

United States Patent

Rudy et al.

[15] 3,650,816

[45] Mar. 21, 1972

- [54] **ADDITIVES FOR CLOTHES DRYERS**
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- [73] Assignee: **Lever Brothers Company**, New York, N.Y.
- [22] Filed: **July 17, 1969**
- [21] Appl. No.: **842,719**

2,784,183	3/1957	Keller et al.....	117/33.5 X
2,822,291	2/1958	Hahn	117/120 X
3,173,841	3/1965	Roth et al.	117/33.5 X
3,401,052	9/1968	Berger et al.....	117/109 X
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3,454,494	7/1969	Clark et al.....	252/8.8
3,468,697	9/1969	Hunter.....	117/121 X
3,485,761	12/1969	Haxby.....	117/33.5 X

- [52] U.S. Cl.....**117/109**, 8/147, 34/12, 117/33.5 T, 117/139.5 A, 117/139.5 C, 117/139.5 F, 118/418, 118/506, 252/8.6, 252/106
- [51] Int. Cl.....**B05c 3/08**, C11d 3/48, D06m 13/00
- [58] Field of Search.....117/109, 120, 33.5 T, DIG. 2; 8/159; 34/12; 252/8.8

[56] **References Cited**

UNITED STATES PATENTS

662,516	11/1900	Barklage.....	117/109
2,612,501	9/1952	Wilson.....	252/301.2 X
2,680,084	6/1954	Ryan.....	8/151.1 X

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[57] **ABSTRACT**

A novel method for applying adjuvants to fabric employing a tumbler-type dryer is disclosed. To achieve uniform distribution of the adjuvant on the fabric, the adjuvant, in accordance with the present invention, is sprayed on to the dryer drum. Spreading agents, distributing agents or carrier may be included in the composition sprayed on to the dryer drum if desired. Novel compositions of matter suitable for use in the practice of this invention are also disclosed.

9 Claims, No Drawings

ADDITIVES FOR CLOTHES DRYERS

This invention relates to a novel method of applying adjuvants to clothing in tumbler-type drying machines.

It has been customary for many years to include various adjuvants in detergents and wash-cycle additives. Germicides, fabric softeners and optical brighteners are among the most common such adjuvants used. However, other materials, such as ironing aids, antistatic agents, stain repellents, soil release agents, wrinkle preventatives, deodorizers, fresheners (e.g., perfumes, etc.), cleaning agents, surfactants, flameproofing agents, mothproofing agents, bleaching agents, etc. are also products which potentially can be applied to fabrics employing the method of the present invention. A particular advantage of the present invention is that it is possible to obtain much more efficient application of the adjuvant to the clothing than can be obtained if the adjuvant is applied in the wash or rinse cycles.

In the wash or rinse cycles, the primary objective is to remove soil, etc. from the cloth being washed by means of detergents, water and emulsifying agents. The presence of detergents and emulsifying agents effective to remove soil from the cloth manifestly renders difficult and less efficient the concurrent application of adjuvants such as fabric softeners or other adjuvants to the same piece of material. Since in the drying cycle following washing and rinsing, the conditions characteristic of the rinsing and washing cycles leading to inefficient application of fabric adjuvants are not present, there is the potential for the much more efficient utilization and application of such adjuvants.

Due to the heat and mechanical action and residual water on the fabrics in the dryer, it might be expected that fabric adjuvants could be easily and uniformly applied in the dryer. Experience demonstrates, however, that this does not readily occur. For example, if clothing to be treated with a fabric softening agent is placed into a dryer together with a pure fabric softening active ingredient such as distearyl dimethyl ammonium chloride, the softener will be somewhat spread throughout the clothing treated, but it will be far from uniformly spread. This may result in unsightly spots on cloth or lead to water repellency. While the problem of nonuniformity of spreading may be alleviated in repeated applications of the adjuvant, more preferable results are obtained if the adjuvant is sprayed on to the surface of the dryer drum in accordance with the present invention.

As discussed in our earlier-filed application Ser. No. 821,476, nonuniformity of distribution of an adjuvant in the clothes dryer may be overcome by including a distributing agent which is ordinarily at least 10 percent of the complete composition, but may be effective if present in a concentration of as little as 5 percent by weight. The compositions described in said copending application may be used in bulk form to treat clothing in a clothes dryer—i.e., in the form of flakes, chips, pellets, tablets and the like.

It has been found in accordance with the present invention that where a spray or a mist of the adjuvant in a suitable solvent is applied to the surface of the dryer drum inclusion of a distributing agent is not necessary to obtain a good distribution in most cases. It will be understood, of course, that a distributing agent may be incorporated in the composition applied to the dryer drum if it is desired to do so.

To be effective in the present invention, the adjuvant deposited after evaporation of the solvent should be a film which adheres to the inner surface of the drum, in the absence of cloth, but releases gradually and transfers to the clothing being dried (or otherwise treated) in the dryer within a period of time from about 5 to 45 minutes when the dryer is rotated. Where the cloth adjuvant forms a waxy film, suitable adjuvants can be readily characterized by their melting point ranges. Typical waxy materials, for example, are fabric softeners, antistatic agents, and combinations of essential oils and fragrances with a suitable waxy carrier such as the C₁₆-C₃₀ fatty acids, fatty alcohols, ethoxylated derivatives thereof, polyethylene glycols, paraffin and the like. Suitable waxy materials generally have melting and softening points between

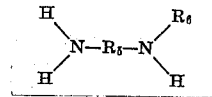
about 70° and 200° F. Preferred materials melt or soften between about 90° and 180° F.

Other adjuvants which may be applied in the present invention such as the optical brighteners or germicides are frequently less waxy in character than those substances mentioned above. Representative germicides and optical brighteners which may be used in the present invention are more fully described below.

In the typical application in accordance with the present invention, the adjuvant to be applied to the dryer drum is formulated in a moderately volatile solvent therefor to provide a liquid solution containing the adjuvant. The liquid is applied by a suitable spray means such as hand sprayer, aerosol spray, or the like, to the surface of the dryer drum. The volatile solvent evaporates leaving behind a relatively hard residue of the fabric adjuvant which is gradually abraded by the clothing as the dryer tumbler operates and becomes uniformly applied to the clothing.

Classes of adjuvants which may be employed in the present invention have already generally been referred to above. More specifically, adjuvants useful in the present invention include, but are not limited to:

1. Fabric softeners such as quaternary ammonium compounds of the formula $N(R_1R_2R_3R_4)_yX$, and the reaction product of about 2 moles of a fatty acid of the formula R_4COOH and hydroxyalkyldiamine of the formula



where R_1 is a C₁₆ to C₂₀ alkyl group, R_2 is a C₁ to C₄ alkyl group, R_3 is selected from the group consisting of R_1 and R_2 , R_4 is a C₁₅ to C₁₉ alkyl group, R_5 is a C₁ to C₃ divalent hydrocarbon radical and R_6 is a hydroxyalkyl group of from about one to three carbon atoms, X is an anion imparting water dispersibility to the cationic ammonium compound, and y is the valency of X.

Typical commercial products commonly available for use in the present invention include distearyl dimethyl ammonium chloride and the reaction product of approximately 2 moles of stearic acid with approximately 1 mole of hydroxyethylene diamine. The last-mentioned product is a mixed chemical structure in view of the multifunctional characteristics of the diamine reactant. Spectral analysis of a commercial product prepared through the fatty acid-diamine reaction indicates that it contains in the order of 25 percent quaternary compounds of the imidazoline type, the balance thereof being mixed esters and amides. Softeners related to this last mentioned compound also include the quaternarized products of about 2 moles of oleic acid reacted with 1 mole of hydroxyethylene diamine and the product of about 2 moles of a mixture of oleic and stearic acids reacted with about 1 mole of hydroxyethylene diamine. Other suitable fabric softening agents which may be used in the present invention include those which have been described in "Proceedings of the American Association of Textile Chemists and Colorists," *American Dyestuff Reporter*, pages P42 and P43, Jan. 28, 1957.

2. Optical brighteners such as disulfonated diaminostilbene compounds disclosed in Alien Property Custodian publication No. 381,856, and in U.S. Pat. No. 2,612,501, and triazole compounds of the type disclosed in U.S. Pat. No. 2,784,183.

3. Essential oils and fragrances. In using materials of this category, many substances are normally in liquid form. Such materials must be combined with a suitable carrier having the desired waxiness, thermal stability, and hardness to obtain a composition suitable for applying to the surface of a dryer drum. Suitable waxy carriers which may be used as needed are discussed below.

4. Antistatic agents which in many cases are compounds of the same general structure discussed above with respect to fabric softening compounds. As disclosed in U.S. Pat. application Ser. No. 468,918, the antistatic properties of quaternary ammonium compounds as well as other fabric softening agents may be enhanced by combining these materials with ethanolamides such as tallow ethanolamide.

5. Germicides such as the halogenated salicylanilides, hexachlorophene, neomycin sulfate, benzalkonium quaternary compounds, and the like. The halogenated salicylanilides which have found the most widespread acceptance are tribromosalicylanilide and polybromosalicylanilide, the latter being a mixture primarily of dibromosalicylanilide and tribromosalicylanilide.

6. Bodying agents such as carboxymethyl cellulose, hydroxyethylcellulose, starch, polyvinyl acetate and the like. Polyvinyl acetate is also effective to improve ease of ironing and may be employed for that purpose.

7. Soil release agents such as the polyacrylic polyvinyl alcohol compositions described, for example, in U.S. Pat. No. 3,377,249. A variety of detergents may also be employed as soil release agents.

In the practice of the present invention, one or more of the foregoing fabric adjuvants will be combined and dissolved in a suitable volatile solvent to form a sprayable solution. In normal practice the adjuvant will be sprayed on to the surface of a relatively cold dryer drum. In order to obtain uniform distribution, it is required that the solution of adjuvant sprayed to the cold drum surface will dry and harden sufficiently that it will not be immediately wiped off on to the clothing which is loaded into the dryer. Accordingly, the solvent system should have sufficient volatility at ambient temperature that it will evaporate rapidly from the solution when applied.

Suitable solvents which may be used in the present invention particularly include those having sufficient volatility to be used also as propellants in aerosol containers of commerce. Such solvent-propellants are particularly efficacious since they may be employed to formulate simple self-dispensing compositions consisting essentially of the adjuvant or adjuvants to be applied together with the solvent-propellant. Other suitable solvents which may be employed include, but are not limited to: halogenated lower alkanes such as methylene chloride and methyl chloride; lower ethers such as dimethyl ether; the lower alkanes such as propane, butane, pentane; lower alcohols such as methyl and ethyl alcohol; etc. It will be recognized that a number of the foregoing solvents are flammable and their use, of course, would be inappropriate in specific commercial applications where flammable solvents are objectionable. In this respect, solvents it may be noted that methods for utilizing flammable solvents in aerosol compositions have been described in the art, for example in U.S. Pat. No. 3,207,386.

When formulating aerosol compositions for use in the present invention it will not always be found that the propellant for the aerosol will be an effective solvent for the adjuvant to be applied. This is particularly true where the chlorinated hydrocarbons are used as the propellant, many of which have been found to lack high-solvency power. In cases where the solvency power of the propellant is inadequate, a volatile secondary solvent may be provided. Suitable secondary solvents would include the volatile alcohols such as methyl alcohol which are effective to dissolve a wide variety of organic compounds.

As indicated already, in the present invention it is desired that the adjuvant applied to the surface of the dryer drum harden relatively rapidly so that it will not be wiped off by the clothing or other cloth articles loaded into the dryer heterogeneously. Typically, therefore, the adjuvant formulation should be one from which the solvent and propellants present will evaporate in the space of a few minutes and dry to a composition having a melting point in the order of 90° to 180° F. Where the adjuvant to be applied is one which is normally liquid, such as, for example, an essential oil or perfume,

or a relatively soft, low-melting point adjuvant, such as, for example, 1-stearylaimidoethyl-1-methyl-2-heptadecylimidazoline methyl sulfate, the adjuvant may be formulated together with a suitable carrier which imparts the necessary hardness to the complete composition. Suitable carriers imparting hardness are preferably waxy organic solids such as stearic acid, stearyl alcohol, palmitic acid, palmityl alcohol, and ethoxylated derivatives of the these acids and alcohols, polyethylene glycol having a molecular weight of 1,000 to 5,000, and hydrocarbons such as paraffin and polyethylene. Where a hardening agent is employed as a carrier, the amount thereof should be sufficient that the adjuvant-carrier mixture will exhibit a melting point of about 75° to 200° F.

The present invention may be further understood by reference to the following examples:

EXAMPLE 1

A solution of 1-stearylaimidoethyl-1-methyl-2-heptadecylimidazoline methyl sulfate was dissolved in ethyl alcohol. The solution was 20 percent active. Sixty parts of this solution was placed in a container fitted with an aerosol discharge valve, and the container was then charged with 40 parts of a fluorinated hydrocarbon propellant. The final composition inside the aerosol container after charging, therefore, contained 10 parts of fabric softener, 40 parts of ethyl alcohol and 40 parts of propellant.

EXAMPLE 2

The aerosol formulation of Example 1 was sprayed on to the interior surface of the dryer drum. The dryer was clothing charged with 6 pounds of spun-dry clothing, and the clothing was dried for a period of 45 minutes. Comparison of the clothing as dried in a dryer sprayed with the aerosol fabric softener of Example 1 with clothing dried in the absence of that softener showed that significantly improved softness was obtained. In a further control, the formulation of Example 1 was modified by including a minor quantity of a blue colorant to determine the uniformity of distribution. It was found that substantially uniform distribution of the product on the dried clothing was obtained.

Further representative fabric softening compositions are the following:

Example 3

The reaction product of mixed stearic and oleic acids with hydroxyethylethylenediamine quaternized with dimethyl sulfate	6%
di(hardened tallow) dimethyl ammonium chloride	4%
ethyl alcohol	40%
fluorinated hydrocarbon propellant	50%

This material is applied as an aerosol sprayed on to the surface of the dryer drum.

Example 4

1-stearylaimidoethyl-1-methyl-2-heptadecylimidazoline methyl sulfate	5%
distearyl dimethyl ammonium chloride condensate of ethylene oxide and a C ₁₂ -C ₁₈ linear fatty alcohol containing about 60% by weight ethylene oxide	5%
ethyl alcohol	1%
fluorinated hydrocarbon propellant	39%
	50%

The foregoing formulation was evaluated in the same manner as the formulation described in Example 2.

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SOIL RELEASE FORMULATIONS

Example 5

Soil release agent	10%
polyethylene glycol, m. w. = 4000	40%
fluorinated hydrocarbon propellant	50%

The composition is applied as an aerosol by spraying the interior surface of the dryer drum.

Example 6

the condensate of ethylene oxide with lauryl alcohol containing about 60% by weight ethylene oxide	10%
ethyl alcohol	40%
fluorinated hydrocarbon propellant	50%

OPTICAL BRIGHTENER FORMULATIONS

Example 7

an optical brightener of the class disclosed in APC publication 381,856	2%
triethanol amine	48%
fluorinated hydrocarbon propellant	50%

This product is applied as an aerosol by spraying the interior surface of the dryer drum.

Example 8

Example 7 may be modified by substituting an optical brightener of the type disclosed in U.S. Pat. No. 2,784,183, for the brightener of Example 7. Example 7 may also be modified by substituting dicocodimethyl ammonium chloride for all or a portion of the triethanol amine.

GERMICIDAL AND SANITIZER FORMULATIONS

Example 9

polybromosalicylanilide	10%
ethyl alcohol	40%
fluorinated hydrocarbon propellant	50%

Example 10

benzalkonium quaternary alcohol	10%
fluorinated hydrocarbon propellant	40%
	50%

Example 11

mixture b 12	
alkyl dimethyl ethyl benzyl	
ammonium chloride and alkyl dimethyl benzyl ammonium chloride	10%
alcohol	40%
fluorinated hydrocarbon propellant	50%

Example 12

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neomycin sulfate	10%
water	80%
isobutane	10%

Example 13

phenyl phenol alcohol	10%
fluorinated hydrocarbon propellant	40%
	50%

The aerosol formulations described in Examples 9 through 13 were sprayed on the interior surface of a dryer drum. The dryer was then charged with 6 pounds of spun-dried cloth and the cloth dried 45 minutes. Portions of the dried cloth treated with germicide were evaluated for antibacterial activity. Treated cloth showed significant antibacterial activity while untreated cloth did not.

WATER AND STAIN REPELLANT FORMULATIONS

Example 14

calcium stearate	10%
ethoxylated alcohols (C ₁₂ -C ₁₈) having about 60% ethylene oxide	2%
ethyl alcohol	38%
fluorinated hydrocarbon propellant	50%

Example 15

linear alkyl benzene sulfonate	10%
isopropyl alcohol	40%
fluorinated hydrocarbon propellant	50%

Example 16

polyoxyethylene sorbitan tristearate	8%
condensate of ethylene diamine with ethylene oxide and propylene oxide	2%
isopropyl alcohol	40%
fluorinated hydrocarbon propellant	50%

BODYING AGENTS

Example 17

polyvinyl alcohol	40%
water	30%
isobutane	30%

We claim:

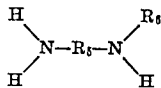
- 65 1. A method for treating cloth with a cloth adjuvant in a clothes dryer having a drum comprising the steps of
 - a. spraying a cloth adjuvant onto the interior surface of said dryer drum, said adjuvant forming an adherent film on said drum surface which is sufficiently hard that it will not be immediately wiped off onto the cloth articles that are loaded into the drum but which is removable by the cloth articles which abrade against said film when said drum rotates in a period between about 5 and 45 minutes, the adjuvant being selected from the group consisting of germicides, fabric softeners, optical brighteners, ironing

aides, antistatic agents, stain repellents, soil release agents, wrinkle preventents, deodorizers, fresheners, cleaning agents, surfactants, flame proofing agents, moth proofing agents and bleaching agents,

b. loading the cloth to be treated in said dryer, and 17 adjuvant said adjuvant

2. A method according to claim 1 for treating cloth with a fabric softener, wherein said cloth adjuvant applied to the interior surface of said dryer drum is a fabric softener having a softening point between 70° and 200° F.

3. A method according to claim 2 wherein said fabric softener is selected from the group consisting of quaternary ammonium compounds of the formula $N(R_1R_2R_3R_4)_yX$ and the reaction product of about 2 moles of a fatty acid of the formula R_4COOH and hydroxyalkyldiamine of the formula



where R_1 is a C_{16} to C_{20} alkyl group, R_2 is a C_1 to C_4 alkyl group, R_3 is selected from the group consisting of R_1 and R_2 , R_4 is a C_{15} to C_{19} alkyl group, R_5 is a C_1 to C_3 divalent hydrocarbon radical and R_6 is a hydroxyalkyl group of from about one to three carbon atoms, X is an anion imparting water

dispersibility to the cationic ammonium compound, and y is the VALENCY of X.

4. A method according to claim 1 wherein said cloth adjuvant is a germicide selected from the group consisting of halogenated salicylanilides, hexachlorophene, neomycin sulfate, and benzalkonium quaternary compounds.

5. A method according to claim 1 wherein said cloth adjuvant is an optical brightener.

6. A method according to claim 1 wherein said adjuvant is employed in combination with a waxy carrier having a softening point between about 70° and 200° F., the waxy carrier being present in an amount sufficient to impart the desired degree of hardness to the composition when said composition is applied to the surface of the dryer drum.

7. A method according to claim 6 wherein said adjuvant is employed in combination with a waxy carrier selected from the group consisting of stearic acid, stearyl alcohol, palmitic acid, palmityl alcohol, and ethoxylated derivatives of these acids and alcohols, polyethylene glycol having a molecular weight of 1,000 to 5,000 and hydrocarbons.

8. A method according to claim 1 wherein said cloth adjuvant is employed in combination with a waxy carrier having a melting point between about 90° and 100° F.

9. A method according to claim 1 wherein said adjuvant is sprayed onto the interior surface of said dryer drum by means of an aerosol spray.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,650,816 Dated March 21, 1972

Inventor(s) Jerome Rudy et al.

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

First page, Item [54] and in column 1, line 1, the title should read -- Method of Applying Adjuvants to Cloth --; last line of Item [56], "Garves" should read -- Graves --. Column 3, line 50, after "respect" the word "solvents" should read -- however, --; line 55, after "invention" insert a comma. Column 4, line 32, after "was", delete "clothing" and substitute -- then --. Column 5 lines 67 and 68, "mixture b-12 alkyl dimethyl ethyl benzyl" should read -- mixture of alkyl dimethyl ethyl benzyl --. Column 7, lines 5 and 6 delete "17 adjuvant said adjuvant" and substitute therefor: -- c. Operating said dryer for a period of time sufficient to effect application of said adjuvant to said cloth. --. Column 8, line 2, "VALENCY" should read -- valency --.

Signed and sealed this 17th day of October 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents