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3,163,493

**PROCESS FOR DISINFECTING DRY CLEANING IN CONVENTIONAL SOLVENTS**

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No Drawing. Filed Dec. 20, 1961, Ser. No. 160,956

Claims priority, application Germany Dec. 23, 1960

3 Claims. (Cl. 8—142)

This invention is concerned with disinfecting by cleaning.

It is known from the work carried out by Chassevant, Farrel and Howles, Ruepp, Virgin, Gabbano, Rimpau, Vierthaler and others that aqueous solvents which are used for dry cleaning purposes, such as light benzine, carbon tetrachloride, trichlorethylene, tetrachlorethylene (perchlorethylene) do not have a disinfecting action. From experiments carried out by Rimpau, on the other hand, it is known that emulsions of trichlorethylene produced by shaking and which are free of emulsifiers and which contain 1% of water show a good disinfecting action against numerous bacteria. Such emulsions are not suitable for dry cleaning.

It is also known from Rimpau and Vierthaler, that emulsions of water in carbon tetrachloride, trichlorethylene and perchlorethylene, which have been stabilised by Turkey red oil, Nekal or the products marked commercially under the trade names of "Products Re 1077" or "Re 297," which are probably quaternary bases, likewise have a good disinfecting action against numerous bacteria. Emulsions of water in solvents, i.e., in solvents with microscopically or macroscopically visible water droplets, are known to be unsuitable for dry cleaning.

A disinfecting dry cleaning process has also been proposed according to which bactericidal and activating agents are added to the solvents, products such as pyridine or methylene chloride and fatty acid glycol esters and aliphatic and aromatic sulphonates of relatively high molecular weight being suitable as activating agents. Formaldehyde is used in particular as a disinfecting agent.

Processes for the disinfecting dry cleaning of textiles, using formaldehyde as disinfecting constituent, are known. Rimpau recommended using 1% formaldehyde as formalin and 1% potassium soap or a mixture of 1% formaldehyde, likewise in the form of formalin, with 1% Turkey red oil, as a disinfecting additive to trichlorethylene. According to the information given by Rimpau, the said mixtures, together with trichlorethylene, form emulsions with the aqueous formaldehyde solution as dispersed phase.

A disinfecting dry cleaning with heavy benzine to which an emulsion of formaldehyde, water and a cation-active compound (Arquad 2 HT) in heavy benzine was added has been proposed by Finch. In this case also, the aqueous formaldehyde solution is present as a milky dispersed phase. It has also been proposed to carry out a disinfecting dry cleaning with formaldehyde, but in the presence of cleaning intensifiers with good water retention. In these processes, formaldehyde as formalin is added to a solution of 35 to 40% formaldehyde, 5 to 10% methanol and 60 to 50% water. The formalin composition fluctuates according to the literature references within the limits indicated, with the proviso that, in winter, the quantity of the methanol necessary for stabilisation would have to be increased.

Experiments carried out by the applicant have shown that the use of formaldehyde and formalin or other basic formaldehyde solutions is largely disadvantageous in dry cleaning and does not offer any guarantee of a reliable disinfecting effect. Literature references show that until

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now no satisfactory disinfecting dry cleaning process has been discovered.

It is known that the quantity of formaldehyde necessary for an effective disinfection is substantially determined by the following factors:

- (1) The nature of the most resistant bacteria,
- (2) The way in which the bacteria are fixed to the fibres, for example whether only loosely adsorbed like dust or firmly adhering by means of pus, faeces, sputum and the like,
- (3) The cleaning process, particularly as regards solvents, cleaning time, cleaning temperature, drying temperature and mechanical handling,
- (4) The nature of the textiles and therewith the maximum permissible relative water content of the solvent,
- (5) The nature of the cleaning intensifier or of the aqueous equilibrium between textile and liquor which results therefrom.

The necessary formaldehyde content must be relatively high when the following factors are present together:

- (1) Resistant bacteria,
- (2) Those bacteria which are embedded in pus, sputum and the like,
- (3) Heavy benzine, which has no disinfecting action, is present as solvent and a short cleaning time a low cleaning temperature and a low drying temperature, for example by drying with cold air, are used and only little mechanical action is used, for example by using rotating drums of small diameter,
- (4) The material to be cleaned, consisting for example of loose hospital blankets, which are only capable of limited cleaning and consequently only stand a relative solvent humidity of 60 to 65%,
- (5) Cleaning intensifiers with a moderate or poor water equilibrium between textile and bath liquid are used.

Conversely, the formaldehyde content can be relatively low when the following factors are present:

- (1) Bacteria which have low resistance,
- (2) Those bacteria which are present are only on the textiles as dust and are not fixed thereto,
- (3) With perchlorethylene, which as a considerable disinfecting action, as solvent, long cleaning times, high drying temperatures, strong mechanical action, for example in machines having drums which comprise driving ribs, have a large diameter and thus produce a considerable fall of the textiles, and a quick change in direction of rotation,
- (4) Textile materials consisting of cotton, polyesters and the like which are capable of unlimited cleaning, even with 80 to 90% relative solvent humidity, are being treated,
- (5) Cleaning intensifiers with very good water equilibrium between textile and bath liquid are used.

All intermediate stages exist in practice between the two extremes which have been described. If cleaning times of more than 30 minutes, relatively high cleaning temperatures of 40° C., old cleaning machines and poor cleaning intensifiers are excluded, the necessary formaldehyde concentrations in the bath liquid still fluctuate between 0.05 and 0.2%.

If formalin is used, then approximately the same quantity of water is positively introduced into the bath liquid. Even an addition of 2% of a good cleaning intensifier (20 g. per litre) to the solvent is not suitable for so combining this quantity of water that it remains in the liquid and does not harm sensitive textiles.

Even when using formalin in the presence of 10 g. of cleaning intensifier per litre of perchlorethylene, a disinfecting dry cleaning cannot be carried out if a 75–85%

relative humidity is not present. For woollen blankets capable of limited cleaning, which can be treated in modern dry cleaning machines with a relative solvent humidity of at most 65-70%, it has not consequently been possible hitherto to carry out a disinfecting dry cleaning with formalin.

It has now been found that also sensitive textiles capable of limited cleaning can be cleaned with formaldehyde cleaning intensifiers and possibly small quantities of water in organic solvents if cleaning intensifiers are used which have the highest possible water retention, in addition the highest possible quantity of water is used, shrinking, matting, or other damage to the textiles being avoided and finally the formaldehyde is added in the form of a solution which is free from or has a low content of water and in such a quantity that all pathogenic germs are killed while carrying out the cleaning process.

Cleaning intensifiers which are suitable according to the invention and have a high water retention are for example anion-active, non-ionic or cation-active products which are completely soluble at 20-30° C. in solvents but are only soluble with an opal to cloudy appearance in water. There are also to be considered however those products which are completely soluble in both solvents and water, as well as products from the class comprising the ampholytes and combinations or products of the said classes. Products which conform to these requirements are for example alkali metal, ammonium or amine salts of sulphonic acids, for example sodium petroleum sulphonates (molecular weight about 380 to 480), sodium dioctyl sulphosuccinate, other diesters of sodium- or potassium-sulphosuccinic acid with a molecular weight of about 400 to 550, alkali metal or ammonium salts of compounds of the type of the so-called Twitchell reagent which decompose fats, salts of aromatic alkyl sulphonic acids, more especially alkyl benzene sulphonic acids, with a molecular weight of at least 380, for example the methoxypropylamine salt of dodecyl-benzene sulphonic acid. Salts of sulphated products can also be used if provision is made, by providing sufficient quantities of suitable buffering agents, so that when the splitting of sulphuric acid, occurs, for example upon distillation mineral acid reaction does not result. Other anion-active products which are suitable are acid alkali or ammonium soaps, more especially of oleic acid, the amine soaps of methoxypropylamine, cyclohexylamine, morpholine and the like. Non-ionic products which have a suitable solubility are for example condensates of, on the one hand, 1 mol each of octylphenol, nonylphenol, coconut fatty alcohol, oleyl alcohol, oleic acid amide, oleic acid, a fatty acid partial ester of glycerine, sorbitol, mannitol and the like and on the other hand 2 to about 10 mols each of ethylene oxide or propylene oxide. Suitable cation-active products have for example molecular weights of at least 380 per basic nitrogen atom, for example diisobutyl-phenoxyethoxyethyl-benzyl-dimethyl ammonium chloride, oleyl-amidopropyl-dimethyl ammonium chloride, oleyl-amidopropyl-trimethylammonium methosulphate, octadecyl-oxethyl-dioxethyl ammonium acetate, tetradecyl-(4,5-dichlorobenzyl)-dimethyl ammonium chloride, didodecyl-dimethyl ammonium bromide. Also suitable are ampholytes such as aminocarboxylic acids with a molecular weight of at least 320, which are obtained by condensation of corresponding primary or secondary amines with chloracetic acid.

Products of the classes of substances as hereinbefore mentioned can also be mixed with other detergents which per se are not suitable, if the mixtures have the required solubility, i.e., hydrophilicity and lyophilicity. For example, a sodium dodecyl benzene sulphonate with a molecular weight of 340, which is practically insoluble in perchlorethylene, can be processed together with a sodium petroleum sulphonate having a molecular weight of 460, it being possible to obtain numerous variations which are soluble in perchlorethylene and have an average molecu-

lar weight of at least 380. Similar combinations are possible with detergents which are insoluble in benzene and chlorinated hydrocarbons, for example with alkali metal soaps, alkali salts or ammonium salts of fatty alcohol sulphates, sulphated oils, fatty acid condensation products, aliphatic sulphonic acids and the like; moreover, non-ionic, cation-active or ampholytic detergents which are insoluble in solvents can also be used for the mixtures under the conditions mentioned.

Mixtures of the products of the aforesaid classes of substances with those from the same or other classes are to be recommended when the essential properties which a cleaning intensifier must have are present and only one or a few properties are not sufficient. For example, two substances, one of which is more hydrophilic and the other more lyophilic, usually give a mixture which has the correct solubility and water retention. Furthermore, mixtures with solution promoters, more especially with alcohols such as ethanol, propanol, butanol, benzyl alcohol, cyclohexanol, oleyl alcohol and the like are often to be recommended in order to improve component properties, but it is to be noted in such cases that such additives very often cause the bleeding of the colours of the textiles during the cleaning. By mixing stoichiometric or sub-stoichiometric quantities of anion-active and cation-active products, it is practically always possible to obtain mixtures which conform to the solubility conditions of Martin and Fulton (Dry Cleaning Technology and Theory, New York, 1958, pages 1953/154) for cleaning intensifiers. It is known that a reaction takes place after the mixing, and salts with large anions and large cations are formed, which are practically always soluble in hydrophobic solvents and sparingly soluble in water. They are usually suitable for taking up other hydrophilic detergents, so that the necessary water retention can easily be established.

Cleaning intensifiers which are preferred according to the invention are those of homogenous components or of several components, the active substance of which is able completely to dissolve half the quantity and at best the same quantity of water in the dry cleaning solvents, and which in addition have a good water retention, which is not to be below 5%, calculated on active substance, and with 80% relative humidity.

Organic solvents for the formaldehyde which are in particular to be mentioned include those which are of unlimited solubility in both the dry cleaning solvents, more especially perchlorethylene, trichlorethylene, carbon tetrachloride, heavy benzene and light benzene, and in water, especially when the formaldehyde solvents contain a small quantity of water, for example up to 5%, and when they have a good dissolving power for formaldehyde. This condition is satisfied by iso-propanol and n-propanol. However, there are other solvents which are suitable, even if with a smaller degree of success or under more difficult conditions. Such solvents are dimethyl formamide, isobutanol and secondary butanol, but possibly also ethanol, n-butanol and butyl glycol.

The solutions of formaldehyde in the said solvents can be prepared by introducing formaldehyde gas into the solvents, preferably until saturation is reached. If the solvents are resistant to alkalis, paraformaldehyde in the solvents can also be depolymerised by the action of a small quantity of caustic alkali solution, the monomeric formaldehyde which is formed remaining in solution.

In order that the invention may be further understood, the following examples are given, by way of illustration only:

#### EXAMPLE 1

An approximately 30% solution of formaldehyde in isopropanol is prepared by stirring 30 parts of paraformaldehyde, 70 parts of isopropanol and 0.5 part of 50% caustic potash solution at 45° C. until a clear solu-

tion has formed. After about 30 minutes, the depolymerisation is completed, whereupon neutralisation is effected with approximately 0.5 part of concentrated hydrochloric acid. The potassium chloride formed as secondary product settles on the bottom as a deposit, so that now the approximately 30% solution of formaldehyde in isopropanol which contains about 0.6% of water, can be decanted off.

#### EXAMPLE 2

Formaldehyde gas is introduced into n-propanol at 20° C., while cooling with water, until no more gas is absorbed and there is then obtained a substantially 28% solution.

#### EXAMPLE 3

6 batches, each comprising 5 kg. of loose hospital blankets, which are only capable of limited cleaning, are cleaned in a Bowe RS machine. The specifications of the machine are:

|                            |                 |      |
|----------------------------|-----------------|------|
| Drum diameter              | mm              | 815  |
| Drum depth                 | mm              | 335  |
| Washing speed              | r.p.m.          | 34   |
| Centrifuging speed         | r.p.m.          | 480  |
| 3 ribs in the drum.        |                 |      |
| Liquid in the washing drum | litres          | 74   |
| Liquid in the filter       | do              | 54   |
| Liquid circulation about   | litres per hour | 3000 |

Arranged on the upper part of the housing of the machine is a union, to which is connected a pipe conduit leading to atmosphere. A fan draws the vapours from the drum housing and forces them through the pipe into the atmosphere. The switch of the fan is operated manually if required. Disposed opposite the union is an adjustable valve, through which air can be drawn. With the valve closed, the air can be drawn in through the filling opening of the machine. The machine is also equipped with an automatic water-proportioning instrument, more especially a Tempo-Aquamatic DGS 3, which is adjusted to 65% relative humidity and is not changed during the 6 batches.

#### EXAMPLE 4

The same working method as in Example 3 is used in other closed machines, for example in a Bowe R15SK or R25SK or R50SK or in a Spencer Junior S20, Major S30 or Senior S50, or in a Hoffmann HS12 or HS22 or HS35 or HS50, or in any suitable closed dry cleaning machine. The same results are obtained.

#### EXAMPLE 5

The same working methods as in Example 3 or 4 are used, employing other cleaning intensifiers with good water retention. By way of example, there is used an intensifier which consists of

- 40 to 60 parts of petroleum sulphonate (sodium or potassium salts; molecular weight 420 to 480),
- 59 to 36 parts of mineral oil,
- 1 to 4 parts of water and small quantities of inorganic salts.

Another good cleaning intensifier consists of:

- 50 parts of sodium dioctyl sulposuccinate,
- 15 parts of cyclohexanol, and
- 35 parts of spindle oil.

Another typical cleaning intensifier contains:

- 50 parts of active substance, consisting of nonyl phenoxy pentaethoxy ethanol and cyclohexylamine dodecyl benzyl sulphonate,
- 25 parts of spindle oil,
- 15 parts of perchlorethylene,
- 10 parts of water.

Another suitable cleaning intensifier consists of:

- 55 parts of coconut fatty acid diethanolamide,
- 5 parts of diethanolamine dodecyl benzene sulphonate,
- 40 parts of perchlorethylene or white spirit.

The same results as in Examples 3 and 4 were obtained.

#### EXAMPLE 6

The same working methods as in Examples 3, 4 or 5 are used, employing carbon tetrachloride or trichlorethylene or trichlorotrifluoroethane or benzene or white spirit as solvent, and the same results are obtained.

##### 1st Batch

The machine is initially supplied with a bath liquid of 120 litres of perchlorethylene, each litre of perchlorethylene having added thereto 10 g. of a cleaning intensifier containing 50% of active substance and 3 ml. of a 40% formaldehyde solution in isopropanol, as obtained according to Example 1. The cleaning intensifier contains

- 30% of sodium petroleum sulphonate (molecular weight 460)
- 15% of sodium dodecyl benzene sulphonate (molecular weight 348)
- 5% of nonyl phenoxy-pentaethoxy ethanol
- 10% of mineral oil (about 4° Engler/50° C.; by-product of the mahogany sulphonate)
- 5% of isopropanol
- 33% of perchlorethylene
- 2% of water, including small amounts of inorganic salts as by-products

The water retention of a solution of 40 g. of the cleaning intensifier in 1 litre of perchlorethylene with respect to wool at 20° C. and 80% relative humidity is 4.0 g., that is to say 20% of the active substance.

Using this bath liquor, the 5 kg. of woolen blankets are now cleaned in the usual manner, after previously depositing kieselguhr on the filter. During the loading of the drum, a stream of air is drawn in through the filling opening by the fan, so that vapours cannot to an appreciable extent pass from the machine into the working chamber.

A strip on which are sewn various pockets containing rags with test bacteria is introduced into the machine together with the woolen blankets. The test bacteria consist of Staphylococci, Coli O 111, Prodigiosus and Soor. It is cleaned for 15 minutes at 65% relative humidity and 25° C. over filters, for 1 minute with the drum rotating, 8 minutes with the drum stationary and finally for another 6 minutes with the drum rotating. The blankets are now centrifuged for 2 minutes and simultaneously the liquid is pumped off. With air suction, the strip with the pockets and test germs is removed from the drum. Drying is then carried out for 15 minutes with hot air in circulation and with interposed spray nozzle coolers and blown for 5 minutes with fresh air.

For the purpose of excluding an after-effect of the formaldehyde liquor, the rags with the test germs are rinsed twice with petroleum ether in known manner, dries in vacuo and subjected to subsequent culture. All germs are killed. The blankets treated in this way are clean, fluffy to handle, have not shrunk and are not matted.

##### 2nd to 6th Batches

Before starting each following batch, the concentration of the cleaning intensifier and formaldehyde is determined and the quantities which are short are made up. The replenishing of the water is left to the automatic mechanism.

It was found that the additives with each batch remain approximately the same. 1 g. of cleaning intensifier and 0.8 ml. of isopropanolic formaldehyde solution according to Example 1 are required as supplement for each 75 litre of bath liquid. The checking of the disinfecting ac-

tion shows that all germs are killed with all batches. The concentration of the formaldehyde at the end of each batch should be approximately 0.4 g. per litre of bath liquid. The cleaning and the feel of all blankets with all batches is equally as good as that of the first batch.

What is claimed is:

1. A process for simultaneously disinfecting and dry cleaning soiled textile articles which comprises applying to said articles a cleaning and disinfecting substantially single phase medium comprising a dry cleaning solvent, a cleaning intensifier, substantially soluble in said dry cleaning solvent and soluble in water, having a water retention capability of at least 5% referred to said intensifier at 80% relative humidity, water in an amount sufficient to produce a 60-90% relative dry cleaning solvent humidity and a solution of formaldehyde in an organic solvent selected from the group consisting of isopropanol, n-propanol, dimethylformamide, isobutanol, secondary butanol, ethanol, n-butanol, and butyl glycol, said formaldehyde being present in a concentration effective for disinfecting, intimately contacting said articles with said cleaning and disinfecting medium whereby said articles

are cleaned and all pathogenic organisms destroyed without the textile article being in any way deleteriously affected.

2. Process according to claim 2 wherein a 65-85% relative dry cleaning solvent humidity is present.

3. Process according to claim 2 wherein said formaldehyde solution is a substantially saturated solution of formaldehyde and isopropanol and said intensifier is a member selected from the group consisting of anion active, cation active, and non-ionic products, and mixtures thereof.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

|           |         |               |
|-----------|---------|---------------|
| 879,375   | Ellis   | Feb. 18, 1908 |
| 1,911,289 | Reddish | May 30, 1933  |
| 2,348,795 | Endres  | May 16, 1944  |
| 2,967,084 | Reitz   | Jan. 3, 1961  |

##### FOREIGN PATENTS

|         |               |               |
|---------|---------------|---------------|
| 14,202  | Great Britain | June 27, 1898 |
| 745,195 | Great Britain | Feb. 22, 1956 |

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,163,493

December 29, 1964

Richard Hess

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 41, after "only" insert -- present --;  
column 4, line 3, for "and chlorinated" read -- or chlorinated --;  
column 7, line 11, after "substantially" insert -- and completely --;  
column 8, lines 4 and 6, for the claim reference numeral "2", each occurrence, read -- 1 --.

Signed and sealed this 18th day of May 1965.

(SEAL)

Attest:

ERNEST W. SWIDER  
Attesting Officer

EDWARD J. BRENNER  
Commissioner of Patents