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3,042,479
CHLOROFLUOROHYDROCARBONS IN DRY
CLEANING COMPOSITIONS AND PROCESS
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This invention relates to a new and improved process for dry-cleaning textile fibers and other garment materials. The invention relates more particularly to the use of halogenated hydrocarbons containing not more than two carbon atoms and at least one fluorine atom per carbon 15 atom in the molecule.

7 Claims. (Cl. 8-142)

Today the common solvents used in the dry-cleaning of textiles and garment materials include such solvents as Stoddard solvent, perchloroethylene, trichloroethylene and carbon tetrachloride. These solvents present various 20 difficulties. For example, carbon tetrachloride because of its high toxicity presents definite health hazards unless used under the most rigid conditions, while cleaning fluids of the Stoddard solvent type are flammable and because of the high boiling range are difficult to remove from the 25 fabrics even with the use of heat. While the perchloroethylene and trichloroethylene being much less toxic than the carbon tetrachloride are still somewhat toxic, they are difficult to remove from the garments, particularly without application of heat, and have deleterious effects on 30 certain plastics and cements used on jewelry ornaments. The application of heat in removing soil from garments presents the problem of setting stains which are subsequently very difficult to remove, and also tends to set wrinkles in the garments which can only be removed by 35 subsequent finishing operations.

These defficiencies of existing dry-cleaning fluids become more pronounced in the newly developed coinoperated dry-cleaning machines, which are not under constant supervision of trained dry-cleaning personnel. Be- 40 cause of the toxicity of the solvents involved, care must be taken in designing the equipment and the installation so that the release of fumes and accumulation of such fumes be avoided. In addition, because of the relatively low volatility of the solvents employed, heat must 45 be applied in the machine to drive the solvent from the clothes, and this drying period requires a substantial amount of time. In addition, heating the garments tends to set stains and also promotes wrinkling of the fabrics. Existing equipment involves a cycle in which the soils 50 are removed from the solvents by constant filtration using filter aids, since distillation with the less volatile of the non-toxic materials involves high temperature heat sources not normally available in these installations.

It is an object of the present invention to provide a 55 of 1,1,2-trichloro-1,2,2-t process for dry-cleaning textile fibers and other garment materials in which a dry-cleaning liquid composition is employed which is non-flammable, which can be readily removed from the garments at normal atmospheric temperatures, and which has an exceptionally low order of toxicity. A more specific object of the invention is to provide a process for dry-cleaning particularly applicable to coin-operated dry-cleaning machines in which a compound of the group consisting of trichlorotrifluoroethanes and trichloromonofluoromethane are used as the principal 65 of 1,1,2-trichloro-1,2,2-to then operated for a 5 high speed extraction additional fresh 65 por carbon for a full rinse of is then followed by high forced air at room tempoperating cycle time is.

The clothes removed free of oil and grease spead trichloromonofluoromethane are used as the principal 65 are dry and wrinkle-free.

It has now been found that the textile fibers and other garment materials may be dry-cleaned in conventional dry-cleaning equipment by employing a halogenated hydrocarbon containing at least one fluorine atom per carbon atom in the molecule as the dry-cleaning liquid, which because of their relatively low boiling points and high

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vapor pressures may be readily removed from the articles being cleaned in a relatively short time without the application of heat, and when required, because of additional savings in cost, can be readily recovered and re-used.

These halogenated hydrocarbons containing at least one fluorine atom are considered to be relatively mild solvents, yet it has been found that they have surprisingly good and rapid cleaning effectiveness when used in drycleaning and have the ability to prevent significant redeposition of soils in the fabric being cleaned. Furthermore, these particular solvents have a substantially reduced tendency to attack plastic buttons and ornaments normally found on garments, and generally do not attack cements which are used in the fabrication of ornaments. Furthermore, it has been found that these solvents have a reduced tendency to bleed colors out of garments, which is quite pronounced with many dry-cleaning solvents particularly on certain types of synthetic fabrics such as acetate, and therefore does not require the close temperature control of the solvent or careful separation of different colored garments in the wash load.

The class of halogenated hydrocarbons employed in the present invention may be exemplified by the following: the trichlorotrifluoroethanes, trichlorofluoromethane, dichlorofluoromethane, 1,1,2-trichloro-2,2-difluoroethane, and 1,2-dichloro-1,1-difluoroethane, the first two being preferred.

These solvents may be used alone or in admixture with each other or with up to about 2% by weight, based on the weight of the solvents, of the usual dry-cleaning emulsifying agents of the non-ionic, cationic and anionic classes, of which the following are examples, isooctylphenyl polyethylene glycols where the number of ethylene glycol units is from 2 to 12; tetrakis-2-hydroxypropylethylenediamine ester of oleic acid quaternized with dimethyl sulfate; and amine salts of dodecyl benzene sulfonic acid. In each case, the solvent comprises a chlorofluorohydrocarbon having a boiling point of from 8° to 75° C., a freezing point below 0° C., and contains not more than 2 carbon atoms and at least one fluorine atom per carbon atom in the molecule.

It is also understood that a small amount of moisture may be present in the dry-cleaning fluid in the same manner as it is employed in the dry-cleaning processes of the prior art. The amount of water should ordinarily not exceed about 1%, based on the weight of the solvent.

Representative examples illustrating the present invention follow. In these examples, a typical automatic front-loading washer-dryer combination was used.

### Example 1

Into a washer-dryer as heretofore described was placed 7 pounds of a wide variety of soiled garments of different textiles and the washer-tub then loaded with 65 pounds of 1,1,2-trichloro-1,2,2-trifluoroethane. The washer was then operated for a 5 minute wash cycle, followed by high speed extraction and subsequent rinsing with an additional fresh 65 pounds of said halogenated hydrocarbon for a full rinse cycle of 1 minute; this rinse cycle is then followed by high speed extraction and drying with forced air at room temperature for 5 minutes. The total operating cycle time is approximately 12 to 13 minutes.

The clothes removed from the washer are essentially free of oil and grease spots, insoluble soil, and the clothes are dry and wrinkle-free

### Example 2

The procedure of Example 1 was repeated with the modification of adding, during the initial loading of the halogenated hydrocarbon, a detergent composition in concentrate form, said detergent composition consisting of about 1 pound of said halogenated hydrocarbon, from

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0% to 2% of an amine salt of dodecyl benzene sulfonic acid as emulsifying agent; and from 0 to 1% water, the percent of said agent and water being based on the total amount of said halogenated hydrocarbon. In addition to the results achieved in Example 1, food spots and water-soluble spots, for example, were also removed. A typical and important example of the latter is a stain resulting from perspiration.

What is claimed is:

1. A process for dry-cleaning textile fibers and other garment materials which comprises washing said material with a dry-cleaning liquid composition comprising a chlorofluoro hydrocarbon having a boiling point from 8° to 75° C., a freezing point below 0° C., and containing not more than 2 carbon atoms and at least 1 fluorine atom per carbon atom in the molecule.

2. The process of claim 1 in which the chlorofluoro hydrocarbon is of the class consisting of trichlorotrifluoro-

ethanes and trichlorofluoromethane.

3. The process of claim 1 in which the chlorofluoro hydrocarbon is 1,1,2-trichloro-1,2,2-trifluoroethane.

4. A cleaning composition consisting essentially of a chlorofluorohydrocarbon solvent containing up to about 2% by weight of an emulsifying agent of the group consisting of non-ionic, cationic and anionic emulsifying 25

agents, said solvent being of the class consisting of a single chlorofluorohydrocarbon and a mixture of chlorofluorohydrocarbons; said solvent comprising a chlorofluorohydrocarbon having a boiling point of from 8° to 75° C. and a freezing point below 0° C.; each of said chlorofluorohydrocarbons present in the solvent containing not more than 2 carbon atoms and at least one fluorine atom per carbon atom.

5. A cleaning composition consisting essentially of 1,1,2-trichloro-1,2,2-trifluoroethane containing up to 2%

by weight of a non-ionic emulsifying agent.

6. A cleaning composition consisting essentially of 1,1,2-trichloro-1,2,2-trifluoroethane containing up to 2% by weight of a cationic emplisiving agent

by weight of a cationic emulsifying agent.

7. A cleaning composition consisting essentially of 1,1,2-trichloro-1,2,2-trifluoroethane containing up to 2% by weight of an anionic emulsifying agent.

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# Disclaimer

3,042,479.—Augustine Hicks Lawrence, Jr., and John H. Dowling, Wilmington, Del. Chlorofluorohydrocarbons in Dry Cleaning Compositions and Process. Patent dated July 3, 1962. Disclaimer filed July 19, 1962, by the assignee, E. I. du Pont de Nemours and Company.

Hereby enters this disclaimer as to claims 1, 2, and 4 of said patent. [Official Gazette August 28, 1962.]