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TREATMENT OF CELLULOSIC FABRICS

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ABSTRACT OF THE DISCLOSURE

Oil composition for treatment of dusting cloths and "walk-off" mats which contains in addition to paraffinic mineral oil, an ammonia phosphorus pentoxide complex as flame retardant, and selected surfactants to emulsify the oil composition in water. The oil composition is exhausted from the aqueous emulsion onto the fabric together with the flameproofing agent, rendering the fabric flameproof. The emulsifying agent includes a non-ionic component in the form of an alkyl phenoxy polyethoxyethanol and a cationic component such as dicocodimethyl ammonium chloride. The formulation may also include hexylene glycol as a penetrant and orthophenyl phenol, which latter serves as a sanitizing agent and also assists in the emulsification.

BACKGROUND OF THE INVENTION

The present invention relates to dust-allaying and dust-wiping compositions and to the treatment of cellulosic fabrics with such compositions for use as mats, rugs, mops, wiping cloths and the like, to render the same flame-retardant.

Oil-treated or impregnated fabrics are extensively used in wiping furniture, floors, walls and other solid surfaces to remove dust and other superficial deposits therefrom. Such impregnated fabrics are most favored which are relatively dry in appearance, which do not smear the wiper surface or leave an oily dust-catching film thereon, and which are capable of picking up dust particles and retaining the same in the cloth by static attraction and adherence.

More recently there have come into rapidly expanding use oil-impregnated cotton mats and rugs, called "walk-off" mats, employed for the purpose of wiping the bottoms of shoes of the wearer before entering into certain areas. In most instances, the oils employed for impregnating these walk-off mats as well as those utilized in wiping cloths and mops are flammable and present a fire hazard in storage or use, as a result of careless contact with a lighted match or cigarette and in some instances fires have been started therein by spontaneous combustion.

Among the objects of the present invention accordingly, are to provide improved oil impregnating compositions for such cellulosic fabrics which overcome or greatly reduce the hazards of flammability yet retain the desirable dust pick-up properties.

In attempting to achieve the desired objects of the present invention extensive experiments and tests were carried out by adding various known flameproofing compounds and mixtures to mineral oils and to previously used preparations adopted for impregnation of wiping cloths. These did not prove satisfactory for the desired treatment for one or more reasons encountered, including among these: incompatibility of the oil and flame retardant, stratification and nonuniformity in deposition on the fabric, loss of dust pick-up properties, failure to pass flame test, or tendering of the fabric structure or the latex backing. As explained in a copending application of the present inventor (Ser. No. 217,548, filed Aug. 17, 1962, now U.S. Patent No. 3,200,036) it is highly advantageous to impregnate fabrics with oil composition by

self-exhaustion or plating from aqueous emulsion. In numerous attempts to apply this desired technique to oil compositions containing various types of flameproofing compounds, only selective deposition of the oil was obtained without accompanying deposition of the flameproofing material in adequate amount or in proper association with the fabric to render the same flameproof.

A further object of the present invention, accordingly, is the provision of an oil composition containing a flameproofing material which can be emulsified in aqueous media and which can be exhausted onto fabric treated therewith to render the oiled fabric flameproof.

In accordance with the present invention the stated objectives are achieved by suitably admixing with a (1) paraffinic oil having a flash point above 350° F. and a fire-point above 400° F., (2) emulsifying and wetting components comprising a selected cationic surfactant and a non-ionic surface-active agent which is sufficiently soluble in light lubricating oils, and (3) a flame retarding agent including an ammonia-phosphorus pentoxide complex having a nitrogen-phosphorus ratio of about 4 to 3 and which is regarded as ammonium hexaphosphate dinitride—$(NH_4)_6P_6N_2O_{15}$—in suitable concentration. Although the said flame proofing compound is highly soluble in water and practically insoluble in mineral oil and in typical organic solvents, it has been surprisingly found that when associated in the emulsion in the manner hereinafter described, the indicated ammonia-phosphorus pentoxide complex is nevertheless retained in the oil phase and deposits in—or as a film or coating over—the oil film impregnating the fabric. The preferred compositions which proved fully successful, as will hereinafter appear, also included orthophenyl phenol and hexylene glycol

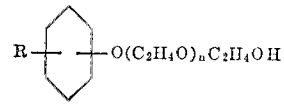
The mineral oil employed must be one that is not too readily volatile and one that has a sufficiently high flash point—above 350° F. While no satisfactory explanation therefor appears, the successful practice of the invention has only been accomplished with paraffinic oils. When using naphthenic oils the treated mats or rugs had a tendency to curl, apparently because of attack on the latex backing, when sufficient flameproofing material was included in the impregnating composition. Thus, commercially available paraffinic oils of the following ranges of properties and characteristics may be used with acceptable results:

	1	2	3
S.G. at 60° F.	0.8639	0.8724	0.8762
Viscosity, SUS at 100° F.	113	213	312
Viscosity, SUS at 210° F.	40	47	53
Flash point, ° F.	380	415	435
Fire point, ° F.	425	470	495
Pour point, ° F.	0	0	0
Aniline point, ° F.	214	224	232
Refractive Index	1.4740	1.4784	1.4801
Visc-gravity constant	0.812	0.817	0.806
Aromatic carbon atoms, percent	2	3	2
Naphthenic carbon atoms, percent	33	33	32
Paraffinic carbon atoms, percent	65	64	66

From overall considerations preference is had for the "heavier," more viscous, oils within the general ranges indicated above, such as those having a viscosity (SUS @ 100° F.) between about 300 and 350 seconds, one readily available example of which is more fully characterized in column 3 of the above table.

The emulsifying and wetting components of the formulation comprise as the cationic surfactant a tetra alkyl ammonium chloride having 10 to 18 carbon atoms in one or more of the alkyl chains and having a total carbon content of 20 to 40 carbon atoms. The non-ionic surfactant is an alkyl phenoxy polyethoxy ethanol (condensa-

tion product of an alkyl phenol with ethylene oxide) or a mixture of these of the general formula



wherein R is an alkyl group of 6 to 12 carbon atoms and *n* is 10 to 12. The preferred non-ionic compounds are those of the above formula having a formula weight of 750±25 (i.e. formula weight 725 to 775) in which the long chain alkyl group contains 8 to 9 carbon atoms. Such compounds are readily miscible in light lubricating oils. The *n* values in the formula given above may represent an average for a homologous mixture of such aryloxy polyether alcohols including individual compounds having in themselves *n* values greater or less than 10 to 12. While certain of such higher homologues may in themselves be insoluble in paraffinic, oil, they are soluble in the lower members of the series which in turn are soluble in the oil. In fact, blended homologues of appropriate lower and higher ethoxy content are often advantageous from the standpoint of stability of the emulsions obtained and the ease of plating out the oil phase of the emulsion onto a fabric leaving behind a relatively clear water phase.

It has also been desirable to include in the formulation a hexylene glycol, such as 4-methyl-2,4-pentane-diol, which serves as a penetrant for the oil, as an emulsifying assistant, and also as a coupling agent which aids in dispersing the otherwise oil insoluble flameproofing component in the oil film deposited in the fabric.

Ordinarily, orthophenyl phenol serves as a sanitizing agent for the surface to which it is applied and also inhibits bacterial growth in the oil. In the present composition, it has been surprisingly found, that the orthophenyl phenol, in addition, was needed to obtain emulsification. When it was omitted from the formulation the oil was not emulsified despite the use of the surface active cationic and non-ionic components described.

The described ammonia-phosphorus pentoxide complex used as the flameproofing agent can be prepared by reacting, at moderately elevated temperature (150–200° C.), anhydrous ammonia in excess with phosphorus pentoxide, thereby effecting molecular condensation to a product having a nitrogen phosphorus ratio of about 1.3, best described as "an ammonium hexaphosphate dinitride." This material can be prepared by the known methods described in U.S. Patent 2,122,122.

A typical formulation of an oily mixture which can be readily emulsified in water and be plated onto a cellulosic fabric from a laundry wash wheel, is as follows:

EMULSIFIER COMPOSITION

	Parts by weight	
	Range	Preferred
Cationic surfactant (di coco-dimethyl ammonium chloride).	40–50	44
Octyl phenol ethylene oxide condensation product (M.W. 750).	25–35	31.66
Hexylene glycol	10–20	15.73
Ortho phenyl phenol	5–10	9.17

The cationic and non-ionic surfactants comprise 65–80% by weight of the preferred emulsified composition, with the cationic component constituting 150–200% by weight of the non-ionic.

Addition of about 12 pounds of the emulsifier composition to 53.5 gallons of paraffinic oil of the type herein above described makes up to about 55 gallons of oil that can be readily emulsified in tap water, for example in a conventional wash wheel, and the oil exhausted from the emulsion onto cotton fabric.

To impart flame resistance to the fabric there is added to the mixture of paraffinic oil and emulsifier composition an amount of the ammonia-phosphorus pentoxide complex in the approximate proportions by weight of about 50–60 parts flameproofing compound to each 50–60 parts of the oil-emulsifier mixture. Preferred compositions are those having about 60 parts of the flameproofing material to 40 of the oil-emulsifier mixture.

The emulsifiable oil composition containing the flameproofing material is thus composed in general of about 38.5 to 48.5 parts of mineral oil, 1.2 to 1.6 parts of the emulsifying agent and about 50 to 60 parts of the flameproofing material. The emulsifying agent in the preferred compositions is made up of the cationic and non-ionic surface active components hexylene glycol and orthophenyl phenol in the proportions above described.

When the ammonia, phosphorus pentoxide complex is added to the oil-emulsifier mixture an exothermic temperature rise of 5 to 10° F. was observed and a faint ammoniacal odor. Without being bound to any specific theory to explain this observation, it appears that there is possibly a reaction taking place between the ammonia-phosphorus complex and some component of the oil mixture.

In a typical application of the above composition to cellulosic material, the wash wheel is run at a 4 to 8 inch water level. Before addition of the oil and emulsifier mixture, there is added to the water in the wheel any conventional laundry sour or other weakly acidic compound in amount sufficient to overcome any alkaline residue in the fabric and to lower the pH of the liquid to about 6. For this purpose one may employ, for example, acetic acid, sodium bifluoride, sodium fluosilicate or the like. Emulsification of the described oil-emulsifier concentrate takes place readily. The cotton material to be treated is then placed in the wheel and the latter rotated. The oil should be completely exhausted from the emulsion onto the cotton material in about ten to fifteen minutes running time.

Fabric of different construction and weight may require somewhat higher or lower amounts of flame retardant. On stranded cotton mop fabrics and heavy cotton rugs good results were obtained using the 60:40 flame retardant/oil composition in an amount equal to about 12% of the dry weight of the cotton material, applied in a quantity of water in the wheel just sufficient to completely cover the cotton articles, running the wheel for ten minutes at 100° F. liquid temperature. Satisfactory operation is had at temperatures as low as 80° F. Temperatures above 100–110° F. are best avoided since possible loss of ammonia may lead to poorer flame resistance. Lighter cotton fabrics may be adequately flame protected with as little as 8% of the described oil composition.

After the emulsion has been exhausted onto the cotton material, the articles are extracted to about 100% "pick-up" to assure adequate flame retardant properties. After extraction the articles are dried in a drying tumbler or by other conventional methods. The drying temperature should not be in excess of about 150° F. nor should the drying be carried to bone-dry state, since the excess tumbling may result in abrasion of some of the protective fire-retardant composition from the fabrics.

Walk-off mats treated in the above-described manner were tested by applying a micro-Bunsen burner with a two inch flame held at a 45° angle to the vertically hung mats for two minutes. Although the area to which the flame was applied became a glowing char, no after flame or after-glow was seen after withdrawal of the flame. The flame did not penetrate through the bottom to the latex backing and no char was visible on the latex.

The flame test applied above is sufficiently severe to compared with other accepted flame testing methods and provides assurance that the treated materials will meet most rigid standards and specifications governing use and storage of such oil-impregnated dust allaying cotton materials.

In the conventional method of applying oils to dust mops and wiping cloths, the cotton material is initially washed to remove size (if new) or soil (if used) from the fabric. The material is then extracted and/or dried

and placed in another wash wheel or tank to soak up the oil, following which the fabric is again extracted to desired "pick-up" and dried in a heated tumbler. In practice of the present invention employing emulsified oil in the wash wheel, the oil composition can be added directly to the wash wheel after the last rinse and exhausted onto the fabric out of the water emulsion. The emulsion method of application therefore affords considerable savings in time and labor as well as in utility costs in eliminating the intermediate extraction and drying operations.

Although numerous other known water soluble flame retarding agents have been tested for the present purpose, none of these showed satisfactory flame proofing properties when associated with an otherwise flammable oil composition in the fabric. It has been found, however, that the treating costs of using the ammonia-phosphorus pentoxide complex can be reduced to significant extent in some instances by substituting a minor part thereof with an ammonium phosphate, preferably a substantially neutral mixture of mono ammonium and diammonium phosphate. Such addition of the ammonium phosphate ordinarily should not exceed 25% by weight of the total fireproofing composition, the balance being ammonia-phosphorus pentoxide complex.

While numerous types of cationic surfactants could possibly be substituted for the described quaternary alkyl ammonium chloride with acceptable results, the proportions of the other components may in such event require considerable modification, to maintain proper balance for exhaustion and to assure desired flameproofing.

Obviously, many modifications and variations of the invention as hereinabove set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

What I claim is:

1. A self-exhausting emulsifiable oil composition for treatment of cellulosic fabrics to render the same nonflammable, consisting essentially of:

(a) about 38.5 to 48.5 parts by weight of paraffinic mineral oil having a flash point above 350° F. and a viscosity (SUS @ 100° F.) in the range of about 113 to 350 seconds;

(b) 1.2 to 1.6 parts by weight of emulsifying agent; and

(c) sufficient flameproofing composition for said purpose; said emulsifying agent consisting essentially of a mixture of o-phenyl phenol with cationic and nonionic surface-active components, said cationic component being present in an amount equal to 150 to 200% by weight of the nonionic component and said cationic component being present in weight ratio of 40–50 parts to 5–10 parts of said o-phenyl phenol; said nonionic component being an alkyl phenoxy polyethoxy ethanol having a formula weight of 725 to 775 and an alkyl chain of 6 to 12 carbon atoms and said cationic component being a tetraalkyl ammonium chloride compound having 10 to 18 carbon atoms in at least one of the alkyl chains thereof and a total of 20 to 40 carbon atoms in said compound; said flame-proofing composition consisting essentially of an ammonium phosphorus pentoxide complex corresponding to the general formula

$$(NH_4)_6P_6N_2O_{15}$$

2. The method of preparing cellulosic materials for use as dust wiping fabrics which comprises emulsifying in a body of water an oil composition as defined in claim **1**, and treating the cellulosic materials with the obtained emulsion to exhaust the oil composition including flameproofing material present therein and onto said cellulosic material in amount sufficient to render the oil impregnated cellulosic material flame retardant.

3. The method of preparing cellulosic materials for use as dust-wiping fabrics, which method comprises admixing with (a) paraffinic mineral oil having a flash point above 350° F. and a viscosity (SUS @ 100° F.) in the range of 113 to 350 seconds (b) an emulsifying composition consisting essentially of

(1) a tetraalkyl ammonium chloride having 10 to 18 carbon atoms in at least one of the alkyl chains thereof and a total of 20 to 40 carbon atoms in said compound as a cationic surface active agent and a lesser amount of

(2) a non-ionic alkyl phenoxy polyethoxy ethanol having an alkyl chain of 6 to 12 carbon atoms and a formula weight of 725 to 775;

and (c) a flameproofing material comprising an ammonia phosphorus pentoxide complex formed by reacting at 150 to 200° C. phosphorus pentoxide with an excess of anhydrous ammonia to effect molecular condensation to a product having a nitrogen to phosphorus ratio of about 1.3, together with (d) orthophenyl phenol and (e) hexylene glycol; emulsifying the obtained mixture with a non-alkaline body of water under agitation, and treating the cellulosic materials in the emulsion to effect exhaustion of the oil onto the cellulosic material accompanied by said flameproofing material.

4. Walk-off mat formed of cellulosic fabric and a latex backing, said mat being impregnated with a non-flammable dust-adhering oil composition consisting essentially of paraffinic mineral oil and an ammonia-phosphorus pentoxide complex corresponding to the general formula $(NH_4)_6P_6N_2O_{15}$, said mineral oil having a flash point above 350° F. and a viscosity (SUS @ 100° F.) of from about 113 to 350 seconds; and said oil composition constituting about 12% of the dry weight of said mat.

5. Walk-off mat as defined in claim **4** in which said oil composition contains orthophenyl phenol.

6. Cellulosic dust-wiping fabrics impregnated with an oil composition consisting essentially of

(a) paraffinic mineral oil having a flash point above 350° F. and a viscosity (SUS @ 100° F.) in excess of 300 seconds,

(b) ammonia-phosphorus pentoxide complex formed by reacting at 150 to 200° C. an excess of anhydrous ammonia with phosphorus pentoxide to effect molecular condensation to a product having a nitrogen to phosphorus ratio of about 1.3,

(c) cationic surface active agent consisting essentially of tetraalkyl ammonium chloride compound having at least 10 to 18 carbon atoms in at least one of the alkyl claims thereof and a total of 20 to 40 carbon atoms in said compound,

(d) non-ionic surface active agent in the form of an alkyl phenoxy polyethoxy ethanol of 725 to 775 molecular weight, in an amount equal by weight to 25–35 parts thereof to 40–50 parts of said cationic agent,

(e) hexylene glycol, and

(f) orthophenyl phenol.

7. A self-exhausting oil composition for treatment of dust-wiping cellulosic materials to render the same nonflammable, said composition consisting essentially of:

(A) 38.5 to 48.5 parts weight of paraffinic mineral oil having a flash point above 350° F. and a viscosity (SUS @ 100° F.) in the range of 113 to 350 seconds;

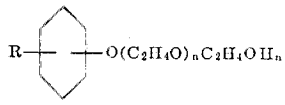
(B) 1.2 to 1.6 parts by weight of emulsifying agent; and

(C) 50 to 60 parts by weight of flameproofing material consisting essentially of an ammonium phosphorus pentoxide complex corresponding to the general formula $(NH_4)_6P_6N_2O_{15}$; said emulsifying agent (B) comprising by weight thereof:

(a) 40 to 50 parts by weight of a tetraalkyl ammonium chloride compound having 10 to 18 carbon atoms in at least one of the alkyl chains

thereof and a total of 20 to 40 carbon atoms in said compound,

(b) 25 to 35 parts by weight of a nonionic surfactant corresponding to the general formula



wherein R is an alkyl group of 6 to 12 carbon atoms and *n* is an integer from 10 to 12 inclusive,

(c) 10 to 20 parts by weight hexylene glycol, and

(d) 5 to 10 parts by weight o-phenyl phenol.

8. Cellulosic wiping material impregnated with a dust adhering and flameproofing oil composition consisting essentially of mineral oil and an ammonia phosphorus pentoxide complex having a nitrogen to phosphorus ratio of about 4/3 formed by molecular condensation reaction of phosphorus pentoxide with excess andhydrous ammonia at 150 to 200° C.; said mineral oil having a flash point above 350° F. and a viscosity in the range of 113 to 350 seconds (SUS @ 100° F.) and a fire point above

400° F.; said oil composition constituting about 8–12% of the dry weight of said cellulosic material.

References Cited

UNITED STATES PATENTS

2,122,122	6/1938	Woodstock	23—106
2,713,536	7/1955	Driskell	252—81 X
2,837,170	6/1958	Armstrong et al.	252—88
3,116,969	1/1964	Coleman	252—88 X
3,247,119	4/1966	Herrick et al.	252—106

OTHER REFERENCES

"Arquads," Quaternary Ammonium Salts, Armour Company, 1956, p. 11.

"Arquads," Armour Company, 1954, p. 3.

"Tergitol," Surfactants, Union Carbide, 1961, pp. 4 and 5.

Rose: Condensed Chemical Dictionary, 6th Ed., 1961, p. 884.

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