Yprite-resistant flexible gloves.

Flexible glove comprising at least a layer of fluoroelastomer with added surface-active agents and/or colloids and/or thickening agents. Preferably the glove has a resistance to yperite and is manufactured by immersing a suitable die into an aqueous dispersion of a compound of fluoroelastomer with the addition of the above cited fillers.
"YPERITE-RESISTANT FLEXIBLE GLOVES"

SPECIFICATION

The present invention is directed to a polymeric flexible glove, in particular to a glove resistant to chemical agents, among which the yperite.

As known, yperite is a blistering gas of strong power, whose presence in a certain ambient can cause lethal effects in the range of few minutes, serious cases of conjunctivitis, further damages which could show themselves with delays from 6 to 24 hours and also later.

It is also known that protective clothing have been provided with various remedies in order to try to withstand said substance with results not completely satisfactory since yperite is a very penetrating substance and penetrates into clothes, leather and rubber.

In some cases there has been reached a certain result, which is acceptable in the protective clothing field, making recourse to manufacturing processes based on the principle of impermeabilizing with polyurethane, for instance the rough leather surface of a shoe.

In other applications it has been found suitable to provide a protective fabric with yperite-resistant characteristics through suitable nitrogenous resins prepared on the fabric itself.

Said manufacturing means and methods are suitable for protective clothing in which the presence of a basic layer having a certain consistency or rigidity as the leather and the fabric, permits the penetration or the impregnation of substances apt to retard in time the permeability of the clothing by yperite.
As it is understood, these circumstances that are in part favourable, do not occur in the glove manufacture whose characteristic of use requiring the manoeuvrability of the user hand, excludes the presence of the layers that easily become impregnated and impermeabilized as already said.

It is also apparent that the technique used for the protective clothing comprising the fabrics or the leather cannot be easily employed in the field of the flexible materials, as gloves which are constituted generally by thin layers of elastomers.

On the other hand there are already known rubber gloves having layers suitably studied to withstand the attack of various substances and gas in ambient with polluted atmosphere.

Generally it has been noted that said elastomeric gloves can be used for a very short time and consequently said gloves are not suitable for being used for a long time in ambients polluted by yperite.

In fact, as known, one of the yperite characteristic is that of having a low reactivity and of being less water-soluble and consequently of having such characteristics so as not being subjected to a quick hydrolysis.

Owing to the above cited reason, yperite can resist in a given ambient for several days and also for weeks and the gloves according to the state of the art unlikely are suitable for being used for instance on those grounds where one zone polluted by yperite must be subsequently occupied by persons having different tasks as it could occur in case of a war or other events or any other calamity.

Moreover it has been found that the gloves according to the state of the art have a certain rigidity which is not completely suitable especially when the operator have to use particulars tools.
Therefore the present invention aims at providing a glove which has a resistance to gas, chemical agents, in particular to yperite, and its relative manufacturing process, devoid of any of the cited drawbacks.

The object of the present invention is a glove of polymeric flexible material, characterized by the fact of comprising at least a layer of fluoroelastomer added with fillers of surface-active agents and/or colloids and/or thickening agents.

A further object of the present invention is a process for manufacturing gloves of polymeric flexible material comprising at least a yperite-resistant layer, characterized by the fact of comprising the steps of:

a) immersing a die corresponding to the outer shape of the glove into a liquid substance formed by a compound of fluoroelastomer added with fillers of surface-active agents and/or colloids and/or thickening agents;

b) drying the layer placed on the die;

c) vulcanizing the layer placed on the die.

In one embodiment, the glove according to the present invention comprises at least a layer of fluoroelastomer alone or in combination with other underlying or overlying layers, with the addition of fillers of surface-active agents and/or colloids and/or thickening agents.

The terms surface-active agents, colloids, thickening agents, referred to in this disclosure, mean fillers or chemical agents in general apt to increase or to improve the affinity between a solid substance and a liquid one or in other words those fillers or elements which tend to encircle a solid substance, for instance in an aqueous dispersion, to increase the wettability degree of the solid substance.

In the considered example, these fillers determine the formation of films both at the air/water interface and
around the solid substances maintaining the various solid substances separated from one another.

In one embodiment of the present invention, the surface-active agents can be of anionic, cationic, non-ionogenic and amphoteric type.

In practice the surface-active fillers used for the purposes of the invention can be selected among salts of organic acids, as for instance stearates, caprylates, oleates, potassium, or sodium or ammonium laurates; ether sulphates of fatty alcohols as lauryl ether sulphate; fatty alcohol sulphates as sodium or potassium or ammonium lauryl-sulphate, or monoethanolamine or triethanolamine lauryl sulphate and in general all the sodium or potassium or ammonium alkyl-aryl sulphates; ammonium salts of carboxylic acids of polyglycolic ethers of fatty alcohols and also quaternary ammonium salts, esters or phosphoric ethers of carboxylic acids or fatty alcohols.

Other examples of used surface-active agents can be selected among those deriving from ethylene oxide as alkyl phenol polyglycolic ethers, fatty alcohol polyglycolic ethers, alkyl phenol thioglycolic ethers, carboxylic acids of polyglycolic ethyls of alkyl phenol or carboxylic acids of polyglycolic ethyls of alkyl phenol or carboxylic acids of polyglycolic ethyls of fatty alcohols alone or in combination with one another.

In one embodiment said colloids can comprise casein, bone glue, alginates salified with various alkali, various gelatine, alone or in combination with one another.

The thickening agents used in addition to the fluor elastomeric layer can comprise: polyvinyl alcohol, carboxylic methyl cellulose, hydroxyethyl or hydroxylpropylcellulose, methyl cellulose, sodium, ammonium, potassium polyacrylates, natural resins as for instance guar
rubber or Karaja rubber, always alone or in combination with one another.

In all the above cited examples, the fillers of surface-active agents or colloids of thickening agents used alone have a light weight or at the most equal to 10% with regard to the weight of the dry fluoroelastomeric compound.

In the embodiment in which all the fillers and i.e. surface-active agents, colloids and thickening agents are used in combination with one another, the total weight of said fillers is at the most equal or less than 30% of the total weight of the dry fluoroelastomeric compound.

In one particular embodiment according to the present invention it has been found suitable to use in addition to the fluoroelastomeric layer a quantity of surface-active agent fillers with a weight comprised between 0.05% and 5% of the total weight of the dry fluoroelastomeric compound.

As said, the invention is not limited to a glove comprising a single layer of fluoroelastomer added with fillers, but can be associated to an inner layer formed by an aqueous dispersion of natural rubber latex comprising on its turn fillers of surface-active agents, colloids, thickening agents, more or less in the seen proportions.

Preferably the two-layer glove comprises two latex aqueous dispersions, the first one of natural rubber forming the inner layer, the second one of fluorinated elastomer, with the further interposition of one intermediate elastomer layer based on a polychloroprene and fluoroelastomer compound.

In particular, the ratio between the polychloroprene and the fluoroelastomer of the intermediate layer is comprised in the range of values from 100/0 and 10/100.
In a practical realization, the two-layer gloves has a thickness of values comprised between 0.6 and 0.9 mm and the thickness of the fluoroelastomeric outer layer can be comprised between 0.1 and 0.2 mm.

Also, in one example the composition of the two-layer glove is as follows:

**NATURAL RUBBER FORMULA**

<table>
<thead>
<tr>
<th>Natural Rubber</th>
<th>Parts by Weight</th>
</tr>
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<tbody>
<tr>
<td>LATEX NATURAL RUBBER</td>
<td>100</td>
</tr>
<tr>
<td>POTASSIUM CAPRYLATE</td>
<td>0.4</td>
</tr>
<tr>
<td>AMMONIUM HYDROXIDE</td>
<td>0.5</td>
</tr>
<tr>
<td>SULPHUR</td>
<td>1</td>
</tr>
<tr>
<td>ZINC DIETHYLDITHIOCARBAMATE</td>
<td>1</td>
</tr>
<tr>
<td>ZINC OXIDE</td>
<td>1</td>
</tr>
<tr>
<td>ANTIOXIDIZING AGENT</td>
<td>1</td>
</tr>
<tr>
<td>ANTIFOAMING</td>
<td>0.1</td>
</tr>
<tr>
<td>THICKENING AGENT</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**INTERMEDIATE COMPOUND FORMULA**

<table>
<thead>
<tr>
<th>Intermediate Compound</th>
<th>Parts by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>POLYCHLOROPRENE</td>
<td>70</td>
</tr>
<tr>
<td>FLUORINATED ELASTOMER</td>
<td>30</td>
</tr>
<tr>
<td>CASEIN</td>
<td>4</td>
</tr>
<tr>
<td>EPOXY RESIN</td>
<td>5</td>
</tr>
<tr>
<td>ZINC OXIDES</td>
<td>7.5</td>
</tr>
<tr>
<td>THICKENING AGENT</td>
<td>4</td>
</tr>
<tr>
<td>STABILIZER</td>
<td>2</td>
</tr>
</tbody>
</table>

**FLUOROELASTOMERIC COMPOUND FORMULA**

<table>
<thead>
<tr>
<th>Fluoroelastomeric Compound</th>
<th>Parts by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLUOROELASTOMER</td>
<td>100</td>
</tr>
<tr>
<td>MgO</td>
<td>15</td>
</tr>
<tr>
<td>DIAK 3</td>
<td>3</td>
</tr>
<tr>
<td>TRITON X 165</td>
<td>1.5</td>
</tr>
<tr>
<td>THICKENING AGENT</td>
<td>4</td>
</tr>
<tr>
<td>CARBON BLACK</td>
<td>10</td>
</tr>
</tbody>
</table>

The manufacture of the glove according to the present invention can be carried out with the aid of porcelain dies.
whose shape corresponds to that of the glove, or making recourse to the use of solutions with solvent or to latex aqueous dispersions of the layers forming the glove.

Generally the processes relating to the formation of the gloves according to the present invention base substantially on the step of immersing the die into the solutions with solvent and into the latex aqueous dispersions and of continuing then to the subsequent drying and vulcanizing steps.

In particular the preferred process for manufacturing gloves according to the invention consists in the steps of immersing the die into a latex aqueous dispersion both of natural rubber and of fluoroelastomer or only of fluoroelastomer in the case of a glove having a single layer.

With respect to the process of immersing a die into a solution with solvent, the process of immersing the die into a latex aqueous dispersion produces the advantage of avoiding to make recourse to the complicated apparatuses necessary for the suction of the solvents.

Also, more in detail a process for manufacturing gloves of flexible polymeric material resistant to chemical agents, particularly to yperite, is characterized by the fact of comprising the steps of:

d) immersing the die into an aqueous dispersion of natural rubber latex containing surface-active agents, colloids, thickening agents;

e) drying the die in which the natural rubber layer has been placed;

f) immersing the die into a compound substantially based on polychloroprene and fluoroelastomer;

g) drying the intermediate polychloroprene and fluoroelastomer compound;
h) immersing the die into an aqueous dispersion formed by a compound of fluororelastomer added with surface-active agents, colloids, thickening agents; i) drying the die with the layers laid down on it; l) vulcanizing.

In some practical carryings into effect of the cited process the die drying step after the immersion into the natural rubber latex compound is carried out in a stove at a temperature comprised between 40° and 100°C, for instance at 60°C.

The further drying step of the compound comprising the fluororelastomer added with surface-active agents, colloids and thickening agents is carried out at a temperature comprised between 40° and 100°C, and in particular also at 60°.

The vulcanizing step is carried out on the die comprising the elastomeric layers placed on it at a temperature comprised between 100°C and 160°C, for instance at 110°C.

The gloves manufactured as indicated have a satisfactory resistance, particularly to yperite.

The results obtained with the invention cannot be completely explained clearly since the addition of the cited fillers to the fluororelastomeric layer and the improvements achieved as regards a greater impenetrability of the glove in presence of yperite also for very long times derive from fortuitous experimentations of complicated interpretation.

Now the Applicant makes a hypothesis in order to try to clarify as much as possible the involved phenomena without said hypothesis being a limitation to the protection of the invention.
Firstly there is to be considered that the improvements can derive both from the manufacturing process of the glove and, in presence of yperite, from the characteristics of the elastomeric layer according to the present invention.

In practice in the manufacturing process there have been found during the experimentations some notches and generally cuts on the dies, especially porcelain dies.

The observation has not been immediate since the number of dies in a production is very high and can reach a few thousands and the same cuts can assume at first low depths and moreover can be present in some and not in all the dies.

Without considering the superficial irregularities due to the manufacturing process it can be stated on good grounds that the presence of cuts can be determined by the chemical attack of the fluoroelastomeric layer placed through the immersion of the porcelain die when the die itself is submitted to the vulcanizing step.

In this step very probably there is a development of hydrofluoric acid from the fluoroelastomeric layer with a consequent chemical attack on the die surface since, as known, said acid is very corrosive.

The attack is slow, but continuous and with passing of time would create on the die surface the cited notches with the consequence of having not only gloves provided with irregularities of different type, as for instance differences in thickness, blisters, incidental overlapping parts, but also the tendency of the fluoroelastomeric glove to excessively adhere to the die with the negative consequence of determining a certain difficulty in the manual removing step of the finished glove from the die and perhaps a certain risk of small tearings.
As understandable, the appearing of irregularities in the finished gloves means a scarce uniformity in the thickness of the layer and therefore a different resistance from zone to zone to yperite.

Moreover the presence of blisters of different type in the finished glove would increase the possibility of tearings on the outer surface of the glove especially when the user acts in an ambient polluted by yperite and is obliged to use tools or to touch articles and the like in his working field.

During the cited experimentations the Applicant has been able to ascertain that the addition of the fillers of surface-active agents, colloids, thickening agents to the fluoroelastomeric layer, improves the resistance to yperite also where said resistance is weak.

This favourable situation could depend on the fact that the cited fillers, owing to their nature, originate the covering of the fluoroelastomeric particles with thin layers, films or lakes and generally they originate very thin layers in the liquid substance in which they are mixed, which laying down on the die surface during the immersing step for obtaining the anti-yperite layers prevent or at least would tend to withstand the superficial attack directed to the die surface by the hydrofluoric acid developped during the vulcanizing step.

Moreover the use of the gloves carried out according to the present invention would show an improved resistance and impermeability for the presence not only of a single barrier, but of two barriers, respectively a first barrier constituted by the fluorinated elastomer and a second barrier constituted by the thin film or the very thin layer determined by the presence of surface-active agents, colloids and thickening agents.
Supposing to use a two-layer glove, i.e. a glove formed as said by an inner and outer layer, of natural rubber and fluoroelastomer, respectively, there are obtained results still more optimal as regards the yperite resistance.

In fact, besides what already said, a greater resistance to the chemical attack of the hydrofluoric acid on the dies of porcelain or like material usually used, should be obtained in consequence of the vulcanizing process.

This favourable situation should depend on the fact that the hydrofluoric acid developed on the fluoroelastomer die is resisted both by the very thin layers or films originated by the presence of the surface-active agents, thickening agents, colloids dispersed in the two layers of the glove, and by the impermeable barrier offered by the first natural rubber layer in which the die has been immersed in the first step of the manufacturing process.

Consequently, the formation of notches and cuts on the outermost die surface is avoided saving thus the glove from thickness irregularities and therefore from having zones with a less resistance to gas, chemical agents in general, in particular to yperite.

Then the presence of the cited surface-active agents, thickening agents and colloids and when required the laying down of a first natural rubber layer on the die by preventing phenomena of a strong attack between the glove and the die, permit favourably the removal of the glove without making recourse to the use of suitable paintings of the outer surface of the die with lubricating substances or anyhow anti-adhesive substances.

Of course the glove of the now described process particularly suitable for being used in ambients polluted by yperite, could be used also in other application fields and in general where a protection is required for the hands
of the user in ambient comprising gas and chemical substances.

Also it is still apparent that the present invention is not directed to a glove comprising one or two layers but, for instance, further solutions could be used in which the number of the layers is higher than two or three, however always following the principle that the glove must comprise at least a layer of fluoroelastomer added with the cited fillers.

Although some particular embodiments according to the present invention have been described, it is understood that the present invention includes in its scope any other alternative embodiment accessible to a technician of the field.
WHAT WE CLAIM IS:

1) Glove of flexible polymeric material resistant to gas, chemical agents, yperite, characterized by the fact of comprising at least a layer of fluoroelastomer added with fillers of surface-active agents and/or colloids and/or thickening agents.

2) Glove as in claim 1, characterized by the fact that said fillers are formed by a mixture of surface-active agents, colloids and thickening agents.

3) Glove as in claim 1, characterized by the fact that each filler of surface-active agents, or colloids or thickening agents is present up to 10% by weight in respect to the weight of the dry fluoroelastomeric layer.

4) Glove as in claim 1 characterized by the fact that the fillers of surface-active agents are selected among salts of organic acids, ether sulphates of fatty alcohols, alcohol sulphates, ammonium salts of carboxylic acids of polyglycolic ethers of fatty alcohols, quaternary ammonium salts, esters or phosphoric ethers of carboxylic acids, fatty alcohols.

5) Glove as in claim 1, characterized by the fact that said colloids are selected among casein, bone glue, gelatine, alone or in combination with one another.

6) Glove as in claim 1, characterized by the fact that said thickening agents are selected among polyvinyl alcohol, carboxymethyl cellulose, hydroxyethyl or hydroxilpropylcellulose, methyl cellulose, sodium, ammonium
or potassium polyacrylates, mineral resins, alone or in combination with one another.

7) Glove as in claim 1, characterized by the fact of comprising an inner layer of natural rubber latex.

8) Glove as in claim 7, characterized by the fact of comprising a further intermediate layer substantially based on polychloroprene and fluoroelastomer between a layer of natural rubber latex and a fluoroelastomeric latex layer.

9) Process for manufacturing gloves of flexible polymeric material comprising at least a yperite-resistant layer, characterized by the fact of comprising the steps of:
   a) immersing a die corresponding to the outer shape of the glove into a liquid substance formed by a compound of fluoroelastomer added with fillers of surface-active agents and/or colloids and/or thickening agents;
   b) drying the layer placed on the die;
   c) vulcanizing the layer placed on the die.

10) Process as in claim 10, characterized by the fact of comprising before steps a), b), c), the steps of:
   d) immersing the die into an aqueous dispersion of natural rubber latex containing surface-active agents, colloids, thickening agents;
   e) drying the die with a natural rubber latex layer;
   f) immersing the die into a compound substantially based on polychloroprene and fluoroelastomer;
   g) drying the polychloroprene and fluoroelastomer layer.
## DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (int. Cl.)</th>
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<tr>
<td>X</td>
<td>IBM TECHNICAL DISCLOSURE BULLETIN, vol. 8, no. 4, September 1965, page 622, New York, US; R.C.GUGGENHEIM: &quot;Gloves for handling corrosive materials&quot;</td>
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<td>A 62 D 5/00 A 62 B 17/00 A 41 D 19/00 A 41 D 31/00</td>
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<td>A</td>
<td>US-A-3 513 064 (M.W.WESTLEY) * Example 1; column 5, lines 38-48; claims *</td>
<td>1,3,4</td>
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<td>US-A-4 190 685 (J.A.HART et al.) * Column 1, line 29 - column 3, line 29; column 9, lines 20-29; claims *</td>
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<td>A</td>
<td>DE-A-2 603 015 (CAMA LATEX GmbH) * Claims; page 4, lines 20-33; page 6, lines 20-24 *</td>
<td>1,7-10</td>
<td>A 62 D A 62 B A 41 D B 32 B</td>
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<td>A</td>
<td>FR-A-1 468 124 (HAMMERSTEINER KUNSTLEDER) * Page 1, left-hand column, lines 9-37; page 2, right-hand column, lines 2-27; claims *</td>
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*TECHNICAL FIELDS SEARCHED (int. Cl.)*

The present search report has been drawn up for all claims.

<table>
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<td>THE HAGUE</td>
<td>08-10-1985</td>
<td>FLETCHER A.S.</td>
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**CATEGORY OF CITED DOCUMENTS**

- **T**: theory or principle underlying the invention
- **E**: earlier patent document, but published on, or after the filing date
- **D**: document cited in the application
- **L**: document cited for other reasons
- **A**: member of the same patent family, corresponding document
- **P**: intermediate document