

1

2,979,157

PROCESS FOR PRODUCING GAS-PROOF AND GAS-ADSORBENT MATERIALS AND THE ARTICLES SO PRODUCED

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This invention relates to gas-proofing compositions and to the gas-adsorbent materials produced therewith and to a process for producing such materials.

In chemical warfare there are employed a variety of gases and smokes which may be classified as vesicants, lung irritants, lachrymators, sternutators and smokes, and mixtures of such gases and smokes. In order to provide for defense against such gases, it has been found desirable to provide gas masks, protective clothing, gas shelters and other protective equipment treated or combined with a gas adsorbent material.

The prerequisites of an ideal gas-proofed material, in particular for use as wearing apparel, are as follows: The material should be such that it adsorbs a relatively large proportion of the various types of war gases while permitting oxygen or air to pass through; the supporting material for the adsorbent should be substantially porous in order to permit perspiration or other liquids to evaporate from the wearer's body; the material comprising the support should substantially retain its flexibility after being combined with the gas adsorbent; the treated material should be of such porosity as to filter out small particles of dust, smoke and oil droplets; the gas adsorbent should be substantially permanently bound to the supporting material in order to prevent the adsorbent from becoming dislodged from the support by rain, laundering or rough usage or by the softening effect of moisture and perspiration. Finally the gas-proofed material should be capable of reuse after decontamination.

It is therefore a general object of the present invention to provide a gas-proofed material in which a gas adsorbent is substantially permanently bound to a fibrous supporting material, the treated material substantially fulfilling the above-mentioned requirements of an ideal gas-proofing material.

Another object of the invention is to combine a fabric with a gas adsorbent in such a manner that it will be substantially resistant to washing and laundering.

It is a more specific object of the invention to provide wearing apparel combined with a gas-adsorbent composition, in such a manner that the wearing apparel retains its porosity, flexibility and is capable of being reused after decontamination.

Another object of the invention is to provide a fibrous material combined with a gas-proofing composition, in such a manner that the gas-proofing composition is substantially permanently bound thereto and the resulting structure forms a combined filter and gas-adsorbing material.

A further object of the invention is to provide a gas-adsorbent composition which is adapted to serve as a permanent finishing agent for sheet materials such as fabrics, felts, paper and the like.

Other objects of the present invention will in part be obvious and will in part appear hereinafter.

According to the present invention fibrous sheet mate-

2

rials are rendered substantially gas-proof by impregnating the fibrous material with an aqueous dispersion of an alkali-soluble water-insoluble cellulosic colloid as a carrier having a gas adsorbent dispersed therein, coagulating this composition on the fibrous material, and drying the treated material to produce a fibrous structure which is substantially porous to air but capable of adsorbing chemical war gases and/or smokes, and which may be reused after contamination and decontamination. Thus the article comprises the comminuted gas adsorbent (e.g. activated carbon), a carrier therefor (the cellulosic colloid) and a support (the fibrous material).

Heretofore it was not thought possible to bind a comminuted gas adsorbent to a support by means of a film-forming colloid because it was thought that the colloid would prevent contact of the gas with the particles of the solid adsorbent and also decrease its adsorptivity. The surprising discovery has now been made that the cellulosic colloids used as the carrier in the present invention do not materially decrease the adsorptivity of the adsorbent even though the particles of the adsorbent are imbedded in and surrounded by the colloid.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others and the article possessing the features, properties and the relation of elements, which are exemplified in the following detailed disclosure and the scope of the invention will be indicated in the claims.

The gas adsorbent which may be employed in the present invention may comprise such adsorbents as carbon, alumina gel, silica gel, manganese dioxide, finely divided metals such as zinc, nickel, platinum and the like which may function as adsorbents or gas-adsorbent catalysts, metallic salts, and other gas adsorbents or mixtures of such gas adsorbents which are known to the art. In the preferred embodiment there is employed as the gas adsorbent an activated carbon of high or low density and preferably in a finely comminuted state.

An acid adsorbent, such as zinc oxide, may be combined with the fibrous material as by impregnation, or mixed or combined with the gas adsorbent and/or the cellulose binder in order to adsorb or neutralize liquid or volatile gaseous acids, for example to neutralize the acid of body perspiration. The acid adsorbent may have the further function of maintaining the efficiency of such gas adsorbent as charcoal, which is known to have its efficiency reduced or destroyed by acid contact.

Alkali-soluble water-insoluble cellulosic materials as a class may be employed as the carrier for the gas-adsorbent material. Such alkali-soluble water-insoluble cellulosic materials comprise cellulose ethers, for example, alkyl-hydroxy-alkyl- and carboxy-alkyl cellulose ethers and the like, mixed cellulose ethers, cellulose ether-esters, alkali-soluble metal salts of the carboxy-alkyl cellulose ethers and mixtures of these cellulose ethers, all of which are capable of being dispersed or dissolved in aqueous alkali. Among the various cellulose ethers which may be employed are methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, propyl cellulose, cellulose glycolic acid ethers, alkali salts of the glycolic acid ethers of cellulose and the like.

In addition to employing the alkali-soluble cellulose ethers as the carrier, there may be employed alkali-soluble celluloses, such as degraded alpha cellulose, beta cellulose and oxy-cellulose which may be produced by degradation and/or decomposition of cellulose by heat, acids, alkali and the like, which treatments result in a product which is soluble in aqueous alkali solution, such as 8 to 10% caustic soda solution upon freezing and thawing the solution. Suitable alkali-soluble water-insoluble cellulosic materials of this class are those disclosed in British Patent No. 507,138 and in the co-pending U.S. applica-

tion Serial No. 427,389 filed January 19, 1942, now Patent No. 2,365,455 issued on December 19, 1944. There may also be employed viscose, cuprammonium solutions of cellulose, and cellulose dissolved in alkaline solutions of zinc salts, as disclosed in U.S. 2,289,085. In the preferred embodiment of the invention there is employed as the carrier for the gas-adsorbent a solution comprising an alkali-soluble water-insoluble cellulose ether, such as hydroxyethyl cellulose.

The dispersion media for the cellulosic carrier may comprise aqueous solutions of strong inorganic alkalis, such as sodium hydroxide, potassium hydroxide, quaternary ammonium hydroxides, and the like, also strong organic bases such as alkyl ammonium hydroxides, and the dispersion may be an emulsion, true solution or colloidal solution. From such dispersions the alkali-soluble cellulosic material may be precipitated by any known coagulant used for coagulating viscose, such as acids, acid-salts, salts and heat.

Fibrous materials constituting the support which may be gas-proofed in accordance with the present invention may be formed in whole or in part of natural fibres such as wood, cotton, hemp, flax, ramie, jute, silk, wool, leather and the like; artificial fibres and filaments formed of regenerated cellulose, such as viscose rayon; or organic cellulose derivatives as a class, such as cellulose ethers, cellulose esters or mixed cellulose ether-esters; synthetic resins as a class such as nylon, vinyl co-polymers, vinylidene chloride polymers; and synthetic rubbers as a class, mineral fibres as a class such as glass fibres, asbestos rock wool and the like. Such fibrous materials may be treated in the form of fibres, yarns, fabrics, in particular wearing apparel, felts, papers, and the like, before, during, or after fabrication. The gas-proofing composition may be applied to such fibrous materials before, during, or after bleaching, dyeing, softening, printing or other treatment. Papers may be treated during or after felting or sheeting.

The finishing composition containing the gas adsorbent may be applied to the fibrous material by spreading, coating, back-filling, padding, impregnating, spraying, or by means of suitable combinations thereof and by means of suitable apparatus known to the art. It is to be understood that the method of applying the composition to the fabric may be varied according to the nature of the fibrous material to be treated, the nature and the viscosity of the binding material and the nature of the final product desired.

The fibrous material may be then washed, stretched, tented or dried in known manner. Care is taken to permit the fibrous material thus treated to substantially retain its porosity and textile characteristics in order that smokes and gases may be permitted to pass therethrough and become adsorbed and/or filtered by the gas-adsorbent material.

The fibrous material may be initially pretreated with a small amount of the dispersion medium or with a suitable wetting agent, and the material then treated while in the pretreated condition in accordance with the process of the present invention. By using a pretreating process, it has been found that the cellulosic composition containing the gas adsorbent is more permanently bound to the fibres and penetration is substantially increased.

The fibrous material and/or the cellulosic composition may be varied by the addition of fillers, plasticizers, waterproofing agents, creaseproofing agents, coloring matter and the like, at any stage during the process. Similarly, the fibrous material may be printed with the composition containing the gas adsorbent.

Generally speaking the ratio of the carrier to the solid adsorbent may range from 1:1 to 1:3. Preferably the carrier constitutes less than 50% of the solids in the composition since it has been found that the smaller the amount of carrier, consistent with good anchorage on

the support, the better will be the adsorbent characteristics of the gasproofed material.

By way of illustrating but not by way of limiting the invention, there will be given the following examples:

Example I

An 80 x 80 bleached cotton cloth was padded with a solution comprising 4% alkali-soluble water-insoluble hydroxy-ethyl cellulose dissolved in 6% aqueous sodium hydroxide solution to which there had been added 16% of comminuted "Norit A" brand activated charcoal. The padded material was partially dried and then passed into an aqueous bath containing 5% acetic acid which coagulated the cellulose ether thus binding the charcoal in dispersed form to the fabric. The cloth was then rinsed, softened, and dried, and otherwise processed in known manner. Upon testing, it was found that the cloth was permeable to air but filtered out a considerable quantity of smoke and substantially entirely adsorbed such chemical war gases as phosgene and the like, for an extended period of time. Furthermore, the fabric was found to retain a majority of the gas adsorbent after laundering and was capable of reuse after decontamination.

Example II

A 64 x 64 cotton sheeting was first backfilled with an unfilled composition comprising 4% alkali-soluble water-insoluble cellulose glycolic acid ether dissolved in 7% aqueous caustic soda solution. The sheeting was partially dried and then backfilled on the same side with a second composition comprising 3% alkali-soluble water-insoluble cellulose glycolic acid ether, 4% aqueous caustic soda solution and 32% finely divided activated carbon. The carbon previously wet with dilute caustic soda solution was added to the composition while stirring. The backfilled sheeting was then treated to coagulate the cellulose ether of both applied compositions by semi-drying, and thereafter passing semi-dried fabric through an aqueous solution comprising 5% sulphuric acid. After coagulation the fabric was washed, dried and otherwise finished in known manner. It was found that the cloth, while still permeable to air, prevented passage of smoke and poisonous gases. The fabric retained such properties even after decontamination.

Example III

The process of Example II was carried out, but with the difference that both of the coatings contained activated carbon.

The gas-proofed materials produced according to the present invention have a wide variety of uses which fall generally into two main classes; (a) for protective purposes, and (b) for filtration and separation of gases. The protective uses include inter alia the use of the material for wearing apparel, in particular for military uniforms, blankets, sleeping bags and other bedding material, surgical dressings to avoid infection by gas gangrene, wrappers and containers of all kinds, in particular for foodstuffs to prevent contamination by mustard gas and other war gases, covers, tarpaulins, tents and curtains, in particular for military use for protection against gas in chemical warfare, and the like.

The uses as a filter include inter alia the use of the material in gas masks, including both the fabric body of the mask as well as the adsorbent in the canister, masks for lacquering and paint spraying, filters in ducts for air-conditioning and in flues for deodorizing flue gases, filters for separating one gas from another, filters in smoking pipe stems, and the like.

It has been found practical to provide a gas mask canister having sections partitioned by discs formed of the gas-proofed fabric, felt or paper rolled into the edges of the container, the spaces between the discs being filled with soda lime for adsorbing and neutralizing acids. Pellets may be formed by coagulating a mixture of the gas adsorbent and the alkali-soluble water-insoluble cellulosic

carrier free of any support, drying the coagulum, and granulating the dried material. Such pellets may be used to advantage in gas mask canisters and in gas and air filters.

Among the advantages which follow from applicant's invention it has been observed that by having the gas adsorbent combined with a fibrous support, various structures may be prepared which would not be possible by using the unsupported adsorbent alone. Moreover, the size of the pores of the fibrous support may be regulated by controlling the amount of the gas-adsorbent composition applied to vary the permeability to air over a wide range. The combination of fibrous material with the gas adsorbent furthermore provides a product which is effective for filtering smoke, particularly if some of the particles of the smoke are so fine as to have little tendency to be adsorbed by the gas adsorbent alone. The invention permits the use of finely powdered activated carbon in place of granular carbon, thus allowing for a greater surface area of the carbon, with a higher adsorptive value per unit weight of carbon.

Since certain changes in carrying out the above process, and certain modifications in the article which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

Inasmuch as the treated fibrous material prevents the passage of gases of various types by its adsorption of these gases the material has been termed "gas-proofed" and the composition "gas-proofing" in the appended claims. Further in the claims the term "felts" includes textile felts and papers.

Having described my invention, what I claim as new and desire to secure by Letters Patent is:

1. A material permeable to air but impermeable to heavy gases comprising a fibrous support combined with an alkali-soluble water-insoluble cellulosic colloid carrying a solid material which is an adsorbent of said heavy gases.

2. A material permeable to air but impermeable to heavy gases comprising a textile combined with an alkali-soluble water-insoluble cellulosic colloid carrying a solid material which is an adsorbent of said heavy gases.

3. A material permeable to air but impermeable to heavy gases comprising a felt combined with an alkali-soluble water-insoluble cellulosic colloid carrying a solid material which is an adsorbent of said heavy gases.

4. A textile material permeable to air but impermeable to heavy gases comprising a fabric impregnated with an alkali-soluble water-insoluble cellulose ether carrying particles of a solid material which is an adsorbent of said heavy gases dispersed therein.

5. A composition for adsorbing heavy gases comprising an aqueous dispersion of an alkali-soluble water-in-

soluble cellulosic colloid and a solid material which is an adsorbent of said heavy gases.

6. A composition for adsorbing heavy gases comprising an aqueous dispersion of an alkali-soluble water-insoluble cellulose and a solid material which is an adsorbent of said heavy gases.

7. A composition for adsorbing heavy gases comprising an aqueous dispersion of an alkali-soluble water-insoluble cellulose ether and a solid material which is an adsorbent of said heavy gases.

8. A composition for adsorbing heavy gases comprising an aqueous dispersion of an alkali-soluble water-insoluble cellulose ether and finely divided activated carbon.

9. In a process for producing a material permeable to air but impermeable to heavy gases, the steps comprising combining a fibrous support with an aqueous dispersion of an alkali-soluble water-soluble cellulosic colloid and a comminuted solid material which is an adsorbent of said heavy gases, coagulating said cellulosic colloid carrying said adsorbent on said fibrous material, the coagulated colloid binding the adsorbent to the support.

10. In a process for producing a fabric permeable to air but impermeable to heavy gases the steps comprising impregnating the fabric with an aqueous dispersion of an alkali-soluble water-insoluble cellulosic colloid and a comminuted solid material which is an adsorbent of said heavy gases, coagulating the cellulosic colloid on said fabric, thus binding the adsorbent to the fabric.

11. In a process for producing a fabric permeable to air but impermeable to heavy gases the steps comprising coating the fabric with an aqueous dispersion of an alkali-soluble water-insoluble cellulosic colloid and a comminuted solid gas-adsorbent carbon, coagulating said cellulosic colloid on said material, thus binding the adsorbent to the fabric.

12. In a process for producing a fabric permeable to air but impermeable to heavy gases the steps comprising backfilling the fabric with an aqueous dispersion of an alkali-soluble water-insoluble cellulosic colloid and a comminuted solid material which is an adsorbent of said heavy gases, coagulating said cellulosic colloid on said fabric, thus binding the adsorbent to the fabric.

13. In a process for producing a material permeable to air but impermeable to heavy gases, the steps comprising combining a fibrous support with an aqueous dispersion of an alkali-soluble water-insoluble cellulose ether and a comminuted carbon, coagulating said cellulose ether carrying said carbon on said fibrous material, the coagulated ether binding the carbon to the support.

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