic tertiary amines. The long chain hydrophobic groups of the betaine or other quaternary

nitrogen compound may be alkyl, alkenyl, alkylaryl, aralkyl, alkyl cycloalkyl, or may contain hetero atoms or hetero groups in the chain, or in an attached heterocyclic ring structure. The heterocyclic compounds are particularly advantageous where the quaternized nitrogen forms a part of the ring, e.g. in pyridinium, piperidinium, and imidazolinium quaternary nitrogen compounds. Where the nitrogen atom is part of an acyclic structure, it contains at least two and not more than three lower molecular weight alkyl, hydroxyalkyl or aryl groups to provide the quaternary ammonium structure. The betaines used in the invention in addition all contain a terminal carboxy (COO) or sulfonic (SO₃) group forming an internal salt with the positively charged quaternary nitrogen atom.

The method of the invention is practiced by charging the drycleaning solvent with a mixture of the cationic detergent and selected non-ionic surfactant. The latter effectively acts as a coupling agent to solubilize the relatively water-soluble cationic agent in the solvent and also exerts some detergent action. Generally, the solvent is charged either before or after its introduction into the wheel, but preferably before contact of the solvent with the soiled garment load. After wetting of the load with the charged solvent, water is introduced in small quantities to perform its function of water-soluble soil removal usually in an amount to provide from 10 to 150 ounces per 100 pounds of garment load. An additional quantity of cationic surfactant is injected as an aqueous solution into the solvent-detergent mixture, the water of the cationic agent solution preferably being a part or all of the water required for maintaining the desired moisture content in the system.

This addition of cationic surfactant in aqueous solution is repeated for each load of garments drycleaned in the solvent and it effectively maintains a uniformly high level of detergency and low level of soil redeposition. Without such addition of cationic agent in aqueous solution with each load, experience demonstrates that detergency rapidly falls below optimum levels and soil redeposition increases. It is, however, a completely unobvious advantage of the method of the present invention that the quantity of cationic agent added with each load, that is, the rate of replenishment is substantially below the observed rate of depletion of the primary cationic detergent from the solvent-detergent-water system when processing repeated loads without replenishment. Moreover, the detergent introduced with the water with each load of clothes processed corresponds only to the cationic portion of the original detergent charged to the solvent, since the non-ionic portion does not exhaust from the solvent bath.

Although it is not intended to limit the invention to any theory or mechanism, the cationic surfactant introduced as a water-solution (without the non-ionic coupling agent) may be rapidly absorbed by the garments and due to its substantivity to the fabric, may effectively loosen and displace the soil from the garments so it is more easily dispersed and suspended in the solvent-water solution. Thus, although the cationic agent introduced in aqueous solution with each load constitutes only a fraction of the required concentration of cationic detergent solubilized in the solvent, it effectively replaces or prevents depletion of the oil-solubilized cationic detergent. Consequently, it maintains a high level of soil removal and suspension while that portion of the cationic surfactant deposited on the fabric effectively reduces soil redeposition and imparts a soft hand and feel to the garment which facilitates pressing and finishing after drycleaning.

In general, the non-ionic and cationic detergent mixture is introduced into the solvent at a level which may range from about 0.1% to 1% of the solvent (expressed as percent by volume).

The quantities of non-ionic component and cationic component in the primary drycleaning detergent mixture will vary depending upon the specific chemical compounds utilized. The non-ionic surfactant is generally used in the

range of from 0.08% to 0.40% by volume of solvent. The cationic surfactant in the mixture is usually within the range of 0.02 to 0.5% of the solvent. As may be seen, this provides a relatively wide range of ratios of cationic to non-ionic detergent.

The quantity of cationic surfactant added in aqueous solution will also vary with the particular chemical utilized. However, it may be stated in general that the quantity of cationic surfactant expressed as active ingredient should range from about 0.5 to 5.0 ounces per 100 lbs. of garment load to maintain the high level of detergency and low soil redeposition obtainable with the method of the invention. Therefore, in the practice of the process with each specific cationic, optimum replenishment quantities within this range may readily be determined. In terms of conventional 30 lb. loads for commercial drycleaning equipment, the quantity of cationic introduced in aqueous solution with each load of clothes is from about 0.17 to 1.7 ounces. Stated otherwise, these quantities are equal to from about 0.03 to 0.30% based on the weight of the garments drycleaned.

The non-ionic surfactant for use in the primary detergent may be selected from several types of such compounds, which may be employed individually or as mixtures. Preferably they are higher molecular weight C₉ to C₂₂ fatty acid partial esters of polyols having from 2 to 4 carbon atoms. Also preferred are the condensates obtained by reaction of lower molecular weight alkanolamines with higher molecular weight C₉ to C₂₂ fatty acids or their methyl esters. Specific examples of such non-ionics are glyceryl monooleate, oleyl monoisopropanolamide, sorbitol dioleate, and alkylol amides prepared by reacting alkanolamines such as monoisopropanolamine, diethanolamine, or monobutanol amine with fatty acids such as oleic, pelargonic, lauric, elaidic and other preferably liquid acids. While the foregoing are preferred, other oil-soluble non-ionic surfactants known in the art are usable in the primary detergent.

Carboxylic betaines are the preferred cationic surfactants for use in the invention, and as indicated above, may be selected from a large class of compounds including aliphatic, carbocyclic, or preferably heterocyclic betaines in which the quaternized nitrogen is a part of the ring. These betaines may be formed according to previously published methods by heating the selected tertiary amine in the presence of a solvent such as water or an alcohol, with an alkaline solution of a halogenated fatty acid, e.g. chloroacetic or chloropropionic acids. However, as disclosed herein below, the present invention also provides an advantageous method for the preparation of the preferred betaines of the invention which are heterocyclic betaines of the imidazolinium type.

Typical of the betaines usable in the invention may be mentioned the following:

Imidazoline betaines, such as 1-hydroxyethyl, 1-carboxyethyl, 2-pelargonyl (nonyl) imidazoline; 1-hydroxypropyl, 1-carboxyethyl, 2-lauryl imidazoline; pyridine betaines, such as N-dodecyl pyridinyl acetic acid; piperidine betaines, such as N-hexadecylpiperidinopropionic acid; aliphatic and carbocyclic betaines, such as

N-dodecyl-N,N-bis-β-hydroxyethylamino-acetic acid;
N-octadecyl-N-β-hydroxyethyl-N-carboxymethylaminoacetic acid;

N-hexadecyl-N,N-bis-carboxymethylaminopropionic acid;

N-dodecyl-N-β,α-bis-hydroxypropyl-N-carboxylpropylaminoacetic acid;

N-heptadecyl-N,N-hydroethoxyethyl-N-carboxymethylaminoacetic acid;

N-decyl-N-β-hydroxyethyl-N-methyl-α-aminosuccinic acid;

N-heptadecyl-N,N-bis-hydroxyethylaminoacetic acid;
N-dodecylphenyl-N,N-bis-hydroxyethylaminopropionic acid;

N,N-bis dodecyl-N-β-hydroxyethylaminoacetic acid; and

betaines with hetero atoms in the hydrophobic chains such as dodecyloxypropyldimethyl aminoacetic acid, and mixed C₁₂ to C₁₈ alkoxyethyltrimethyl aminopropionic acid.

The quarternary ammonium salts suitable for the invention may also be of the aliphatic, carbocyclic or heterocyclic type, but the anion must be derived from an acid with a pK greater than 2. Representative acids are acetic, propionic, lactic, dialkyl phosphoric, alkyl sulfuric.

Typical of the quarternary ammonium compounds may be mentioned cetyl pyridinium acetate; methyl cetyl piperidinium propionate, hydroxyethyl octadecyl morpholinium methosulfate, octyltrimethyl ammonium phosphate, N-oleyl-amidopropyl N,N, trimethyl ammonium dimethophosphate, p-stearamidophenyl trimethyl ammonium ethosulfate, N,N dilauryl, N,N dimethyl ammonium diethophosphate.

The invention is described in greater detail and its advantages illustrated in the following examples of complete specific embodiments of the invention and in comparative test results tabulated below.

EXAMPLE 1

A conventional drycleaning machine was charged with 125 gallons of perchloroethylene as the drycleaning fluid and 0.39% (0.5 ounce per gallon) of the following cationic-nonionic primary detergent in an acidified water-solvent mixture was added to the main body of the solvent:

22% of 1-hydroxyethyl, 1-carboxyethyl, 2-oleyl imidazoline, as a 66.7% solution in butyl Cellosolve(mono-butylether of ethyleneglycol)
59% of oleyl monoisopropanolamide
0.7% phosphoric acid
6.3% water
12.0% perchloroethylene

30 lbs. of garments were introduced into the rotating drum after which the drum was filled with the detergent-charged solvent. At this time, the filtration cycle was started and 3.75 ounces of a 30% aqueous solution of the same betaine cationic as above-described acidified with 1.2% phosphoric acid were injected into the solvent along with an additional 11.25 ounces of water. The drycleaning filtration cycle was continued for fifteen minutes after which the clothes were centrifuged to remove excess solvent and dried by heating. This operation was repeated for twenty loads of soiled garments using the original detergent-solvent mixture with injection of cationic agent solution and water as above-described with each new load of clothes.

The detergency or soil removal effectiveness of the solvent system was measured by including with each load of soiled clothes a linen towel on which 4" by 4" test swatches of white wool flannel were attached. The test swatches are artificially soiled by placing them in a steel drum containing an iron oxide pigment and sand mixture where they are rotated so the pigment is milled into the fabric surface to provide a very uniform soiling of the wool. Excess pigment is removed by means of an air stream. Reflectance measurements with a Gardner Reflectometer are used to determine the soil removal from the test swatches using the following formula:

$$\text{Detergency} = \frac{R_c - R_s}{R_o - R_s} \times 100$$

where:

R_o=reflectance of original test swatch before soiling,
R_s=reflectance of test swatch after soiling, and
R_c=reflectance of test swatch after cleaning.

The average detergency measured as described for the twenty cycles in the foregoing example was 63.7%.

EXAMPLE 2

The improvement in detergency provided by the cationic detergents and method of the invention are further

illustrated by comparison with anionic drycleaning detergent systems in the following tests.

Drycleaning runs of at least twenty loads each were made as reported in Table I below with (A) perchloroethylene and (B) Stoddard solvent utilizing the following detergents:

(1) Petroleum (mahogany) sulfonates, a commonly used oil-soluble anionic drycleaning detergent designated in Table I as Anionic No. 1. It was formulated as 35% active surfactant in a mixture of mineral oil and Stoddard solvent.

(2) A commercially available anionic and non-ionic detergent blend which combines a non-ionic amide-ester reaction product of diethanolamine and oleic acid with an anionic diethanolamine salt of dodecyl-benzene sulfonic acid, designated as Anionic No. 2. It was formulated as a 60% solution in Stoddard solvent.

(3) A primary detergent of the invention consisting of equal parts of glycerol monooleate as the non-ionic surfactant and N-oleylamidopropyl, N,N,N-trimethyl ammonium dimetho phosphate, as the cationic surfactant designated Cationic No. 1. The above was formulated as a 60% solution in mineral oil.

(4) One of the preferred heterocyclic betaines (the cationic agent designated as Cationic No. 2 and formulated as in Example 1 above), namely 1-hydroxyethyl, 1-carboxyethyl, 2-oleyl imidazoline.

In the tests recorded in Table I, the general test procedure of Example 1 was followed with differences in batch size and cleaning time being noted in the table.

Additions for each load of clothes in each test were as follows:

Anionic No. 1—Water only

Anionic No. 2—Water plus a detergent booster consisting of 12.5 parts of diethanolamine condensates of coconut oil fatty acids (2 to 1 mol ratio), 8 parts Anionic No. 2 detergent, 5 parts amyl alcohol and 7 parts mono-butylether of ethylene glycol, as coupling agents and the balance water.

The anionic detergents do not deplete from the cleaning bath as do the cationic detergents of the present invention and therefore do not require replenishment, as shown with Anionic No. 1. The detergent booster is only added to Anionic No. 2 to augment its soil redeposition performance and it is not required for maintaining the concentration level of Anionic No. 2.

Cationic No. 1—20% aqueous solution of the quaternary ammonium compound defined above.

Cationic No. 2—Aqueous solution as described in Example 1.

Detergency was measured with swatches as described in Example 1.

TABLE I.—DETERGENCY OF ANIONIC AND CATIONIC DRYCLEANING DETERGENT SYSTEMS

	Anionic		Cationic	
	1	2	1	2
Detergent:				
Percent active.....	35	60	60	80
Percent detergent in solvent.....	1.0	1.0	0.78	0.39
A. Solvent—perchloroethylene (125 gallons, 30 pound load, 15 minutes):				
Total aqueous additions ¹ (oz./100 lbs. clothes)	50	20	50	50
Surfactant additions (oz./100 lbs. load)	0	0.8	2.7	2.5
Percent detergency.....	39.7	45.9	64.6	58.9
B. Stoddard solvent (260 gallons, 65 pound load, 30 minutes):				
Total aqueous additions ¹ (oz./100 lbs. clothes)	50	33	-----	50
Surfactant additions (oz./100 lbs. clothes)	0	1.32	-----	2.5
Percent detergency.....	45.5	32.8	-----	60.7

¹ Includes surfactant solution additions.

It may be seen from the results of Table I that superior detergency is obtained by utilizing the cationic detergents and method of the invention.

EXAMPLE 3

Soil redeposition tests

The reduction in soil redeposition accomplished by the present invention is illustrated in the tests recorded below. In these tests different swatches of bleached cotton fabric and white cellulose acetate fabric were individually exposed to one and to five drycleaning cycles, respectively in the presence of soiled garments, predominantly of cotton and acetate fabric. These drycleaning cycles were performed under conditions as described in Example 2

of the rate of depletion of the cationic agent originally charged in the primary detergent where there is no replenishment. The tests were carried out by the drycleaning method described in Example 1 with detergent formulations of Cationic 1 and 2 as previously described, and replenishment additions as shown in column 4 of Table III "Cationic, Additions in Aqueous Solution (oz./100 lbs.)." The concentration of the cationic agent was determined by standard analytical method, that is, titration with Aerosol OT (sodium dioctyl sulfosuccinate) using Methylene Blue as the indicator.

TABLE III

Detergent	Solvent	Original cationic concentration, oz./100 gal.	Cationic additions in aqueous solution, oz./100 lbs.	Final cationic concentration, oz./100 gal.	Rate of cationic depletion, oz./100 lbs.	Performance			
						Percent detergency		Percent redeposition	
						Orig.	Final	Orig.	Final
Cationic 1	Perchloroethylene	30	0	24.8	4.3	¹ 62.7	² 58.7	¹ 7.6	² 8.8
	do	30	2.7	31.0	0	³ 64.6		³ 4.3	
Cationic 2	Stoddard	10	0	3.1	5.1	¹ 60.1	² 54.2	¹ 3.8	² 7.5
	do	10	2.5	10	0	³ 62.5		³ 0.8	

¹ Average for first of five loads.

² Average for last five of twenty-five loads.

³ Average of twenty-five loads.

above. The reflectance of the fresh swatches was first measured on the Gardner Reflectometer and then after drycleaning the swatches were recovered, pressed on a steam press and their reflectance was again measured. The percent soil redeposition is calculated from the following formula:

$$\text{Percent redeposition} = \frac{Ro - Rc}{Ro} \times 100$$

where:

Ro is the measured reflectance of the fresh swatch, and Rc is the reflectance of the swatch after exposure to the drycleaning cycles.

The redeposition values given in the Table II below are an average from readings taken on five swatches each of which was exposed to a different fabric load.

TABLE II.—COMPARISON OF SOIL REDEPOSITION OF ANIONIC AND CATIONIC SYSTEMS

	Percent redeposition			
	Cotton		Acetate	
	Cation-ic 2	Anion-ic 2	Cation-ic 2	Anion-ic 2
A. Perchloroethylene (125 gallons, 30 pound loads, 15 minutes):				
Cleaned once	0.5	4.3	0.8	
Cleaned five times	9.0	11.4	1.5	
B. Stoddard solvent (260 gallons, 65 pound loads, 30 minutes):				
Cleaned once	1.5	12.8	1.1	5.7
Cleaned five times	6.5	19.7	2.6	9.7

The foregoing results indicate that in either petroleum solvent or perchloroethylene, the cationic drycleaning detergents used according to the invention provide significant reduction in soil redeposition on a one-load basis. The results also indicate, that although soil redeposition increases with both the cationic and the anionic detergents after drycleaning repeated loads, the increase is by no means as severe with the cationic detergent as with the anionic.

EXAMPLE 4

As indicated above, the method of the invention not only provides exceptional detergency, but does so with an unexpectedly low requirement for replenishment of the cationic agent. The results of tests set forth in Table III below amply demonstrate that the replenishment required for maintenance of superior detergency is only a fraction

The results clearly demonstrate that by the method of the present invention detergency at a high level and redeposition at a low level may be maintained with an unexpectedly small quantity of cationic agent added in aqueous solution form with each load. The rate of depletion of the original cationic agent in the detergent is shown to be far in excess of the replenishment quantities set forth in the table. In addition, the value for the detergency in the last five of the twenty-five loads processed without replenishment is substantially reduced, while both the original and the final redeposition values without replenishment are far in excess of the redeposition when practicing the method of the invention.

EXAMPLE 5

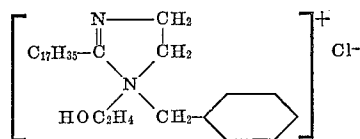
The cationic surfactants suitable in the invention have been defined as mildly cationic. In order to demonstrate that strong cationic detergents do not provide suitable results when used according to the present invention, the tests described below were conducted. The imidazoline base for the preferred betaine surfactants of the invention was prepared by the reaction of oleic acid with N-aminoethylethanolamine, as described in detail in Example 6 below. The resulting product, 1-hydroxyethyl, 2-oleyl imidazoline was then quarternized with benzyl chloride to form a strong cationic quaternary salt, 1-benzyl, 1-hydroxyethyl, 2-oleyl imidazolinium chloride whose anion is derived from an acid (hydrochloric) with a pK less than 2. This strong cationic was used in drycleaning tests conducted in Stoddard Solvent in a laboratory Launderometer and compared with cationic detergents of the invention.

The Launderometer is a piece of test equipment which simulates drycleaning in a commercial machine by agitating jars containing test swatches immersed in the solvent-detergent mixture. The jars contain 1/4" stainless steel balls to assist in "tumbling" the swatches. The Launderometer is run for a period of thirty minutes for each drycleaning test. The swatches are then solvent rinsed until the solvent runs clear, centrifuged to remove solvent, then dried and steam pressed after which reflectance measurements are obtained on the Gardner Reflectometer.

The detergents in these laboratory tests were dissolved in 100 ml. of solvent and water was added to the solvent-detergent mixture prior to the test by mixing in a Waring Blender for thirty seconds, the quantity of water being 0.1%. Table IV shows the detergency and soil redeposition performance of the strong cationic surfactant compared to a cationic quaternary salt and a betaine of the

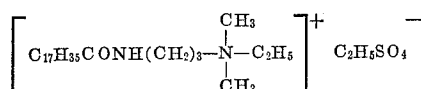
invention. The chemical identity of the cationics and their detergent formulations are as follows:

Cationic 3—1-benzyl, 1-hydroxyethyl, 2-oleyl imidazolinium chloride



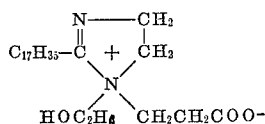
Cationic 3 was formulated into a 30% active solution with 30% oleyl monoisopropanolamide as the non-ionic coupler (See Example 1) and 40% of a diluent consisting of an inert hydrocarbon (Kerr-Magee Deep Rock Oil).

Cationic 4—N-oleylamidopropyl, N-ethyl, N,N dimethyl ammonium ethosulfate



Cationic 4 was used in a 50-50 mixture with oleyl monoisopropanolamide.

Cationic 5—1-hydroxyethyl, 1-carboxy ethyl, 2-oleyl imidazoline



Cationic 5 was formulated like Cationic 3 as a somewhat less concentrated 23% active cationic solution combined with 25% oleyl monoisopropanolamide and 52% Kerr-Magee Deep Rock Oil diluent.

TABLE IV.—DETERGENCY AND SOIL REDEPOSITION USING STRONG VS. MILD CATIONIC DETERGENT

	Cationic		
	3	4	5
Stoddard solvent:			
Detergent concentration (percent volume of solvent).....	1.0	0.6	1.0
Percent detergency.....	26.9	43.0	54.2
Percent redeposition.....	19.1	11.7	19.1

The foregoing results clearly demonstrate that the strong quarternary Cationic 1 provides much lower detergency than either of the milder cationics. This difference is particularly striking relative to Cationic 3 which is chemically identical to Cationic 1 except that the latter is quaternized with benzyl chloride and the former with beta-propiolactone.

BETAINES PREPARATION

As mentioned above, the invention also provides a novel solventless method for the preparation of the preferred quarternary betaine surfactants by reaction of beta-propiolactone and a tertiary amine represented by the formula $\text{R}_1\text{R}_2\text{R}_3\text{N}$ wherein R_1 , R_2 and R_3 are organic radicals, each providing a carbon-nitrogen linkage and in which at least one and not more than two of the radicals R_1 , R_2 , R_3 includes a hydrophobic C_8 to C_{22} hydrocarbyl group and at least one and not more than two of such radicals are lower alkyl, hydroxyalkyl, aryl or alkaryl. All tertiary amines are suitable for the reaction with the beta-propiolactone, but for use as surfactants those having proper hydrophobic-hydrophilic balance are required. Suitable tertiary amines may be further described as those which produce any of the propio-betaines whose structures are described in detail above. Thus, they may be acyclic, such as alkyl amines, or carbocyclic, such as aryl or alkaryl, or heterocyclic and particularly those heterocyclics where the nitrogen of the tertiary amine is a part of the ring structure such as the imidazo-

lines, pyridines and piperidines mentioned above. The beta-propiolactone reacts with the amine so that the beta carbon atom of the lactone is directly connected to the nitrogen of the tertiary amine to form the corresponding propio-betaine.

It has been found essential in the method of the invention where no solvent is employed to maintain the tertiary amine in liquid phase and to gradually add the lactone to avoid undue heating due to the exothermy of the reaction and to repress polymerization of the beta lactone. On the other hand, it was found necessary in the method of the invention to maintain the temperature for the reaction substantially above those previously used when employing solvents in the reaction system. Temperatures are maintained at from at least about 50° C. up to 100° C., preferably from about 50 to 75° C. This is accomplished by the gradual addition of the lactone reactant and by the provision of positive cooling where necessary.

The following example provides a complete specific embodiment of the method applied to the preparation of the propio-betaine of 1-hydroxyethyl, 2-oleyl imidazoline.

EXAMPLE 6

First, the imidazoline tertiary amine was prepared as follows:

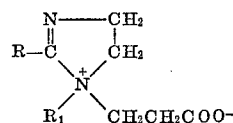
695 lbs. oleic acid and 305 lbs. of N-aminoethylethynol-amine are charged into a reaction vessel equipped with an agitator, fractionating column, vacuum pump and nitrogen supply. The materials are heated to 90° C. and the pressure is reduced to 5-10 mm. Hg. Heating is then continued at a slow rate, preferably not exceeding 1/2° C. per minute, until the temperature reaches 250 to 260° C. The reaction mixture is then cooled to 100° C. under vacuum after which nitrogen is admitted over the reaction mixture before discharge from the reaction vessel. The yield is 906 lbs. of 1-hydroxyethyl, 2-oleyl imidazoline.

The propiobetaine was then prepared as follows:

830 lbs. of 1-hydroxyethyl, 2-oleyl imidazoline is reacted with 170 lbs. of beta-propiolactone in the following manner. The imidazoline is charged into an open kettle equipped with an agitator (sweep-type) and a heating and cooling jacket. The liquid beta-propiolactone (B.P. 160° C.) is slowly added through a polyethylene tube below the surface of the imidazoline with constant agitation and cooling is initiated to maintain the temperature at 50-75° C. Addition of the lactone is completed in approximately two hours and reaction is continued at 60-70° C. until samples have an amine number (by HCl titration) of 20 or less. This represents a product yield of 85% in the form of a viscous liquid imidazoline propiobetaine. To improve handling characteristics and to reduce viscosity, an appropriate diluent is usually added to the betaine. In this example, 500 lbs. of butyl cellosolve (monobutyl ether of ethylene glycol) were mixed with the imidazoline betaine reaction product.

The foregoing betaine preparation method provides a distinct advantage over the prior art methods of preparation in solvents, such as dimethylformamide and acetonitrile. It avoids solvent recovery which would be necessary since such solvents cannot be tolerated in systems where the surfactant will come in contact with skin or textile articles. Moreover, the solvent recovery problem is compounded by the presence of the betaine exerting its surfactant properties.

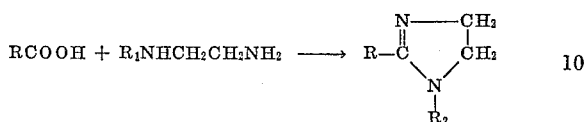
The preferred cationic surfactants for use in the invention are the imidazoline propiobetaines derived by the above-described method and corresponding to the following structural formula:



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in which R is a C₈ to C₂₁ hydrocarbyl group, and R₁ is lower alkyl, hydroxyalkyl or R CONH— (lower alkylene).

The imidazolines for preparation of the propiobetaines prepared by known reaction of a higher fatty acid and a polyamine, as specifically exemplified in Example 6 above, and as generally illustrated by the following equation:



where R is a C₈ to C₂₁ hydrocarbyl group and R₁ is lower alkyl, hydroxyalkyl or aminoalkyl, and R₂ is the same as R₁, except when R₁ is aminoalkyl R₂ is R CONH (lower alkylene).

The resulting imidazolines tertiary amines are then converted to the quaternary betaine surfactants of the invention by reaction with beta-propiolactone as described above.

As mentioned above, other diluents and coupling agents are appropriate for use with the cationic detergents of the invention such as alcohols of C₁ to C₅ chain length, e.g. methanol, ethanol, isopropanol and butanol, as well as glycols and glycol ethers such as ethylene glycol, diethylene glycol monoethyl ether, ethylene glycol monobutyl ether, hexylene glycol, and the like.

The invention has been described above in relation to (1) the preferred cationic surface-active agents suitable for use in the method of the invention, (2) the solventless method of preparation of the preferred propiobetaines and (3) the improved method of drycleaning made possible by use of the cationic and non-ionic combination as primary detergent, and the aqueous solution of cationic agent added as replenishment to maintain a uniform and optimum level of detergency and redeposition. This method advantageously lends itself to conventional drycleaning operations and equipment as described above.

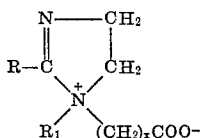
Repeated reference is made herein to addition of cationic agent in aqueous solution with each load of clothes. It must be understood that the cationic agent may alternatively be added to the drycleaning solvent in solution in a polar solvent such as those mentioned above as diluents and couplers. The water required in the system may thus be added separately from the cationic agent.

There are many substitutions or modifications which will occur to those skilled in the art that may be made in the practice of the invention and which are intended to fall within the scope thereof as defined in the appended claims.

I claim:

1. In a drycleaning method wherein soiled garments are agitated in a drycleaning solvent and multiple loads are processed in said solvent, the improvement comprising initially charging the solvent with from 0.1 to 1 percent by volume of a primary detergent consisting essentially of a mixture of

- (a) an oil soluble non-ionic surfactant; and
- (b) a betaine selected from the group consisting of imidazoline betaines having the structural formula:



wherein R is a hydrocarbyl radical containing from 8 to 21 carbon atoms, and R₁ is a lower alkyl or hydroxyalkyl radical and x is 2 or 3,

N-dodecyl pyridinyl acetic acid,
N-hexadecylpiperidinopropionic acid,
N-dodecyl-N,N-bis-β-hydroxyethylaminoacetic acid,
N-octadecyl-N-β-hydroxyethyl-N-carboxymethylaminoacetic acid,

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N-hexadecyl-N,N-bis-carboxymethylaminopropionic acid,

N-dodecyl-N-β, α-bis-hydroxypropyl-N-carboxylpropylaminoacetic acid,

N-heptadecyl-N,N-hydroethoxyethyl-N-carboxymethylaminoacetic acid,

N-decyl-N-β-hydroxyethyl-N-methyl-α-amino-succinic acid,

N-heptadecyl-N, n-bis-hydroxyethylaminoacetic acid,

N-dodecylphenyl-N,N-bis-hydroxyethylaminopropionic acid,

N-bis-dodecyl-N-β-hydroxyethylaminoacetic acid,
Dodecyl-oxypropyl-dimethyl aminoacetic acid,

and mixed C₁₂ to C₁₈ alkoxyethyl-dimethyl amino-propionic acid, the ratio of said betaine to non-ionic surfactant being 1:20 to 6:1;

wherein with each load of garments drycleaned an additional quantity of said betaine is added to the amount of from 0.5 to 5.0 ounces per hundred pounds of garment load.

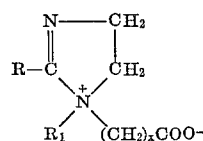
2. A method as in claim 1 wherein the non-ionic surfactant is selected from the group consisting of C₉ to C₂₂ fatty acid partial ester of C₂ to C₄ polyhydric alcohols, condensates of C₉ to C₂₂ fatty acids with lower alkanolamines, condensates of the methyl esters of C₉ to C₂₂ fatty acids with lower alkanolamines and mixtures thereof.

3. A method as in claim 1 wherein water is added with each load of garments drycleaned to provide from 10 to 150 ounces of water per hundred pounds of garment load.

4. A method as in claim 3 wherein the imidazoline betaine is selected from the group consisting of 1-hydroxyethyl, 1-carboxyethyl, 2-oleyl imidazoline and 1-hydroxypropyl, 1-carboxyethyl, 2-lauryl imidazoline.

5. A drycleaning detergent consisting essentially of the combination of:

- (a) an oil soluble non-ionic surfactant selected from the group consisting of C₉ to C₂₂ fatty acid partial esters of C₂ to C₄ polyols and C₉ fatty acid amides of lower molecular weight alkanolamines and
- (b) a betaine selected from the group consisting of imidazoline betaines having the structural formula:



wherein R is a hydrocarbyl radical containing from 8 to 21 carbon atoms, and R₁ is a lower alkyl or hydroxyalkyl radical and x is 2 or 3,

N-dodecyl pyridinyl acetic acid,
N-hexadecylpiperidinopropionic acid,

N-dodecyl-N,N-bis-β-hydroxyethylamino-acetic acid,
N-octadecyl-N-β-hydroxyethyl-N-carboxymethylaminoacetic acid,

N-hexadecyl-N,N-bis-carboxymethylaminopropionic acid,

N-dodecyl-N-β,α-bis-hydroxypropyl-N-carboxylpropylaminoacetic acid,

N-heptadecyl-N,N-hydroethoxyethyl-N-carboxymethylaminoacetic acid,

N-decyl-N-β-hydroxyethyl-N-methyl-α-amino-succinic acid,

N-heptadecyl-N,N-bis-hydroxyethylaminoacetic acid,
N-dodecylphenyl-N,N-bis-hydroxyethylaminopropionic acid,

N-bis-dodecyl-N-β-hydroxyethylaminoacetic acid,
Dodecyl-oxypropyl-dimethyl aminoacetic acid,

and mixed C₁₂ to C₁₈ alkoxyethyl-dimethyl amino-propionic acid, the ratio of the oil soluble non-

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ionic surfactant of (a) to the betaine of (b) being
20:1 to 1:6.
6. The detergent of claim 5 wherein said betaine is 1-
hydroxyethyl, 1-carboxyethyl, 2-oleyl imidazoline.

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5 MAYER WEINBLATT, Primary Examiner

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252—153, 524, 528, 542, 547; 260—309.6, 501.11