3,335,093

DRY CLEANING PROCESS AND COMPOSITION

Herman Spencer Gilbert, Angleton, and John Henry Brown, Jr., Lake Jackson, Tex., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

No Drawing. Filed Feb. 8, 1965, Ser. No. 431,205
10 Claims. (Cl. 252—170)

The present invention relates to a new process and composition for cleaning textile materials. More specifically, this invention is concerned with improving the brightness of dry cleaned materials by inhibiting the deposition of metallic impurities on such materials during a cleaning process.

It has been discovered that polyvalent metal ions, generally present in dry cleaning solvent systems, tend to deposit on fibrous materials cleaned therein. Such deposits, it has been found, are responsible for decreasing the brightness of the cleaned materials.

In general dry cleaning practice a solvent system comprising essentially a halogenated organic dry cleaning solvent is commonly employed, e.g. chlorinated hydrocarbons such as perchloroethylene, trichloroethylene and the like, and is frequently formulated to contain detergents or soaps and other additives. The term "solvent system" is used herein to designate these commonly used solvents and formulated solvents.

In the present invention, deposition of polyvalent metal ions from a solvent system onto fibrous materials being cleaned therein is inhibited by addition of minor amounts of a lower alkanedione or cycloalkanedione to the solvent system employed in the dry cleaning process. It is believed that this dione additive, which is soluble in the solvent system in the amounts used to practice the present invention, reacts with polyvalent metal ions present to form soluble complexes thus preventing deposition of these metallic impurities on the fibrous materials in the solvent system.

The following examples illustrate the detrimental effect on the brightness of materials caused by deposition of polyvalent metal ions onto the material. The tendency of polyvalent metal ions to deposit on materials from the contacting dry cleaning solvent system is also demonstrated.

EXAMPLE 1

After the discovery that polyvalent metal ions tend to be deposited from dry cleaning solvent systems onto materials cleaned therein and that such deposits adversely effect the brightness of the cleaned materials, experiments were conducted to determine quantitative effects of this unexpected phenomenon. Investigation revealed that the polyvalent metal ion deposit is in most instances, especially marked where moisture is present in the material. Moisture, of course, is normally present in materials being cleaned and additional moisture is generally present in the formulated dry cleaning solvent initially introduced into the dry cleaning system.

A series of forty loads of clothes, averaging about eight pounds per load, were cleaned in a regular commercial dry cleaning machine employing a standard perchloroethylene dry cleaning solvent system used in the cleaning industry. A number of new, 4" by 11" swatches of cotton, wool, viscose taffeta and spun acetate materials were cleaned together with the series of 40 loads of clothes and the deposit of polyvalent metal ions thereon was determined by emission spectroscopy. A portion of each of the swatches was moistened with a few drops of deionized water prior to each cleaning cycle to demonstrate the effect of moisture, present in the material being cleaned, on the tendency of the metal ions to deposit on the cloth. The original metal content of these new swatches provides a standard for determination of the amounts of metal deposited during cleaning. The results are shown in Table I, below, where metal content is reported as parts per million (p.p.m.), weight of cloth basis.

TABLE I

Swatch	Description	Metal Content (p.p.m.)							
		Ca	Mg	Fe	Cu	Ti	Zn	Pb	Cd
Cotton	New	47	15	14	1	5	20	10	23
	Wet area	420	27	25	35	10	65	30	24
	Dry area	160	21	22	33	13	42	30	20
	Wet-dry interface	800	55	47	80	15	340	85	65
Wool	New	56	7	14	1	1	47	2	2
	Wet area	50	1.5	12	40	10	220	12	36
	Dry area	52	6	13	1	9	40	9	6.5
Viscose Taffeta	New	500	48	13	1	------	20	35	3
	Wet area	330	30	12	35	------	100	70	15
	Dry area	520	65	28	12	------	20	50	13
Spun Acetate	New	150	48	2	1	------	20	10	2
	Wet area	150	34	2	1	------	20	10	16
	Dry area	230	70	30	1	------	20	10	10

The largest increase in metal content was at the wet-dry interface and this area also showed the greatest loss of reflectance as compared with the new sample. This may possibly explain the difficulty encountered in removing the border line portion of water spots; a frequent problem in dry cleaning of materials. This high metal content at the wet-dry interface is believed due primarily to wet area deposition with subsequent capillary action (similar to paper partition chromatography) depositing a large portion of the wet area metal species in the ring forming the wet-dry interface.

EXAMPLE 2

This experiment illustrates the correlation between reflectance loss and the presence of polyvalent metals in a dry cleaning solvent system used to clean swatches of material.

A series of cloth swatches was agitated for extended time periods in quantities of three different commercially available dry cleaning solvent systems. In each case the reflectance readings of swatches agitated in samples of the new, uncontaminated dry cleaning solvent system were compared with reflectance readings of swatches agitated in portions of the same dry cleaning solvent system which had been saturated with Zn, Cu, Fe, and Mg ions. These saturated portions were prepared by extended stirring of water soluble salts of these metal species with the dry cleaning solvent employed. The reflectance readings, taken on a standard reflectometer, are tabulated in Table II, below, as taken initially and at the end of one, two and three days of agitation in the solvent. In the following table, Solvent 1 is perchloroethylene; Solvent 2 is a chlorinated hydrocarbon dry cleaning solvent, containing a petroleum sulfonate base detergent, widely used in commercial, coin-operated, dry cleaning machines; Solvent 3 is a formulated perchloroethylene solvent containing a phosphate base detergent additive.

TABLE II.—REFLECTANCE READINGS

	1 day	2 days	3 days
Spun Acetate Swatches: [1]			
Solvent 1			
Metals absent	84.5	84.5	84.5
Metals present	84.0	82.5	81.5
Solvent 2			
Metals absent	84.5	84.0	84.0
Metals present	83.0	80.5	78.5
Solvent 3			
Metals absent	83.5	83.0	83.0
Metals present	82.0	78.5	78.5
Worsted Gabardine Wool Swatches: [2]			
Solvent 1			
Metals absent	73.0	73.0	73.0
Metals present	70.0	68.0	67.5
Solvent 2			
Metals absent	73.0	72.5	73.0
Metals present	71.5	67.5	65.0
Solvent 3			
Metals absent	72.5	72.5	72.5
Metals present	71.0	69.5	69.5

[1] Initial reflectance readings—85 units.
[2] Initial reflectance reading—73.5.

As shown by the comparative reflectance readings in Table II, above, the presence of the polyvalent metal ions (which were the only contaminants present in the test samples of solvent) cause a significant loss of whiteness in the swatches.

In practice of the present invention, a quantity of from about 0.1 to 3 parts by weight of a lower alkanedione or a cycloalkanedione is added to 100 parts by weight of a dry cleaning solvent system to form a new composition of the present invention. This new composition is utilized to inhibit the previously described deposition of metallic impurities on fibrous materials during dry cleaning operations. The term "lower alkanedione" is used herein to designate an alkanedione containing from 1 to 6 carbon atoms, inclusive. The term "cycloalkanedione" as used herein includes cycloalkanediones having one or more alkyl substituents, which substituents contain from 1 to 4 carbon atoms, inclusive. These new compositions of the present invention may also be employed for purposes, other than usual dry cleaning procedures, where solvent systems are utilized. Examples of such uses include water repellant formulations, spotting agent, moth proofing and static eliminator systems and sizing solutions.

Specific examples of lower alkanediones and cycloalkanediones employed in practice of the present invention include acetylacetone, 2,3-butanedione, 2,4-pentanedione, 2,5-hexanedione and 5,5-dimethyl-1,3-cyclohexanedione.

The following examples describe completely representative specific embodiments of the method and compositions of the present invention. These examples, however, are not to be interpreted as limiting the invention other than as defined in the claims.

EXAMPLE 3

A series of four glass containers holding 100 ml. quantities of a fresh solvent system and either cotton or spun acetate cloth samples was prepared. A commercially available solvent system, widely used in coin-operated dry cleaning machines and containing small amounts of a petroleum sulfonate base detergent, was employed. A quantity of analytical reagent grade zinc, magnesium, iron and copper (0.2 gram each) was added to each glass container. A quantity of 1000 parts per million (p.p.m.) of acetylacetone, based on the solvent system, was added to one container holding cotton swatches and one container holding spun acetate swatches. The four containers were then agitated for 90 hours after which the reflectance of the cloth swatches was measured. The cotton swatches

agitated in the container having acetylacetone present were 3.8 reflectance units brighter than those swatches agitated in the solvent system containing no acetylacetone. Similarly, the addition of acetylacetone to the solvent system containing spun acetate swatches was responsible for a reflectance reading 6.4 units higher than that obtained on spun acetate swatches agitated in the control solvent system containing no acetylacetone. The initial reflectance of the cotton swatches, before treatment, was 75 units. A number of repeat experiments confirmed the above improvement in brightness of these materials when acetylacetone was present in the solvent system.

EXAMPLE 4

In the manner of the preceding experiment, a quantity of galvanized metal was employed in place of the Zn, Cu, Fe and Mg used above. Table III, below, shows the reflectance readings of cotton swatches, after various time periods, agitated in solvent systems with and without acetylacetone present. The initial reflectance of the cotton swatches, before treatment, was 75 units.

TABLE III

	Reflectance Reading After—				
	1 day	3.7 days	6 days	7 days	11 days
Acetylacetone absent	69.6	67.3	67.0	66.5	66.1
Acetylacetone present	-------	68.9	-------	68.8	68.7

While the improvement in reflectance readings is not as marked in this example as in Example 3, it must be noted that Cu and Mg were not present in this example.

EXAMPLE 5

In this example the procedure of Example 3 was employed with the following exceptions; no iron was present, agitation time was 24 hours after which reflectance was measured, the solvent system employed was perchloroethylene and the diketones used in place of acetylacetone are as indicated in Table IV, below. Cotton swatches were used.

TABLE IV

Additive	Reflectance Reading
Control (no metals or additive)	70.0
Control (metals present—no additive)	68.0
2,3-butanedione (1,000 p.p.m.)	70.5
2,4-pentanedione (1,000 p.p.m.)	69.5
2,5-hexanedione (1,000 p.p.m.)	69.0
5,5-dimethyl-1,3-cyclohexanedione (1,000 p.p.m.)	70.5

As previously noted a quantity of from about .01 to 3 parts by weight of a lower alkanedione or cycloalkanedione is dissolved in 100 parts by weight of a dry cleaning solvent system to provide a new composition of the present invention. This solvent system, as stated before, comprises essentially a halogenated organic dry cleaning solvent base well known to the art. In addition there may be present relatively small amounts of other additives such as soaps or detergents, water, brighteners, anti-static agents, etc. While these relatively small amounts of additives have no marked effect on the formation of the diketone-metal complexes, each plays a role in improving or providing other desirable features in a dry cleaning process. The new compositions of the present invention, which consist essentially of a major amount of dry cleaning solvent and a minor amount of a lower alkanedione or cycloalkanedione, will therefore usually contain small amounts of one or more detergents, water, and other agents as described above.

We claim:

1. In a method of cleaning fibrous materials in a dry cleaning solvent by contacting the material with said dry cleaning solvent, the improvement wherein the sol-

vent contains an agent which prevents the deposition of metallic ions upon the material being cleaned, said agent being a diketone selected from the group consisting of acetylacetone, 2,3-butanedione, 2,4-pentanedione, 2,5-hexanedione, and 5,5-dimethyl-1,3-cyclohexanedione, said agent being present in an amount of from 0.01 to 3 weight percent.

2. The method of claim **1** wherein said diketone is acetylacetone.

3. The method of claim **1** wherein said diketone is 5,5-dimethyl-1,3-cyclohexanedione.

4. The method of claim **1** wherein said diketone is 2,3-butanedione.

5. The method of claim **1** wherein said diketone is 2,4-pentanedione.

6. The method of claim **1** wherein said diketone is 2,5-hexanedione.

7. The method of claim **2** wherein said halogenated dry cleaning solvent consists essentially of perchloroethylene.

8. The method of claim **2** wherein said halogenated dry cleaning solvent is perchloroethylene containing a petroleum sulfonate base dry cleaning detergent.

9. The method of claim **2** wherein said halogenated dry cleaning solvent is perchloroethylene containing a phosphate base dry cleaning detergent.

10. In the method of cleaning fibrous materials in a halogenated dry cleaning solvent system the improvement which comprises employing a chlorinated hydrocarbon dry cleaning solvent containing from about 0.01 to 3 weight percent of a diketone selected from the group consisting of acetylacetone, 2,3-butanedione, 2,4-pentanedione, 2,5-hexanedione and 5,5-dimethyl-1,3-cyclohexanedione.

References Cited

UNITED STATES PATENTS

1,911,289	5/1933	Reddish	252—161
2,388,962	11/1945	Flett	252—161
2,476,554	7/1949	Lincoln et al.	252—171 XR
2,517,895	8/1950	Larcher et al.	252—171
3,117,152	1/1964	Michaels	252—171

LEON D. ROSDOL, *Primary Examiner.*

J. T. FEDIGAN, *Assistant Examiner.*