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(54) **Spot removal compositions for use in aerosol dispensers**

Aerosolzusammensetzungen zur Entfernung von Flecken

Compositions en aérosol pour détachage

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GB-A- 2 247 894 **US-A- 3 354 092**
US-A- 4 460 489 **US-A- 4 711 739**
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• **PATENT ABSTRACTS OF JAPAN** vol. 014, no.
334 (C-0742), 18 July 1990 (1990-07-18) & JP 02
123199 A (TAKEHARA:KK), 10 May 1990
(1990-05-10)

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DescriptionTechnical Field

5 **[0001]** The present invention relates to compositions suitable for use in aerosol dispensers for removing spots and stains from textiles.

Background Art

10 **[0002]** Stains and spots can be removed from many textiles by aqueous washing media, as in conventional laundering. However many textiles are adversely affected if brought into contact with water, and an extended drying time may be needed if a conventional aqueous washing medium is used.

It is known to remove stains and spots from textiles by the use of so-called "dry cleaning " sprays in which a non-aqueous medium is sprayed on the textile from an aerosol dispenser using a propellant to force the cleaning medium from the dispenser. The liquid medium may contain an absorbent solid. Halogenated hydrocarbons have been used as the cleaning fluid. Halogenated hydrocarbons have also been used as aerosol propellants. Such halogenated hydrocarbons are no longer acceptable in products released to the atmosphere because of their adverse effect on the ozone layer. Hydrocarbon propellants, e.g. propane or butane, have been used in place of halogenated hydrocarbons and hydrocarbon solvents have been used as the cleaning liquid. However the use of these hydrocarbons introduces a fire hazard because of their flammability. It should be noted that the hydrocarbon solvents, although less volatile than the propellant, must be sufficiently volatile to evaporate readily from the surfaces on to which they are sprayed. There is also a problem of the generation of static electricity if the aerosol canister is punctured and thus releases the contents. A spark may be produced which may ignite the hydrocarbons.

15 **[0003]** US-A- 5 269 958 discusses these problems and proposes to overcome them by eliminating the hydrocarbon propellant and solvents. The composition disclosed contains a small amount of water, together with major amounts of dimethyl ether as propellant and dimethoxymethane to remove oil-based stains, a co-solvent, e.g. isopropanol, and a particulate absorbent.

20 **[0004]** GB-A-2 247 894 discloses prewash cleaning compositions in the form of water-in-oil-microemulsions/and/ include hydrocarbon solvent, water, nonionic surfactant and dimethylether.

25 **[0005]** The oxygenated solvents are relatively expensive and it would be highly desirable to be able to produce a spray cleaning composition which made use of the cheaper and more readily available hydrocarbon solvents but which reduced the disadvantages associated with the use of hydrocarbons.

Disclosure of Invention

30 **[0006]** According to the present invention there is provided a self-pressurized aerosol composition for spot dry cleaning of a textile, said composition comprising

- 35
- a) a propellant,
 - 40 b) a volatile hydrocarbon solvent for removing stains, wherein the solvent is an alkane having from 5 to 8 carbon atoms in the molecule or is a mixture of such alkanes,
 - c) a particulate absorbent capable of absorbing a stain from a textile on to which it is sprayed,
 - d) a water-in-oil microemulsion in an amount from 5% to 50% by weight of the total composition including propellant,

45 said microemulsion containing from 2.5 % to 25. % by weight of water based on weight of the total composition including propellant, wherein the water-in-oil microemulsion has a continuous phase which is an aliphatic hydrocarbon.

[0007] The propellant may be a liquefied petroleum gas (LPG). The propellant is preferably dimethyl ether (DME). This is water-soluble and is less flammable than the hydrocarbon propellants.

50 **[0008]** The quantity of propellant may for example be 2.0 to 50 % by weight of the total composition, preferably 30 to 45 % by weight, e.g ca. 35% by weight.

[0009] The volatile organic solvent is preferably an alkane having from 5 to 8 carbon atoms in the molecule or a mixture of such alkanes. An example of a suitable volatile organic solvent is a pentane/heptane blend. Such a blend is commercially available as Exxsol 45/100 from Exxon.

55 **[0010]** The quantity of solvent is preferably in the range 10 to 50% by weight of the total composition, more preferably 15 to 45% by weight of the total composition.

[0011] The particulate absorbent capable of absorbing a stain from a textile on to which the composition is sprayed is one which has a particle size which permits it to be sprayed from a self-pressurized aerosol dispenser. Examples of such particulate absorbents are fumed or pyrogenic silica, precipitated silica, surface-treated silica, calcium silicate,

calcium carbonate, magnesium silicate, starch, clays, talc, magnesium oxide. The nature of the particulate absorbent is discussed in detail in US-A-5 269 958.

[0012] The quantity of particulate absorbent is preferably 1% to 10%, preferably 5% to 9%, more preferably from 6% to 8% of the total weight of composition.

[0013] Water is incorporated into the composition in the form of a microemulsion in which water is the internal phase. Despite the water being in the form of droplets within an organic continuous phase it has been found that the presence of a relatively small amount of water has a significant effect on flammability and prevents the production of static electricity if the can is punctured.

[0014] Water-in-oil emulsions suitable for use in the present invention are available from the firm of Dow under the name "Invert Solvents". Emulsions in which the continuous phase is an aliphatic hydrocarbon phase are used, preferably a low flash point hydrocarbon phase which evaporates readily, e.g Dow "Invert 1000". Thus the boiling point is preferably less than 90 °C, and the viscosity is preferably less than 7 cps at 25°C, and the flash point (closed cup) is preferably below 0°C.

[0015] The water content is preferably in the range 45% to 55% by weight of the microemulsion.

[0016] The quantity of water-in-oil emulsion in the composition is in the range 5 to 50%, preferably 15 to 40%, e.g. 10 to 30 % of the total weight of composition.

[0017] The absorbent solid when used in the conventional aerosol composition using hydrocarbon solvents and hydrocarbon propellants usually shows no tendency to cake or clump and can be readily dispersed in the composition by shaking. In the compositions of the present invention it has been found that there is a tendency for the particulate absorbent to cake or clump. This can be overcome by including an anti-caking agent in the composition. An example of a suitable anti-caking agent is diammonium phosphate. This may be present, for example, in an amount in the range 0.2 to 1.5% by weight of the total composition, e.g. 0.5% by weight.

[0018] It may be desirable to include some dimethoxy methane (also known as methylal) in the composition in order to assist in the removal of oil based stains. This preferably constitutes not more than 5% of the composition.

Best Mode of Carrying Out the Invention

Example 1

[0019] A self-pressurized spot remover composition suitable for use in an aerosol dispenser for removing stains from textiles was prepared as follows. An intermediate composition was first prepared from the following ingredients.

Ingredient	Amount (% wt of final product)
Hydrocarbon solvent	35.550
Microemulsion	20.000
Absorbent	07.500
Anti-caking agent	00.500
Silicone oil	00.200
Surfactant	01.000
Ammonia 25%	00.250

[0020] The hydrocarbon solvent was a pentane/heptane blend available from Exxon under the trade name "Exxsol DSP 45/100".

[0021] The microemulsion was a water-in-oil microemulsion supplied by Dow under the name "Invert 1000". It contained about 50% by weight of water with the continuous phase being a low flash point aliphatic hydrocarbon. It had a boiling point of 84°C, a freezing point of -2°C, a vapour pressure of 34.9 mm Hg at 20°C, a viscosity of 6.2 cps,

[0022] The absorbent was a precipitated silicon dioxide from Akzo available under the trade name "Ketjensil SM604" and with an average particle size of 12µm.

[0023] The anti-caking agent was diammonium phosphate. In addition to having an anti-caking effect it acts as a corrosion inhibitor and has a quenching effect on flammability.

[0024] The silicone oil was silicone oil with a viscosity of 1000 cps at 25 °C is included to provide a lubricating effect for the absorbent solid in the plastic channels of the valve and actuator of the dispensing device used to dispense the composition.

[0025] The surfactant was a 70% solution of sodium dioctyl sulphosuccinate in petroleum distillate commercially available from Cytec under the trade name "Aerosil OT-S". It acts as an additional emulsifier and helps to remove water-based stains.

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[0026] The ammonia was a 25% by weight aqueous solution. It is used to increase the pH of the composition to about pH 8.5 to minimize corrosion of aerosol canisters.

[0027] The intermediate product was prepared by mixing the liquids, then adding the two solids and agitating with a Silverson-type mixer until a smooth particle free mixture was obtained.

5 [0028] Propellant (dimethyl ether) was then added in an amount corresponding to 35% of the total composition (i.e. the composition after the dimethyl ether had been added).

Example 2

10 [0029] A composition was prepared as in Example 1 except that the intermediate composition was prepared using the amounts of ingredients set out below.

Ingredient	Amount (% wt of final product)
Hydrocarbon solvent	40.549
Microemulsion	15.000
Absorbent	07.500
Anti-caking agent	00.500
Silicone oil	00.200
Surfactant	01.000
Ammonia 25%	00.250

Example 3

25 [0030] A composition was prepared as in Example 1 except that the intermediate composition was prepared using the amounts of ingredients set out below.

Ingredient	Amount (% wt of final product)
Hydrocarbon solvent	30.549
Microemulsion	25.000
Absorbent	07.500
Anti-caking agent	00.500
Silicone oil	00.200
Surfactant	01.000
Ammonia 25%	00.250

Example 4

40 [0031] A composition was prepared as in Example 1, but with the intermediate composition as set out below, and using Liquefied Petroleum Gases (LPG 48) as propellant.

Ingredient	Amount (% wt of final product)
Hydrocarbon solvent	26.520
Microemulsion	20.000
Absorbent	07.500
Anti-caking agent	00.500
Silicone oil	00.200
Ammonia 25%	00.250

[0032] The quantity of LPG used was 45.00% of the weight of the total composition.

55 Flammability tests

[0033] The flammability of the compositions of Examples 1, 2, 3 and 4 was assessed. This was done using modifications of the test procedures described on page 380 of the Aerosol Handbook, 1st edition, M. A. Johnsen et al., Wayne

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E. Dorland Company, Caldwell, N. J., 1972. The modified tests are described in US Patent 5 269 958 in columns 10 and 11.

[0034] The same valve system was used with the aerosol container used to dispense the composition in all the tests. The discharge rates vary in some cases because the narrow channels in the valve system can become partially clogged with powder particles. The weights of sample sprayed are however sufficiently close for the tests to provide useful results.

Example 1

[0035]

Drum Test	
Discharge rate	0.641 g/s
Weight of sample sprayed	16.09 g
Time taken for explosion	27.9 s
Discharge rate	1.06 g/s
Weight of sample sprayed	16.33 g
Time taken for explosion	12.91 s
Discharge rate	0.636 g/s
Weight of sample sprayed	15.09 g
Time taken for explosion	19.13 s
Ignition distance	30 cm

[0036] Flame extension 50 cm, no flashback, not self sustaining.

Example 2

[0037]

Discharge rate	0.665 g/s
Weight of sample sprayed	15.67 g
Time taken for explosion	23.19 s
Discharge rate	0.598 g/s
Weight of sample sprayed	14.86 g
Time taken for explosion	25.03 s
Ignition distance	20 cm

[0038] Flame extension 40 cm, no flashback, not self sustaining.

Example 3

[0039]

Discharge rate	0.633 g/s
Weight of sample sprayed	16.62 g
Time taken for explosion	26.10 s
Discharge rate	0.602 g/s
Weight of sample sprayed	18.85g
Time taken for ignition	24.15 s

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(continued)

Ignition distance	25 cm
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[0040] Flame extension 55 cm, no flashback, not self sustaining.

Example 4

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[0041]

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Weight of sample sprayed	14.5 g
Time taken for explosion	15.43 s
Weight of sample sprayed	14.32g
Time taken for ignition	26.53 s
Weight of sample sprayed	14.54g
Time taken for ignition	27.32 s
Ignition distance	55-60 cm

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[0042] Flame extension 50 cm, flashback 10-12 cm, not self sustaining.

Comparative Test A

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[0043] Average flammability results for a commercially available composition intended for spray dry cleaning based on a hydrocarbon solvent without water, LPG as propellant, and containing an amine as an anti-static agent tested as in the Examples above are set out below.

[0044] In these tests the discharge rate was approximately 0.8g/sec. The time to explosion was 22.4 s and the weight of sample sprayed was 10.4 g. Flashback was observed (12 cm) and the flame was self-sustaining.

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Stain removing tests

[0045] The compositions of Examples 1, 2, and 3 gave satisfactory removal of stains from textiles without excessive drying times and without adversely affecting the textile because of the presence of water on a variety of oil-based and water-based stains.

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[0046] A comparison of the flammability results shows that compositions based on the microemulsions and using dimethyl ether as propellant gave the best flammability results. Better flammability results compared with conventional aerosol dry cleaning compositions are obtained using compositions containing microemulsions even when using hydrocarbon propellants.

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[0047] The compositions containing microemulsions will eliminate the risk of static electricity discharge leading to ignition if the aerosol dispenser is accidentally punctured. Conventional compositions can reduce the risk of static electricity discharge by incorporating organic antistatic agents but these are believed to be more dependent on the ambient atmospheric conditions (temperature, humidity) for successful results.

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Claims

1. A self-pressurized aerosol composition for spot dry cleaning of a textile, said composition comprising:

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- a) a propellant;
- b) a volatile hydrocarbon solvent for removing stains, wherein the solvent is an alkane having from 5 to 8 carbon atoms in the molecule or is a mixture of such alkanes;
- c) a particulate absorbent capable of absorbing a stain from a textile on to which it is sprayed; and
- d) a water-in-oil microemulsion in an amount from 5% to 50% by weight of the total composition including

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propellant, said water-in-oil microemulsion containing from 2.5 % to 25 % by weight of water based on weight of the total composition including propellant, wherein the water-in-oil microemulsion has a continuous phase which is an aliphatic hydrocarbon.

- 5 2. A composition according to claim 1 wherein the propellant is dimethyl ether.
3. A composition according to claim 1 or claim 2 wherein the microemulsion has a boiling point of less than 90°C.
- 10 4. A composition according to any one of the preceding claims wherein the viscosity of the microemulsion is less than 7 cps at 25°C.
5. A composition according to any one of the preceding claims wherein the microemulsion has a flash point (closed cup) below 0°C.
- 15 6. A composition according to any one of the preceding claims wherein the microemulsion has a water content in the range 45% to 55% by weight.
7. The composition according to any one of the preceding claims which contains from 15 to 40 % by weight of the microemulsion.
- 20 8. The composition according to any one of the preceding claims which contains from 10 to 50 % by weight of volatile hydrocarbon solvent.
- 25 9. The composition according to any preceding claim which contains from 15 to 45% by weight of volatile hydrocarbon solvent.
10. The composition according to any one of the preceding claims wherein the composition further contains an anti-caking agent.
- 30 11. The composition according to claim 10 wherein the anti-caking agent is diammonium phosphate.

Patentansprüche

- 35 1. Unter Eigendruck stehende Aerosol-Zusammensetzung zur Trocken-Fleckentfernung aus Textilien, mit:
 - a. einem Treibmittel;
 - b. einem flüchtigen Kohlenwasserstoff-Lösungsmittel zur Fleckentfernung, bei dem es sich um ein Alkan mit 5 bis 8 Kohlenstoff-Atomen im Molekül oder um eine Mischung solcher Alkane handelt;
 - 40 c. einem teilchenförmigen Absorptionsmittel, das einen Fleck aus einem Textilartikel absorbieren kann, auf den es aufgesprüht wird; und
 - d. einer Wasser-in-Öl-Mikroemulsion in eine Menge von 5 bis 50 Gew.-% der Gesamtzusammensetzung einschließlich des Treibmittels, wobei die Wasser-in-Öl-Mikroemulsion 2,5 bis 25 Gew.-% Wasser relativ zum Gewicht der Gesamtzusammensetzung einschließlich des Treibmittels enthält, wobei die Wasser-in-Öl-Mikroemulsion eine kontinuierliche Phase aufweist, bei der es sich um einen aliphatischen Kohlenwasserstoff handelt.
- 45 2. Zusammensetzung nach Anspruch 1, bei der das Treibmittel Dimethyläther ist.
- 50 3. Zusammensetzung nach Anspruch 1 oder 2, bei der die Mikroemulsion einen Siedepunkt von unter 90 °C hat.
4. Zusammensetzung nach einem der vorgehenden Ansprüche, bei der die Viskosität der Mikroemulsion weniger als 7 cP bei 25 °C beträgt.
- 55 5. Zusammensetzung nach einem der vorgehenden Ansprüche, bei der der Flammpunkt (geschlossener Tiegel) der Mikroemulsion unter 0 °C liegt.
6. Zusammensetzung nach einem der vorgehenden Ansprüche, bei der der Wassergehalt der Mikroemulsion im

Bereich von 45 bis 55 Gew.-% liegt.

7. Zusammensetzung nach einem der vorgehenden Ansprüche, die 15 bis 40 Gew.-% der Mikroemulsion enthält.
- 5 8. Zusammensetzung nach einem der vorgehenden Ansprüche, die 10 bis 50 Gew.-% des flüchtigen Kohlenwasserstoff-Lösungsmittels enthält.
9. Zusammensetzung nach einem der vorgehenden Ansprüche, die 15 bis 45 Gew.-% des flüchtigen Kohlenwasserstoff-Lösungsmittels enthält.
- 10 10. Zusammensetzung nach einem der vorgehenden Ansprüche, die weiterhin einen ein Zusammenbacken verhindernden Wirkstoff enthält.
- 15 11. Zusammensetzung nach Anspruch 10, bei der der ein Zusammenbacken verhindernde Wirkstoff Diammoniumphosphat ist.

Revendications

- 20 1. Composition en aérosol auto-pressurisée pour le nettoyage à sec de taches d'un textile, ladite composition comprenant :
- a) un propulseur ;
- 25 b) un solvant hydrocarboné volatil pour éliminer des taches, dans lequel le solvant est un alcane ayant de 5 à 8 atomes de carbone dans la molécule ou est un mélange de tels alcanes ;
- c) un adsorbant particulaire capable d'absorber une tache d'un textile sur lequel il est pulvérisé ; et
- d) une micro-émulsion eau-dans-huile dans une quantité de 5 % à 50 % en poids de la composition totale comprenant le propulseur, ladite micro-émulsion eau-dans-huile contenant de 2,5 % à 25 % en poids d'eau rapportés au poids de la composition totale comprenant le propulseur, dans laquelle la micro-émulsion eau-dans-huile présente une phase continue qui est un hydrocarbure aliphatique.
- 30 2. Composition selon la revendication 1, dans laquelle le propulseur est le diméthyléther.
3. Composition selon la revendication 1 ou la revendication 2, dans laquelle la micro-émulsion présente un point d'ébullition inférieur à 90°C.
- 35 4. Composition selon l'une quelconque des revendications précédentes, dans laquelle la viscosité de la micro-émulsion est inférieure à 7 cps à 25°C.
- 40 5. Composition selon l'une quelconque des revendications précédentes, dans laquelle la micro-émulsion a un point éclair (bol fermé) inférieur à 0°C.
6. Composition selon l'une quelconque des revendications précédentes, dans laquelle la micro-émulsion présente une teneur en eau dans l'intervalle de 45 % à 55 % en poids.
- 45 7. Composition selon l'une quelconque des revendications précédentes qui contient de 15 à 40 % en poids de la micro-émulsion.
8. Composition selon l'une quelconque des revendications précédentes qui contient de 10 à 50 % en poids de solvant hydrocarboné volatil.
- 50 9. Composition selon l'une quelconque des revendications précédentes qui contient de 15 à 45 % en poids de solvant hydrocarboné volatil.
- 55 10. Composition selon l'une quelconque des revendications précédentes, dans laquelle la composition contient en outre un agent anti-prise en masse.
11. Composition selon la revendication 10, dans laquelle l'agent anti-prise en masse est le phosphate de diammonium.