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DRY CLEANING METHOD AND COMPOSITION

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The present invention relates to a new dry cleaning method and compositions for use therein. More specifically, the present invention is concerned with a method for decreasing the amounts of metallic ion impurities introduced into the solvent systems generally employed in dry cleaning processes.

It has been discovered that the presence of polyvalent metal ions 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. It was found that reduction of the polyvalent metal ion content of a solvent system improved the brightness (as indicated by higher reflectance readings) of fibrous materials cleaned therein.

In the method of the present invention, a protective coating is imparted to those metallic surfaces of a dry cleaning apparatus which come into contact with the solvent system used in the dry cleaning process, advantageously by reaction between a compound dissolved in the solvent system and said metal surfaces whereby a surface coating non-reactive with the solvent system is formed. This protective coating inhibits the introduction of metallic impurities from the metal surfaces to the contacting solvent system and materials cleaned therein show significantly and consistently higher reflectance readings than those obtained when no such protective coating is provided.

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 commonly used solvents and formulated solvents.

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 frequently heaviest 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.) based on the cloth analyzed.

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 expediment 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 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) causes a significant loss of whiteness in the swatches.

In practice of the method of the present invention, metal surfaces of a dry cleaning apparatus which are exposed to the solvent system are contacted with a compound capable of forming a protective metal surface coating which inhibits the previously discussed introduction of metallic impurities into the solvent system. Examples of such compounds, conveniently employed as additives to the solvent system used in the dry cleaning apparatus, include formic acid, acetic acid, propionic acid, butyric acid, dimethyl hydrogen phosphite, diethyl hydrogen phosphite, dipropyl hydrogen phosphite, dibutyl hydrogen phosphite, dimethyl mono acid orthophosphate, diethyl mono acid orthophosphate, dipropyl mono acid orthophosphate, dibutyl mono acid orthophosphate, 4,4'-dithiodimorpholine, 2,2'-dithiobisbenzothiazole and mixtures thereof. A quantity of from about 1 to 50 parts by weight of one or more compounds selected from the above group is added to 1000 parts by weight of a dry cleaning solvent system to furnish a new composition of the present invention. This solvent system, as previously noted, comprises essentially an organic dry cleaning solvent base selected from volatile hydrocarbons and chlorinated hydrocarbons well known to the art. In addition there may be present relatively small amounts of other additives such as soaps or detergents, water, anti-redeposition agents, brighteners, anti-static agents, etc. While these relatively small amounts of additives have no marked effect on the formation of the protective metal coating, 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 a dry cleaning solvent and a minor amount in the range of from about 0.1 to 5.0 weight percent of one or more of the previously listed compounds will therefore usually contain small amounts of one or more detergents, water, and other agents as described above.

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 galvanized metal test coupon, approximately ½" x ½" square, was immersed for several days in a sample of a commercially available, perchloroethylene base, dry cleaning solvent system after addition of 1 part by weight of acetic acid to 1000 parts by weight of the solvent system. The solvent system, widely used in commercial, coin-operated dry cleaning machines, contained small amounts of a petroleum sulfonate base detergent and water. An adherent protective coating, presumably zinc acetate, was formed on the galvanized metal test coupon by this treatment. A control coupon was prepared by the same treatment but omitting the acetic acid addition. The test and control coupons were then agitated for extended periods of time in separate 100 ml. portions of the solvent system described above which also contained swatches of cotton cloth. Table III, below, shows the reflectance readings of such cotton swatches after four, six and seven day periods of agitation in these solvent systems containing either the control or test coupons. The initial reflectance readings of the cotton swatches, before treatment in the solvent system, was 75 units. Reflectance measurements were made on a standard reflectometer.

TABLE III

	Reflectance Readings		
	4 days	6 days	7 days
Control run	67.4	66.6	65.9
Test run	70.6	69.8	70.0

As indicated by the data above, the presence of a protective coating on the galvanized metal coupon in contact with the solvent system inhibited the introduction of polyvalent metal ions into the solvent system. This is shown by the higher reflectance readings of the cotton swatches in the test run as compared to those in the control run.

Example 4

In this experiment a piece of copper wire (5.7 grams) was immersed for 24 hours in 50 mls. of perchloroethylene containing 1 ml. of acetic acid. An identical piece of copper wire was immersed for the same length of time in 50 mls. of perchloroethylene which contained no acetic acid. These two pieces of wire were rinsed with fresh perchloroethylene and placed in perforated polyethylene bags. Each bag was placed in separate portions of the solvent system used in Example 3, above, which also contained 2" x 2" cotton swatches. A control experiment containing no copper wire was also conducted. Table IV, below, shows the reflectance readings of cotton swatches removed from the three portions of solvent system after agitation therein for twelve days.

TABLE IV

Description:	Reflectance readings after 12 days
No Cu wire present	69.8
Untreated Cu wire present	67.8
Treated Cu wire present	69.4

The above data show (1) the adverse effect on brightness of the cloth when copper metal is in contact with the solvent system employed to dry clean cloth, and (2) the inhibition of this adverse effect by treatment of the copper metal to form a protective coating.

Example 5

In the following experiment a series of galvanized metal coupons were immersed in portions of the solvent system described in Example 3, above, which contained 1000 p.p.m. (based on the weight of the solvent system employed) of various additives. These additives provided protective coatings on the coupons. Each coupon was immersed for eleven days in an additive-containing solvent system and then rinsed and dried. Each treated coupon (2" x ½" x 1/16") was then agitated for five days in 100 mls. of fresh solvent system containing 2" x 2" cotton swatches. Control experiments employing (1) an untreated coupon and (2) a coupon immersed for eleven days in perchloroethylene containing no additive, were also run. Table V, below, shows the reflectance readings of cotton swatches after five days' agitation in the described solvent system.

TABLE V

Description	-additive	Reflectance Readings
Untreated coupon	(1) control	68.4
Do	(2) control	68.4
Treated coupon	-dimethyl mono acid orthophosphate.	71.5
Do	-dibutyl mono acid orthophosphate.	69.6
Do	-diethyl hydrogen phosphite	69.7
Do	-4,4'-dithiodimorpholine	69.4
Do	-2,2'-dithiobisbenzothiazole	69.4

In each case, above, treatment of the galvanized metal coupon with the indicated additive produced a protective metal coating. The uniform and consistent improvement in reflectance readings of cotton swatches agitated in solvent systems exposed to such coated metals as compared to use of non-coated metals demonstrates the value of such treatment of metal surfaces exposed, in a dry cleaning apparatus, to the solvent system. In the preceding experiments (Examples 3, 4 and 5) glass containers were employed to hold the solvent systems.

In the manner of Example 5, above, treatment of metal surfaces exposed to a solvent system in dry cleaning operations with formic acid, propionic acid, butyric acid, dimethyl hydrogen phosphite, dipropyl hydrogen phosphite, dibutyl hydrogen phosphite, diethyl mono acid orthophosphate, or dipropyl mono acid orthophosphate produces similarly advantageous results, i.e., a protective coating is formed on such exposed metal surfaces which decreases polyvalent metal ion content of the contacting solvent system by inhibiting the introduction of metal species into the solvent system. In each case the improvement in the brightness of clothes cleaned in a solvent system which is in contact with metal surfaces containing a protective coating as previously described in significant and consistent.

I claim:

1. In a method for cleaning textile materials with an organic dry cleaning fluid employing a metallic apparatus for containing the said fluid and the textile, the improvement for increasing the brightness of the textile which comprises maintaining in contact with the surfaces of the metallic apparatus a solution of from 0.1 to about 5.0% by weight of at least one member selected from the group consisting of formic acid, acetic acid, propionic acid, butyric acid, 4,4'-dithiodimorpholine, 2,2'-dithiobisbenzothiazole and mixtures thereof, in a dry cleaning solvent.

2. An improved dry cleaning solvent composition which consists essentially of a major amount of a dry cleaning solvent and a minor amount in the range from about 0.1 to 5 weight percent of 4,4'-dithiodimorpholine.

3. An improved dry cleaning solvent composition which consists essentially of a major amount of a dry cleaning solvent and a minor amount in the range from about 0.1 to 5 weight percent of 2,2'-dithiobisbenzothiazole.

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