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DRY CLEANING METHOD

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ABSTRACT OF THE DISCLOSURE

The present invention concerns the method of contacting a dry cleaning solvent formulation after use to the action of a cation exchange resin or a chelating agent to remove or chemically bind the metal ions in said solvent formulation in a form such that they are removed from the solvent formulation before the formulation is reused.

It has now been discovered that the presence of polyvalent metal cations in dry cleaning solvent systems is detrimental to the effectiveness and efficiency of dry cleaning operations. This surprising and unexpected discovery resulted from observations that the reflectance readings of cloth samples were influenced by the polyvalent metal ion content of the dry cleaning solvent system in which the samples had been cleaned.

In general dry cleaning practice a solvent system comprising essentially an organic dry cleaning solvent is employed, e.g. chlorinated hydrocarbons such as perchloroethylene, trichloroethylene and the like, or volatile hydrocarbons such as benzene, naphtha 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 comonly used solvents and formulated solvents.

In the present invention the polyvalent metal ion content of the dry cleaning solvent system is reduced by contacting the solvent system with a material capable of tying up or precipitating polyvalent metal ions in a form suitable for removal from the solvent system by filtration. Examples of materials found suitable for establishing the ions in a form for removal, as for example by filtration, include cation exchange resins, which tie up polyvalent metal ions through ion exchange, and compounds or compositions which react with polyvalent metal ions to form precipitates in the solvent system.

Although the concentration of polyvalent metal ions in dry cleaning solvents may be quite low initially, there is a rapid build-up of these metal ions, together with other impurities, during repeated cleaning operations which remove these impurities from the fibrous materials cleaned. In usual practice, the dry cleaning solvent is continually or periodically filtered in order to remove the various suspended or dispersed impurities, such as soil particles and the like, which accumulate in the solvent during cleaning operations. The interfering polyvalent ions are not removed by this filtration. However, in practice of the method of the present invention the undesirable metal ions are established in a form removable by such a filtration step. Similarly, the desired removal of polyvalent metal ions, which have been precipitated from the solvent system, is accomplished by separate filtration of the solvent system prior to re-use in further cleaning operations. In an alternative method of the present invention the contaminated dry cleaning solvet system is brought into intimate contact with a cation exchange resin to effect ion exchange removal of the polyvalent metal ions.

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 affect 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 this 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 and 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 re-

flectance 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 tabulaed 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 day	3 day
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 reading—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.

As previously noted, one procedure for reducing the polyvalent metal ion content of the solvent system involves contacting the solvent system with compounds or compositions which react with these metal ions to form precipitates which are removed from the solvent system as, for example, by filtration. The compounds or compositions employed for this purpose are those which possess the property of forming chelates or complexes with polyvalent metal ions. Any of the wide variety of known polyvalent metal ion chelating compounds may be employed for this purpose, such as, for example, the tetrasodium salt of ethylenediaminetetraacetic acid, the pentasodium salt of diethylenetriamine pentaacetic acid, the trisodium salt of N-hydroxyethylenediaminetriacetic acid and the sodium salt of N,N-di(2-hydroxyethyl)glycine. Since these well known chelating agents are insoluble in the dry cleaning solvent system, except for very small amounts which would tend to dissolve in moisture present, it is necessary that only sufficient agitation or mixing of the insoluble compound and solvent system occur to bring the compound into reactive contact with the polyvalent metal ions present.

In another procedure, polymers of cyclic amides, such as polyvinylpyrrolidone, polyvinylmorpholinone, poly-5-methyl-3-vinyl-2-oxazolidinone and mixtures thereof, are added to the solvent system, with agitation, to form polyvalent metal ion-polymer complexes which are insoluble in the solvent system and which form precipitates removable by filtration.

In an alternative procedure the solvent system may be agitated with a cation exchange resin, or passed through an ion exchange column of such a resin to reduce the polyvalent metal ion concentration by ion exchange.

The following examples describe completely representative specific embodiments of procedures for accomplishing the method of the present invention, i.e. reducing polyvalent metal ion content in a dry cleaning solvent system. These examples, however, are not to be interpreted as limiting the invention other than as defined in the claims.

EXAMPLE 3

In this experiment various compounds and compositions within the scope of the invention were employed as additives to a dirty, i.e. "mature," solvent system. A quantity of 11.4 grams of the additive was added to a 12 liter sample of mature dry cleaning solvent system which had previously been used to dry clean clothing. In each case, a quantity of 21 grams of diatomaceous earth was also introduced to serve as a filter medium. After thorough mixing of the mature solvent system and additive, the mixture was filtered and the residue remaining from evaporation of a 100 ml. portion of the filtrate was analyzed for metal content by emission spectroscopy. Table III, below, indicates the additive employed and the metal content analysis. The control sample run was identical to the test sample runs with the exception that no additive was utilized therein.

TABLE III

Sample	Metals present (p.p.m.) Ca	Mg	Si
Control	2,000	60	50
Sodium salt of N,N-di(2-hydroxyethyl) glycine	520	30	25
Polymer 1[a]	850	32	16
Polymer 2[b]	1,100		42

[a] Polymer of 5-methyl-3-vinyl-2-oxazolidinone.
[b] 50–50 mixture (by weight) of polyvinylpyrrolidone and polyvinylmorpholinone.

EXAMPLE 4

A 55 ml. quantity of a mature solvent obtained from a commercial dry cleaning establishment was agitated for 16 hours with 10 grams of a sulfonated styrene-divinylbenzene cation exchange resin (H^+ form) sold under the trademark Dowex 50 resin (a product of The Dow Chemical Company, Midland, Mich.). The liquid phase was filtered off and analyzed for metals by emission spectroscopy. Table IV, below, shows the percent of various metal ions removed by this treatment based on the amounts of metal ions originally present. Original metal ion content was determined by an analysis of a control sample before treatment with the ion exchange resin.

TABLE IV

Percent removal of metal ions

Cd	40
Cr	20
Cu	28
Zn	40
Ti	16.6
Ca	22
Pb	26
Mg	33
Fe	25
Si	58

I claim:

1. In the method of cleaning textile materials in an organic dry cleaning solvent system in which an organic dry cleaning solvent is contacted with said textile, removed from said textile and the solvent reused, the improvement which consists essentially of the step of reducing the polyvalent metal ion content of the solvent

system by contacting the solvent before reuse as a cleaning agent with a sulfonated styrene-divinyl benzene acid form of a cation exchange resin which is insoluble in said system, said resin being employed in an amount from about 180 grams to about 0.95 gram per liter of solvent to remove at least some of the dissolved metal ions from the solvent, while in contact with said solvent, and returning the so treated solvent for reuse in said dry cleaning system.

2. In the method of cleaning fibrous materials in an organic dry cleaning solvent system in which an organic dry cleaning solvent is contacted with said textile, removed from said textile and the solvent reused, the improvement of reducing the polyvalent metal ion content of the solvent system by treatment of said solvent before reuse with an organic chelating agent to form an insoluble complex with said polyvalent metal ions dissolved in said solvent and removing by filtration the so-formed complex from the solvent system, said agent being employed in an amount from about 180 grams to about 0.95 gram per liter of solvent to remove at least a part of said dissolved metal ions, and returning the so treated solvent for reuse in said dry cleaning system.

3. In the method of dry cleaning fibrous materials in a dry cleaning solvent system which comprises the successive steps of introducing the fibrous material into the solvent system, circulating the solvent through the fibrous material and filtering the solvent for subsequent re-use in cleaning additional fibrous materials, the improvement which comprises the step of reducing the polyvalent metal ion content of said solvent system prior to said re-use by contacting the solvent before reuse and filtering with either a sulfonated styrene divinyl benzene acid form cation exchange resin or an organic metal chelating agent in an amount from about 180 grams to about 0.95 gram per liter of solvent to remove at least a part of the dissolved metal ions from the solvent prior to reuse by exchange from solution with said cation exchange resin or the formation of a solid complex with said chelating agent.

4. In the method of cleaning textile materials in an organic dry cleaning solvent system in which an organic dry cleaning solvent is contacted with said textile, removed from said textile and the solvent reused, the improvement which consists essentially of the step of reducing the polyvalent metal ion content of the solvent system by contacting the solvent before reuse as a cleaning agent with a cation exchange resin which is insoluble in said system, in an amount from about 180 grams to about 0.95 gram per liter of solvent to remove at least some of the dissolved metal ions from the solvent, and returning the so treated solvent for reuse in said dry cleaning system, which cation exchange resin is a sulfonated styrene-divinyl benzene cation exchange resin hydrogen ion form.

5. In the method of cleaning fibrous materials in an organic dry cleaning solvent system in which an organic dry cleaning solvent is contacted with said textile, removed from said textile and the solvent reused, the improvement of reducing the polyvalent metal ion content of the solvent system by treatment of said solvent system with an organic metal chelating agent to form a solid complex with said polyvalent metal ions and removing the so-formed solid complex from the solvent system and returning the so treated solvent for reuse in said dry cleaning system, said chelating agents are employed in amounts of from about 180 grams to about 0.95 gram per liter of solvent and are selected from the group consisting of tetrasodium salt of ethylenediamine tetraacetic acid, trisodium salt of N-hydroxyethylenediaminetriacetic acid, sodium salt of N,N-di(2-hydroxyethyl)glycine, and the polyvinylpyrrolidone, polyvinylmorpholinone, poly-5-methyl-3-vinyl-2-oxazolidinone, and mixtures of the polymers.

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