

United States Patent[15] **3,644,142****Rauch et al.**[45] **Feb. 22, 1972****[54] PROTECTIVE GARMENT AGAINST
WHITE PHOSPHORUS****[72] Inventors:** Francis Clyde Rauch, Stamford, Conn.;
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Conn.**[22] Filed:** Dec. 11, 1968**[21] Appl. No.:** 783,152**[52] U.S. Cl.**.....117/138.8UF, 117/31, 117/138,
117/160 R, 117/169 R**[51] Int. Cl.**.....B32b 27/20, A62b 17/00**[58] Field of Search**.....117/31, 138.8, 138, 160, 169;
161/162, 168, 169, 174, 403**[56] References Cited****UNITED STATES PATENTS**

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Primary Examiner—William D. Martin*Attorney*—Gordon L. Hart**[57] ABSTRACT**

Protective garment fabric impervious to burning phosphorus is made with fibrillated polytetrafluoroethylene containing an incorporated copper adjuvant which consists of metallic copper or a copper compound, e.g., copper sulfate, cuprous or cupric oxide and the like. The fabric comprises 10 to 95 per-cent weight of the copper adjuvant. In preferred embodiments the fabric may also include inorganic fibers, e.g. asbestos. In-corporated polytrifluorochloroethylene improves strength of the fabric. Protective garments can be fashioned from the new fabrics.

5 Claims, No Drawings

PROTECTIVE GARMENT AGAINST WHITE PHOSPHORUS

The invention relates to protective garment fabric and particularly to fabric for protection against burning white phosphorus. The fabric comprises a fibrillated polytetrafluoroethylene lattice or web with an incorporated copper adjuvant. More specifically, the invention provides a protective fabric of fibrillated polytetrafluoroethylene in which is incorporated a copper adjuvant which constitutes from about 10 percent to about 95 percent of the total weight of the protective fabric. A garment made from this fabric has been found to be uniquely effective in protecting a user against burning white phosphorus. Other materials, such as heavy leather and certain ablative polymers, which have been proposed to provide some protection against burning white phosphorus are based upon placing a large mass of material between the hazard and the wearer with the result that a garment of such other protective material is necessarily uncomfortable due to its bulk and weight and its poor breathing ability. Such a garment also possesses such limited flexibility that it restricts the wearer's movements and so would impair his ability to guard against dangerous conditions.

An object of this invention is to provide fabric for making a garment which affords effective protection against burning white phosphorus and also possesses other qualities desirable in a garment fabric such as lightweight, good flexibility and porous breathing ability. When this fabric is exposed to burning phosphorus, the copper compound and the burning phosphorus react to produce a resistant shield in the fabric which is inert to further chemical action by burning phosphorus, thereby providing continuing protection to the wearer. By way of comparison in other known fabrics for phosphorus protection, such as phenolic nylon, the protective properties are depleted by action of burning phosphorus.

As used in a protective garment, a fabric according to the invention may be effectively employed merely by draping a sheet of the fabric about a wearer or by cutting the fabric into panels and sewing or bonding the panels together to make a fitted garment or by molding sheets of the fabric into a shaped garment or by sewing or bonding sheets of the fabric to an existing garment such as an apron or a pair of coveralls.

In a preferred method for making a fabric of the invention, a selected copper adjuvant in finely divided form is mixed into a pliable dough which is made by blending an aqueous dispersion of polytetrafluoroethylene with a second resinous polymer which is soluble in a selective solvent. The entire mixture is mechanically worked on a rubber mill for sufficient time to thoroughly mix all the components. This step is carried out at a temperature below the sintering temperature of the polytetrafluoroethylene components. When polymethylmethacrylate is the second resin, the mechanical working temperature is preferably in the range from about 170° C. to about 200° C. The thoroughly mixed composition is then removed from the mill, cooled, and ground into pellets of size less than ¼-inch diameter. These pellets are injection molded into plaques which are then pressed at a temperature of about 200° C. into a sheet of desired thickness. The sheets are then removed from the press and washed in a selective solvent, which is a solvent for the second resinous component but not for polytetrafluoroethylene and the copper components. This wash removes the second resinous component leaving a fabric sheet of porous, unsintered, fibrillated polytetrafluoroethylene, with the copper adjuvant dispersed through the fabric. Mechanical working of the mass in the milling and molding and pressing steps has fibrillated the polytetrafluoroethylene. Other mechanical working steps may be substituted or added to effect fibrillation of the polyTFE component during or prior to final shaping of the sheet. Such mechanical working steps effect fibrillation by internal shearing stress which might be produced by one or more processes such as high stress, blending, milling, extruding, pressing, kneading, injection molding, repeated stretching and folding, drawing, twisting and the like.

It has been found advantageous in some embodiments to incorporate a proportion of another fluorinated hydrocarbon polymer, such as polytrifluorochloroethylene, with the polytetrafluoroethylene. This additional component assists the fibrillation of the polytetrafluoroethylene and also improves the mechanical strength of the fabric for service under severe conditions. The additional fluorinated hydrocarbon polymer may also be added as a colloidal dispersion. Also, in some preferred embodiments it will be advantageous to incorporate a high-temperature-resistant and fire-resistant fibrous component such as asbestos, nylon, and the like. When these other fibrous components are added to the polytetrafluoroethylene fabric, in some instances the effective protection against burning phosphorous will be obtained with a smaller proportion of copper adjuvant than would otherwise be needed. Such fiber additives will be effective when used in amounts constituting 1 percent to 50 percent by weight of the fabric. In our most preferred embodiments asbestos may constitute 10-30 parts by weight of the fabric.

Copper adjuvants useful in accordance with the invention include metallic copper; cuprous and cupric salts, such as copper sulfate, cupric phosphate, cupric carbonate, cuprous and cupric halides, i.e., chlorides, iodides and bromides, cupric acetate, cupric formate; cuprous and cupric oxides, and other compounds of copper. The adjuvant will be present in a finely divided solid form which is dispersed throughout the body of the fabric. Copper sulfate is an especially preferred copper adjuvant for this invention.

The polytetrafluoroethylene that forms the fibrous web in the fabric is introduced as a colloidal dispersion of poly TFE in aqueous dispersion. Any colloidal dispersion of poly TFE may be used; a commercially available suspension suitable for the purpose is DuPont Teflon aqueous dispersion No. 30 B, 60 percent solids, which also contains a surface active wetting agent in small amounts as a dispersant. The shape of the colloidal particles is changed from globular particles to fibrillated strands by mechanical working in the second resinous polymer which is selected for its softening point, its high viscosity, and its selective extractability. Although molten polymethylmethacrylate is especially well suited for use as this second resinous polymer, another resin may be substituted such as poly (ethylene oxide), alkali metal shellacate, rosinate or talate, and the like. The selected second resin should soften to a highly viscous pliable plastic state at a temperature below the sintering temperature of the polytetrafluoroethylene so the poly TFE can be readily dispersed and mechanically worked therein to effect fibrillation. Further, the polymer used must be extractable by a selective liquid solvent or by other selective extraction means (e.g., by evaporation or sublimation).

Following are examples presented to set forth the best mode contemplated for carrying out the invention by reference to specific details of certain preferred embodiments. The following also includes several examples not embodying the invention, for purpose of comparison. Full scope of the invention may extend beyond specific details of the following examples.

EXAMPLE 1

A Farrell 1 lb. rubber mill is heated with high pressure steam to 170° C. The rolls are closed and polymethylmethacrylate pellets (Rohm & Haas Plexiglas U.S. -100) are poured between the rolls and allowed to soften for 2-3 minutes. The rolls are then started and as the polymethylmethacrylate begins to develop into a sheet the rolls are adjusted to form a bead at the nip of the rolls about ½ inch to ¾ inch in diameter. To 350 parts by weight polymethylmethacrylate is added 17.5 parts polytetrafluoroethylene solids (in DuPont Teflon dispersion No. 30 B, 60 percent solids), 17.5 parts polytrifluorochloroethylene (in 3-M Kelf-F dispersion K×631, 0.75 g. solids/cc.), 315 parts anhydrous copper sulfate, fine powder. The mixture is prepared as follows. The PTFE dispersion is dispersed in a fine stream evenly back and forth across the rolls after the PMMA sheet has formed in the

rolls. As fibrous material begins to develop the rolls are readjusted to maintain bead size. After all of the PTFE has been added the same procedure is used to slowly add the Kel-F dispersion. After all the polytrifluorochloroethylene has been added, the copper compound is added in the same manner and any excess that falls through the rolls is collected and added again until all the copper compound is milled into the sheet. After all of the components have been added and thoroughly mixed the rolls are operated for 5 minutes more with adjustment of the rolls every 1 to 2 minutes in known manner so as to transfer the sheet to one roll. The entire sheet is then removed from the mill, folded crosswise and returned to the mill. This folding operation is repeated four times before the milling has been completed. The sheet is then removed from the mill cut into small squares and cooled. These small squares are then ground in a Cumberland Model O blade grinder into pellets of less than 1/4-inch particle size. These pellets are then injection molded into rectangular plaques 5 inches by 2 inches by one-quarter inch in a Van Dorn Model H-200 injection molder and then pressed at 200° C. in a Carver Model K laboratory press into sheets of 5 1/2 inches square and 0.030 inches thick. These sheets are removed from the press, fastened into a frame and dipped into acetone or methylethylketone for several hours to extract the polymethylmethacrylate leaving a porous, unsintered completely fibrillated polytetrafluoroethylene fabric which contains polytrifluorochloroethylene and copper sulfate and is resistant to penetration by burning white phosphorus.

EXAMPLE 2

The components of Example 1 are mixed, with the exception that additional poly TFE is substituted on weight for weight basis for the polytrifluorochloroethylene and a fabric is produced by the same process described in Example 1. The resulting fabric, then, has a composition of 35 parts by weight polytetrafluoroethylene and 315 parts copper sulfate. This fabric is resistant to penetration by burning white phosphorus. It is, however, not mechanically as strong as the fabric described in Example 1.

EXAMPLE 3

The process of Example 1 is repeated with the same ingredients but in different proportions and with addition of fibrous asbestos. Fibrous asbestos is added on the rubber mill in the same manner that the copper sulfate is added, that is by spreading the fibers across the operating rolls so that the asbestos fibers are dispersed into the pliable sheet. The finished sheet has a fabric composition of 227 parts by weight asbestos, 315 parts by weight copper sulfate, 20.7 parts polytetrafluoroethylene and 14 parts polytrifluorochloroethylene. This fabric is demonstrated to be resistant to penetration by burning phosphorus and possesses good mechanical fabric strength.

EXAMPLE 4

The process of Example 3 is repeated with the same ingredients in the same proportions by weight except that nylon fiber (DuPont Nomex) is substituted for asbestos. A fabric of the following composition is produced: 227 parts nylon, 315 parts copper sulfate, 20.7 parts polytetrafluoroethylene and 14 parts polytrifluorochloroethylene. This fabric is resistant to penetration by burning white phosphorus.

EXAMPLE 5

The process of Example 1 is repeated with the same ingredients and proportions except that finely divided metallic copper powder is substituted for copper sulfate. A fabric of the following composition is produced: 315 parts copper, 17.5 parts polytetrafluoroethylene, and 17.5 parts polytrifluorochloroethylene.

EXAMPLE 6

The process of Example 1 is repeated with the same ingredients except that cuprous oxide is substituted for copper sulfate and the proportions are varied as indicated below. A fabric of the following composition is produced: 225 parts cuprous oxide, 12.5 parts polytetrafluoroethylene and 12.5 parts polytrifluorochloroethylene.

EXAMPLE 7

The process of Example 1 is repeated with the same ingredients except that cupric oxide is substituted for copper sulfate and the proportions are varied. A fabric of the following composition is produced: 166 parts cupric oxide, 9.5 parts polytetrafluoroethylene and 9.5 parts polytrifluorochloroethylene.

EXAMPLE 8

The process of Example 1 is repeated with the same ingredients except that cupric chloride is substituted for copper sulfate. A fabric of the following composition is thereby prepared, 315 parts copper chloride, 17.5 parts polytetrafluoroethylene and 17.5 parts polytrifluorochloroethylene.

EXAMPLE 9

The process of Example 1 is repeated with the same ingredients except that cupric carbonate is substituted for copper sulfate. A fabric of the following composition is thereby prepared, 315 parts copper carbonate, 17.5 parts polytetrafluoroethylene and 17.5 parts polytrifluorochloroethylene.

EXAMPLE 10

The process of Example 1 is repeated with the same ingredients except copper sulfate is omitted. Fabric of the following composition is thereby prepared: 17.5 parts polytetrafluoroethylene and 17.5 parts polytrichlorofluoroethylene. Upon being exposed to burning phosphorus, this fabric was heat resistant and fire retardant but did not stop penetration of the fabric by burning phosphorus.

EXAMPLE 11

The process of Example 1 is repeated with the same ingredients except that titanium dioxide is substituted for copper sulfate. A fabric of the following composition is thereby prepared, 90 parts titanium dioxide, five parts polytetrafluoroethylene and 5 parts polytrifluorochloroethylene. Upon exposure to burning phosphorus, this fabric did not prevent penetration.

EXAMPLE 12

The process of Example 1 is repeated with the exception that activated charcoal is substituted for copper sulfate. A fabric is thus prepared which has the following composition, 150 parts charcoal, 100 parts polytetrafluoroethylene and 50 parts polytrifluorochloroethylene. Upon exposure to burning phosphorus, this fabric did not prevent penetration.

EXAMPLE 13

Samples of the fabric produced in Examples 1 through 12 are subjected to burning phosphorus in the following manner. A piece of white phosphorus about the size of one-half inch by one-half inch by one-quarter inch is placed on the fabric and allowed to ignite. All of the test fabrics except those produced in Examples 10, 11 and 12, which contain no copper compound, are effective in preventing penetration through the fabric by burning white phosphorus. Results of this test are tabulated in Table 1 in column headed Burning Test. Exam-

ples 10-12 are not embodiments of the invention and are presented for comparison with the invention.

EXAMPLE 14

Samples of the fabrics of Examples 1 and 3 above are placed on a form which supports them at a distance of 3 feet from an explosive charge of which phosphorous which consists of two standard ordnance white phosphorus grenades. The grenades are exploded and both samples are proved effective in preventing penetration by the burning white phosphorus scattered by the grenades. Results of this test are tabulated in Table 1 in the column headed Grenade Test.

All of the fabrics produced and tested in the above examples are porous and air-permeable so that they have the property of breathing ability which increases comfort of a garment made from the fabric. All of these fabrics are pliant and flexible enough so that a fitted garment of the fabric will not seriously restrict movement of the wearer. Bulk and weight of the fabrics are not excessive for making a protective garment. All factors considered, a protective garment of any of these fabrics will provide protection against burning white phosphorus and at the same time will be reasonably comfortable for the wearer. The fabric may be combined in a garment with other fabrics, such as an absorbent underlayer or a water-proof outer-layer in addition to a layer of the protective fabric.

In producing fabric for making a garment, the mechanical working steps in the above examples can be changed or modified to produce sheets of larger size. For example, after the components of the mixture have been thoroughly worked so that water and other volatiles have been removed and the components have been thoroughly mixed the final steps might consist of extruding a continuous strip and calendering the strip to desired width and thickness through a series of pressure rolls. These steps would be followed by a solvent wash step to remove the filler resin and produce the finished fabric.

TABLE I

Sample	Burning Test	Grenade Test
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Ex. 1	PTFE + PTFCE + CuSO ₄	Effective	Effective
Ex. 2	PTFE + CuSO ₄	Effective	—
Ex. 3	PTFE + PTFCE + CuSO ₄ + asbestos	Effective	Effective
Ex. 4	PTFE + PTFCE + CuSO ₄ + nylon	Effective	—
Ex. 5	PTFE + PTFCE + Cu	Partially Effective	—
Ex. 6	PTFE + PTFCE + Cu ₂ O	Effective	—
Ex. 7	PTFE + PTFCE + CuO	Effective	—
Ex. 8	PTFE + PTFCE + CuCl ₂	Partially Effective	—
Ex. 9	PTFE + PTFCE + CuCO ₃	Effective	—
Ex. 10	PTFE + PTFCE	Not Effective	—
Ex. 11	PTFE + PTFCE + TiO ₂	Not Effective	—
Ex. 12	PTFE + PTFCE + charcoal	Not Effective	—

Note: PTFE is polytetrafluoroethylene

PTFCE is polytrifluorochloroethylene

We claim:

1. Garment fabric resistant to penetration by burning phosphorus, said fabric comprising a porous and air-permeable web of fibrillated polytetrafluoroethylene and dispersed in said web fine particles of copper sulfate.

2. Garment fabric defined by claim 1 wherein said copper sulfate constitutes from 10 to 95 percent by weight of the fabric.

3. Garment fabric defined by claim 1 further comprising fibers of other heat-resistant, fire-retardant material dispersed in said web.

4. Garment fabric defined by claim 1 further comprising polytrifluorochloroethylene in mixture with said polytetrafluoroethylene.

5. Garment fabric defined by claim 1 further comprising asbestos fibers dispersed in said web.

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