(54) Title: RUBBER ARTICLES HAVING A MODIFIED POLYMER LAYER OF ETHER AND ESTER UNITS

(57) Abstract

There is disclosed a body contacting article, e.g. a surgeon's glove which comprises a first layer of a natural or synthetic elastomer and thereupon a layer of polymer comprising repeating units of the formula: [-CH₂-(OR)] and [-CH(CO₂H)-CH(CO₂R¹)] (I) or [-CH₂-CH(R²)] and [-CH(CO₂H)-CH(CO₂R²)] (Ia), wherein R is a lower alkyl group and R¹ is a lower alkyl group or a (lower) alkoxy (lower) alkyl group, and R² is hydrogen or a phenyl group.
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RUBBER ARTICLES HAVING A MODIFIED POLYMER LAYER OF ETHER AND ESTER UNITS

DESCRIPTION

This invention relates to body contacting articles fabricated from natural or synthetic elastomeric materials e.g. natural or synthetic rubbers or polyurethanes. More particularly, the invention relates to medicinal gloves and especially to surgeon's gloves.

In order to improve the donning properties of gloves such as thin rubber or polyurethane gloves of the type used in medical examinations or surgical procedures, it has been customary to incorporate a donning aid at least at the hand contacting surface of the glove. Conventional donning aids have been powders such as talc or starch. However, the use of such particulate donning aids has the disadvantage that particles may drop off the glove into the wound possibly resulting in a granuloma. In order to avoid the use of donning powders other attempts to improve the donning properties of the glove have included the treatment of the hand contacting surface of the glove by halogenation or by lamination with another material having better donning properties than the base rubber. Other articles of natural or synthetic elastomeric materials also suffer problems associated with application due to the frictional resistance of the natural or synthetic elastomeric material employed in the manufacture of the article and the body portion with which it is to be contacted.

Delamination caused during stretching or flexing of the glove has been a problem associated with such laminated gloves particularly when the glove is donned when the hands are wet.

Attempts to improve resistance to delamination have included treatment of the natural or synthetic
elastomeric base material surface for example by acid priming so that the laminated material keys well to the base material and remains adhered whilst the base material is stressed. In US Patent No. 4499154 there is disclosed a process for producing a flexible rubber article in which the formed rubber article is subjected to an acid priming step and a neutralising step prior to a polymer coating step.

The present invention seeks to mitigate the disadvantages of the prior art and to provide body contacting articles such as surgeon's gloves having good donning properties, by using polymers which can be applied directly to the natural or synthetic elastomeric surface without the necessity of pre-treating that surface.

Thus the present invention provides a process which is simpler and more economical than those hitherto known.

According to the present invention there is provided a body contacting article which comprises a first layer of a natural or synthetic elastomer and thereon a layer of a polymer comprising repeating units of the formula:

\[
[-\text{CH}_2-\text{CH(OR)}-] \text{ and } [-\text{CH(CO}_2\text{H)}-\text{CH(CO}_2\text{R}^1)-] \text{ (I)}
\]
or

\[
[-\text{CH}_2-\text{CH(R}^4)-] \text{ and } [-\text{CH(CO}_2\text{H)}-\text{CH(CO}_2\text{R}^1)-] \text{ (IA)}
\]

wherein R is a lower alkyl group and R^1 is a lower alkyl group or a (lower) alkoxy (lower) alkyl group, and R^4 is hydrogen or a phenyl group.

Aptly R is a lower alkyl group containing up to 4 carbon atoms. More suitably R is a methyl group. Aply R^1 is a lower alkyl group containing up to 9 carbon atoms (e.g. methyl, propyl, butyl, pentyl, hexyl, octyl or nonyl) more aptly up to 4 carbon
-3-

atoms; or an alkoxy alkyl group having up to 4 carbon atoms in the alkoxy part and up to 4 carbon atoms in the alkyl part (e.g. a propoxyethyl group). Suitably, when R is a methyl group, R¹ is a propyl or butyl group. More suitably R¹ is a -(CH₂)₃CH₃ group.

The natural or synthetic elastomer preferably comprises a natural rubber or a polychloroprene (e.g. Neoprene), a nitrile rubber, a styrene butadiene rubber or a polyurethane.

The polymers for use in the polymer layer favourably comprise or consist essentially of repeating units of formula (I) or (IA). Such polymers may be referred to as copolymers of a vinyl alkyl ether and a maleic ester (I), or of an alkylene and a maleic ester (IA).

Preferably the body contacting article is a surgeon's glove.

According to a further embodiment of the invention there is also provided a surgeon's glove which comprises a rubber glove which has on the hand contacting surface thereof a layer of a polymer comprising repeating units of the formula:

[-CH₂-CH(OCH₃)-] and [-CH(CO₂H)-CH(CO₂R²)-] (II)

wherein R² is lower alkyl group. Suitably R² is an alkyl group containing up to 9 carbon atoms, more suitably up to 4 carbon atoms. Preferably R² is a propyl or butyl group. More preferably R² is an n-butyl or a -(CH₂)₃CH₃ group.

The preferred polymers for use in the polymer layer favourably comprise or consist essentially of repeating units of the formula II. Such polymers may be referred to as copolymers of vinyl methyl ether and a maleic ester.

Polymers having repeating units of formula I or
II are commercially available and are sold under the trade name GANTREZ (available from GAF Corporation). Apt polymers are those of the GANTREZ ES series of resins and are described as alkyl monoesters of poly(methyl vinyl ether - maleic acid). Suitable resins of this series are the isopropl and n-butyl esters sold under the trade names ES-335, ES-425 and ES435.

Other polymers may however be suitable and these includes polymers of:

(i) the butyl half ester of poly(ethylene/maleic acid)- which is a rubbery material that laminates satisfactorily to rubber.

(ii) the butyl half ester of Scripset 520 (butyl half ester of poly (Styrene/maleic acid) which is a glassy material.

(iii) SMA 2625 (partly esterified poly(styrene/maleic acid)) - which is a glassy material that laminates satisfactorily to rubber.

(Scripset 520 is a trade mark and relates to a substance obtainable from Monsanto).

The polymers having repeating units of formula I, IA or II may be applied directly to formed articles having a natural or synthetic elastomer surface.

Accordingly therefore there is also provided a method for producing a body contacting article comprising a first layer of a natural or synthetic elastomeric material, which method comprises applying to said first layer a layer of a polymer having repeating units of the formula I, IA or II as hereinabove defined.

The method of the present invention may be employed as part of the article manufacturing process. For example, where the article is a glove such as a
surgeon's glove, the glove may be first formed by a conventional dipping procedure wherein a suitably shaped former is first dipped into a coagulant and thereafter into a latex solution comprising the natural or synthetic elastomer, e.g. natural rubber from which the article is to be formed. After withdrawal from the dipping bath the article may then be subjected to a conventional washing or leaching step prior to application of the polymer layer.

In a preferred aspect of the process of the present invention the formation of the polymer layer on the natural or synthetic elastomer surface takes place prior to final curing of the elastomer. Thus in a conventional glove dipping process, the process train may be modified by incorporating the process of the invention as an intermediate step between the leaching and curing steps.

Thus in accordance with an embodiment of the invention there is provided a process for the production of dipped articles in which a layer of a polymer having repeating units of formula (I), (IA) or (II) is applied to a natural or synthetic elastomer surface of the article prior to final curing of the rubber article.

Aptly, the polymer may be applied to the elastomer surface as a solution. Suitably the solution employed is an alcoholic solution. Preferred alcohols for forming the polymer solution include alkanols such as ethanol and isopropanol.

The polymer content in such solutions should not be more than 50% by weight of the solution, aptly up to about 15% by weight of the total solution, and preferably up to about 8% by weight. Generally, the polymer contact of the solution will be at least 2% by
weight of polymer. Preferably polymer contents of from 4 to 6% by weight may be used.

The elastomers can be obtained as latices, which can then be dipped and coated. Cosolvents can be used in the preparation of the latices and the elastomer may be initially present in an emulsion, e.g. a polyurethane emulsion.

The polymer layer may be formed by conventional solution coating procedures but is aptly formed by dipping the article into a solution of the polymer.

The polymer solution may be employed at temperatures below the boiling range of the polymer solvent and may suitably be used at ambient temperatures.

Although the polymer may be used alone, additional hydroxyl containing compounds may be added to the polymer solution. Aptly such hydroxyl containing compounds may include water or polyhydroxy compounds such as polyethylene glycol.

Aptly water may be present in the polymer solution in amounts up to 50% by weight based upon the weight of the solution.

Preferred polyethylene glycols for inclusion with polymers having repeating units of formula (I), (IA) or (II) are those commercially available under the tradename CARBOWAX. Polyhydroxy compounds, as typified by the carbowaxes, may be present in amounts up to about 30% by weight of the polymer aptly in amounts up to 10%, possibly up to 5%, up to 1% or up to 0.5% by weight of the polymer.

After application of the polymer layer, the article may be dried and cured according to conventional procedures.

The article may thereafter be subjected to post-
curing treatments such as halogenation in order to impart desired physical properties to the product. We have found that further improvements in the hand donning properties may be obtained by treatment with an agent such as a surfactant. An apt surfactant for use with the invention is cetyl pyridinium chloride (CPC). Although this surfactant may be employed alone, it may suitably be employed as a complex with a long chain acid, more suitably with a fatty acid. Preferred fatty acids include stearic acid. Lauric acid is especially preferred. CPC in admixture with fatty acid derivatives such as lauryl sulphonate may also be used but these mixtures are less preferred.

Suitable complexes may be formed by adding each of the constituents to water and applying the aqueous complex to the article. A preferred complex may be formed by admixing CPC and lauric acid in water and heating such that each constituent is present in amounts of about 2% by weight of the aqueous complex.

The complex may be applied either by spraying it onto the elastomer surface of the article or by immersing the article in the aqueous complex. Suitably the complex is applied at elevated temperature. Spraying is preferred. In a preferred embodiment the spraying is carried out at elevated temperature, aptly at about 130°F. Dipping applications may be carried out at temperatures of about 100°F.

Other donning aids such as silicones used either along or in combination with the CPC containing complexes may also be used with advantage.

Thereafter the treated article is dried.

Examination of the elastomer surface and the
polymer layer thereon, for example by a Scanning Electron Microscope (SEM) shows the polymer to be distributed over the whole of the rubber surface.

The articles of the invention may have flat polymer coatings. However, in preferred form of the invention, the polymer layer, whilst being continuous has raised areas (domains) which are thicker than the surrounding polymer layer. In these preferred forms of the invention the thickness of the raised domains may be up to 25\(\mu\)m thicker than that of the remaining areas, favourably up to about 7\(\mu\)m thicker. The remaining areas may be less than about 8\(\mu\)m thickness, aptly between 6 and 7\(\mu\)m, more aptly less than 1\(\mu\)m.

The occurrence of raised domain architecture of the polymer surface depends mainly upon the condition of the elastomer surface to which the polymer is applied.

We have found that if the elastomer surface contains moisture, for example after the leaching stage in a conventional dipping process train, a raised domain architecture will occur when the polymer is applied. Thus it is preferred to apply the polymer between the leaching and curing stages when the articles are produced by a dipping process.

Further improvements in the donning preparation of articles such as gloves when produced in accordance with the invention have been determined when a polymer has repeating units of the formula

\([-\text{CH}_2-\text{CH(C}_6\text{H}_5)\text{-}]\) and \([-\text{CH} (\text{CO}_2\text{H})\text{CH(CO}_2\text{R}^3\text{-}]\) \text{III}

where \(R^3\) is an alkyl group. Aptly \(R^3\) is a lower alkyl group, more aptly \(R^3\) is an alkyl group, containing up to 4 carbon atoms. Suitable polymers having repeating units of formula (III) are sold under the trade name
SCRIPSETS (available from Monsanto). Preferred grades are those sold under the designations SCRIPSETS 540 and SCRIPSETS 550.

Other similar and suitable polymers may be those sold under the trade name SMA resin (available for Atochem) e.g. the polymer sold under the trade name SMA 2625, which is effective in combination with the polymers having repeating units of formula I and II.

Polymers having repeating units of formula (III) may be incorporated directly into the solution of the polymer having repeating units of formula (I), (IA) or (II). Aptly polymer (III) may present in the polymer (II) solution in an amount of greater than about 5% by weight of the total solids content of the solution. Preferably the concentration of polymer III will be about 20% by weight or less of the solution solids.

In favoured form the solution for forming the polymer layer on the article will comprise or consist essentially of 94% by weight of ethanol, 4.8% by weight of a polymer having repeating units of formula (I) or (IA) and 1.2% be weight of a polymer having repeating units of formula (III).

The surface morphology of articles having the above described modified polymer layer shows that the raised areas have further raised areas thereon.

Gloves produced with said modified layers have good donning properties especially wet hand donning properties.

In addition to having the modified polymer layer thereon, the donning properties body contact articles may further improve by the use of donning aids, for example as hereinbefore described.
The invention will now be illustrated by the following examples.

Example 1

An alcoholic coagulant solution was prepared according to the formulation:

- Industrial Methylated Spirits: 3469 lbs
- Calcium Nitrate: 71 gals (US)
- Triton X-100: 1.153 Kg
- Carbowax 600: 17.7 lbs
- Calcium Carbonate: 250 lbs
- Surfynol TG (An acetylenic surfactant): 450.2 gm

Glove formers, for moulding a surgeon's glove, were immersed in the coagulant solution for 1 minute. The temperature of the coagulated solution was maintained at 110°F.

The coagulant treated former was then dipped into a latex solution for 1 minute. The temperature of the latex was ambient temperature and the solution had the following composition:
Water  3600 lbs
Natural rubber Latex  9750 lbs
Modicol (elemental sulphur dispersion)  3 lbs
DPTT\textsuperscript{1} Dispersion  210 lbs
ZMBT\textsuperscript{2} Dispersion  46 lbs
MZ\textsuperscript{3} Dispersion  30 lbs
Lowinox\textsuperscript{4} Dispersion  148 lbs

1 - Dipentylmethylene thiuram tetrasulphide
2 - Zinc Mercaptobenzothiazole
3 - Methyl Zimate
4 - a hindered phenol antioxidant.

The final solids content of the latex solution was reduced by the addition of a further 800 lbs of water.

Upon removal from the latex solution the coated formers are then immersed in a leaching bath, maintained at 160°F, for 2 minutes.

The leached coated formers were immersed in a polymer bath, maintained at ambient temperature before passage to a curing oven where they were dried at 240°F for 20 minutes.
The polymer solution was prepared by diluting an ethanolic solution of GANTREZ ES-425 copolymer to 4% by weight solids content with industrial methylated spirits. GANTREZ ES-425 has repeating units of Formula (II) in which \( R^2 \) is a \((CH_2)_3CH_2\) group. To the 4% resin solution was added a polyethylene glycol (Carbowax 600) in an amount of 20% by weight based on the weight of the resin.

After curing all the gloves were removed from the formers and subjected to a conventional halogenation procedure and then sprayed with a donning aid consisting of:

- Cetyl Pyridinium Chloride - 2% by weight
- Lauric Acid - 2% by weight
- Water qs 100%

The temperature of the spraying solution was 100°F. The gloves were then dried at 140°F for 5 minutes.

The thus produced gloves exhibit good hand donning properties.
Examples 2-5

Example 1 was repeated except that the polymer solution consisted essentially of a 4% solution of GANTREZ ES 425 in industrial methylated spritis. The thus treated polymer gloves were subjected to the post treatments summarised in the following table.

<table>
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<tr>
<th>Example No</th>
<th>Halogenation</th>
<th>CPC/Lauric Acid</th>
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<tr>
<td>2</td>
<td>Yes</td>
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<td>3</td>
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</tr>
<tr>
<td>4</td>
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<td>5</td>
<td>No</td>
<td>Yes</td>
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</table>

The thus produced gloves exhibit good hand donning properties.

Example 6

Examples 2-5 were repeated except that the polymer solution consisted of:

GANTREZ 425 - 4.8% by weight
SCRIPTSET 550 - 1.2% by weight
Industrial Methylated Spirit - 94% by weight

The gloves thus produced exhibited good wet and dry hand donning properties.
The surface morphology of gloves produced in accordance with Examples 3 and 6 was examined together with that of a control sample which is a conventional halogenated glove having no polymer treatment in accordance with the invention.

Surface roughness measurements and surface traces were obtained by surface profilometry using a Rank Taylor-Hobson TALLYSURF 10 profilometer.

Glove samples were taken from the middle finger of each glove for the control samples and the glove of Example 3 the amplification (V_v) was x5000 whereas (because of the increase in difference between the lowest and highest points of the probe) that for the glove for Example 6 was V_v = x1000. The V_h setting was 0.8mm (cut-off) in each case.

The surface roughness (averaged in three readings) was

Example 3  -  0.55 \mu m
Example 6  -  2.92 \mu m
Control  -  0.49 \mu m
Fig. 1 in the accompanying drawing depicts the surface trace for each glove over a length of 3cm ($V_h \times 10$ and $V_v \times 1000$).

**Example 7**

**The Application of Gantrez ES-425/Scripset 540 Coatings to Synthetic Latices**

The synthetic latices shown in table 1 below, were coagulation dipped, as described below, and coated with a solution (an industrial Methylated Spirits) of 2.8% by weight GANTREZ ES-425, 1.2% by weight SCRIPTSET 540 and 0.8% by weight CARBOWAX 600 (referred to as 70/30 blend of Gantrez ES-425 and Scripset 540).

**Table 1**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Polymer</th>
<th>Brand Name</th>
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<tr>
<td>1</td>
<td>Polychloroprene</td>
<td>Neoprene 671</td>
<td>Du Pont</td>
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<tr>
<td>2</td>
<td>Styrene butadiene Rubber</td>
<td>Revinex 26W10</td>
<td>Doverstrand</td>
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<tr>
<td>3</td>
<td>Nitrile rubber</td>
<td>Revinex 99G41</td>
<td>Doverstrand</td>
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<td>4</td>
<td>Polyurethane</td>
<td>BIP L9009</td>
<td>BIP</td>
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<tr>
<td>5</td>
<td>Polyurethane</td>
<td>Cydrothane HP5035</td>
<td>Cyanamid</td>
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Preheated (to 115°C) ceramic glove formers were used to prepare coated latex gloves using the steps shown in Table 2. All the dipping operations were carried out by hand.

### Table 2

<table>
<thead>
<tr>
<th>Process Details</th>
<th>Temperature</th>
<th>Time</th>
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<tr>
<td>Dip into coagulant(^1)</td>
<td>60°C</td>
<td>Zero dwell</td>
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<td>Air Dry</td>
<td>Room</td>
<td>1 min</td>
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<tr>
<td>Dip into latex(^2)</td>
<td>Room</td>
<td>10 sec dwell</td>
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<tr>
<td>Air dry</td>
<td>Room</td>
<td>1 min 30sec</td>
</tr>
<tr>
<td>Dip into leach(^3)</td>
<td>70°C</td>
<td>2 min dwell</td>
</tr>
<tr>
<td>Air dry</td>
<td>Room</td>
<td>1 min</td>
</tr>
<tr>
<td>Dip into coating(^4)</td>
<td>room</td>
<td>zero dwell</td>
</tr>
<tr>
<td>Air dry</td>
<td>Room</td>
<td>1 min</td>
</tr>
<tr>
<td>Oven Dry</td>
<td>115°C</td>
<td>30 min</td>
</tr>
</tbody>
</table>

(1) the coagulant consisted of calcium nitrate, calcium carbonate powder and distilled water

(2) the latices were used in their as supplied form

(3) the leach consisted of distilled water

(4) the coating solution consisted of a 70/30 blend of Gantrez ES-425 and Scripset 540 dissolved in a 80/20 blend of Industrial Methylated Spirits (IMS) and
Isopropyl alcohol (IPA). Samples were dipped only half way in the coating solutions.

Both the coated and uncoated latex surfaces were examined using optical microscopy. This revealed that roughened coatings were present on the synthetic latices. These roughened coatings, give rise to good damp hand donning performances.

**Example 8**

*The Application of a Range of Partly Esterified Maleic Anhydride Derived Polymers to Natural Rubber (NR) Latex*

The polymers listed below were applied onto coagulation dipped natural rubber latex surfaces.

1. Gantrez ES 225 (Acid primed latex)
2. Isopropyl half ester of Gantrez AN169
3. Propoxethyl half ester of Gantrez AN169
4. n-Hexyl half ester of Gantrez AN169
5. n-Nonyl half ester of Gantrez AN169
6. n-Butyl half ester of polyethylene/maleic acid
7. SMA 2625

Preheated (to 115°C) ceramic glove former were used to prepare samples using the procedure set out in Table 3 below. The dipping operations were carried out on the Cotswold Dipping Machine and Glove Coating Rig.
Table 3

<table>
<thead>
<tr>
<th>Process Details</th>
<th>Temperature</th>
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<td>Dip into coagulant¹</td>
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<tr>
<td>Air dry</td>
<td>Room</td>
</tr>
<tr>
<td>Dip into latex²</td>
<td>Room</td>
</tr>
<tr>
<td>Air dry</td>
<td>Room</td>
</tr>
<tr>
<td>Dip into leach³</td>
<td>70</td>
</tr>
<tr>
<td>Air dry</td>
<td>Room</td>
</tr>
<tr>
<td>Dip into coating⁴</td>
<td>Room</td>
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<td>Air dry</td>
<td>Room</td>
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<tr>
<td>Oven dry</td>
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(1) the coagulant consisted of calcium nitrate, calcium carbonate powder and distilled water.
(2) the latex used was as supplied Perry Style 42 or Dermaguard latex.
(3) the leach consisted of distilled water.
(4) the coating solutions used consisted of 4 to 6% polymer solids dissolved in Industrial Methylated Spirits.

Satisfactory hand donning characteristic results were obtained with the isopropyl half ester of Gantrez AN169 and with the n-butyl half ester of polyethylene/maleic acid. The other materials gave even better results.

Example 9

A glove former for moulding a surgeon's glove was dipped into Witco # A 127-71 polyurethane without coagulant. The resulting film was dried for 5 mins at 130°F and then overdipped with an overdip formulation, comprising:-
2.8% Gantrez ES-425
1.2% Scripset 540
0.8% Carbowax 600

Examination of the Gantrez-Scripset surface by scanning electron microscope was carried out and the results are shown in Figures 2 (40 x magnification) and 3 (100 x magnification), from which it can be seen that domains were formed. The glove was found to exhibit good hand donning properties.

**Example 10**

The process described in Example 9 was repeated, but using Du Pont Neoprene 571 latex instead of polyurethane and including an extra step of dipping the glove former in coagulant and drying it before dipping into the Neoprene latex.

Examination of the Gantrez-Scripset surface by scanning electron microscope was carried out and the results are shown in Figures 4 (150 x magnification) and 5 (500 x magnification), from which it can be seen that domains were formed. The glove was found to exhibit good hand donning properties.

**Example 11**

The process described in Example 9 was repeated but using Reichhold Nitrile (TYLAC 68-060-00) latex instead of polyurethane and using 12 dips into the latex instead of 1. A further difference was that after drying the nitrile coating and before overdipping the sample was leached at 160°F for 2 mins.

Examination of the Gantrez-Scripset surface by scanning electron microscope was carried out and the results are shown in Figures 6 (150 x magnification)
and 7 (500 x magnification), from which it can be seen that domains were formed. The glove was found to exhibit good hand donning properties.

Additional detail of some of the abovementioned coating polymers is given below:

**Gantrez ES-225 and Half Esters of Gantrez AN169** are believed to contain repeating units of the formula:

```
               OCH₃
              |    
CH₂ – CH — CH — CH — 
    |    |    |    |    
CO₂H  CO₂R
```

where R = ethyl (ie. Gantrez ES-225)
- R = isopropyl
- R = Propoxyethyl
- R = n-pentyl
- R = n-hexyl
- R = n-octyl
- R = n-nonyl

**n-Butyl Half Ester of Poly/ethylene/maleic acid** is believed to contain repeating units of the formula:

```
\[ \text{CH}_2 - \text{CH} \] \quad \text{and} \quad \text{CH} \quad \text{CH} \\
\text{CO}_2\text{H} \quad \text{CO}_2\text{C}_4\text{H}_9
```

Scripset 540 and 550 and Butylated Scripset 520 are believed to contain repeating units of the formula:-

\[ \begin{array}{c}
\text{CH}_2 - \text{CH} \quad \text{CH} - \text{CH} \\
\text{CO}_2 \text{H} \quad \text{CO}_2 \text{R}
\end{array} \]

where \( R = n\text{-butyl} \) (for Scripset 540)
\( R = \text{ethyl/n-butyl mixture} \) (for Scripset 550)
\( R = n\text{-butyl} \) (for Butylated Scripset 520)

for Butylated Scripset 520 the ratio of the number of the first units to the number of the second units is 1:1, Scripsets 540 and 550 the ratio is 1:<1.

SMA 2625 is believed to be

\[ \left[ \begin{array}{c}
\text{CH}_2 - \text{CH} \quad \text{CH} - \text{CH} \\
\text{CO}_2 \text{H} \quad \text{CO}_2 \text{R}
\end{array} \right]^m \]

where \( m = 1 \) to 3
\( n = 6 \) to 8

where \( R \) is a low alkyl group.
1. A body contacting article which comprises a first layer of a natural or synthetic elastomer and thereupon a layer of polymer comprising repeating units of the formula:

\[-\text{CH}_2-\text{CH(OR)}-\] \text{and} \[-\text{CH(CO}_2\text{H)}-\text{CH(CO}_2\text{R}^1)-\] (I)

\[-\text{CH}_2-\text{CH(R}^4)-\] \text{and} \[-\text{CH(CO}_2\text{H)}-\text{CH(CO}_2\text{R}^1)-\] (IA)

wherein \(R\) is a lower alkyl group and \(R^1\) is a lower alkyl group or a (lower) alkoxy (low) alkyl group, and \(R^4\) is hydrogen or a phenyl group.

2. An article according to claim 1, wherein \(R\) is a methyl group.

3. An article according to claim 2, wherein \(R^1\) is a propyl or butyl group.

4. An article according to claim 2, wherein \(R^1\) is a \(-(\text{CH}_2)_3\text{CH}_3\) group.

5. An article according to any one of claims 1 to 4, wherein said polymer layer comprises a polymer having repeating units of formula (I) or (IA), wherein \(R\) and \(R^1\) are as defined in any one of claims 1 to 4 and a polymer having repeating units of the formula:

\[-\text{CH}_2-\text{CH(C}_6\text{H}_5)-\] \text{and} \[-\text{CH(CO}_2\text{H)}-\text{CH(CO}_2\text{R}^3)-\] (III)

wherein \(R^3\) is an alkyl group.

6. An article according to any one of the preceding claims, wherein said elastomer comprises natural rubber, a polychloroprene, a nitrile rubber, a styrene-butadiene rubber or a polyurethane.

7. A surgeon's glove which comprises a glove comprising a natural or synthetic elastomer, which has on the hand contacting surface thereof a layer of
polymer comprising repeating units of the formula:

\[ (-\text{CH}_2-\text{CH}(\text{OCH}_3)-) \text{ and } (-\text{CH}(\text{CO}_2\text{H})\text{CH}(\text{CO}_2\text{R}^2)-) \] (II)

wherein \( \text{R}^2 \) is a lower alkyl group.

8. A glove wherein \( \text{R}^2 \) is a \( -(\text{CH}_2)_3\text{CH}_3 \) group.

9. A glove according to claim 7 or 8, wherein said polymer layer comprises a polymer having repeating units of formula (II) wherein \( \text{R} \) and \( \text{R}^1 \) are as defined in claim 1 and a polymer having repeating units of a polymer of formula (III) where \( \text{R}^3 \) is as defined in claim 5.

10. A glove according to any of claims 7 to 9, wherein said elastomer comprises natural rubber, a polychloroprene, a nitrile rubber, a styrene butadiene rubber or a polyurethane.

11. A method for production of a body contacting article which article comprises a first layer of a natural or synthetic elastomer which method comprises forming a layer of a polymer comprising repeating units of the formula:

\[ (-\text{CH}_2-\text{CH}(\text{OR})-\text{H}) \text{ and } [\text{CH}(\text{CO}_2\text{H})\text{CH}(\text{CO}_2\text{R}^1)-] \] (I)

or \[ (-\text{CH}_2-\text{CH}(\text{R}^4)-) \text{ and } [\text{CH}(\text{CO}_2\text{H})\text{CH}(\text{CO}_2\text{R}^1)-] \] (IA)

wherein \( \text{R}, \text{R}^1 \) and \( \text{R}^4 \) are as defined in any one of claims 1 to 4, upon said first layer of natural or synthetic elastomer.

12. A method according to claim 11, wherein the first layer is derived from a latex.

13. A method according to claim 11 or 12, wherein the polymer is applied as a solution in ethanol or isopropanol.

14. A method according to claim 13, wherein the
polymer content is from 4 to 6% by weight of the polymer solution.

15. A method according to claim 13 or 14, wherein the polymer solution contains at least one other hydroxyl compound selected from water and a polyethylene glycol.

16. A method according to any one of claims 11 to 15, wherein the polymer further comprises a polymer having repeating units of the formula:

\[ \text{[-CH}_2\text{-CH(C}_6\text{H}_5\text{-]} \text{ and [-CH(CO}_2\text{H)}\text{-CH(CO}_2\text{R}^3\text{-]} \text{ (III)} \]

wherein \( R^3 \) is an alkyl group.

17. A method according to claim 16, wherein the polymer comprises up to 20% by weight of a polymer having repeating units of formula (III).

18. A method according to any one of claims 11 to 17, wherein the polymer layer is treated with a surfactant comprising a mixture of cetyl pyridinium chloride and lauric acid.

19. A method as claimed in any one of claims 11 to 18, wherein the elastomer comprises natural rubber, a polychloroprene, a nitrile rubber, a styrene butadiene rubber or a polyurethane.

20. A surgeon's glove according to any one of claims 6 to 10, wherein the polymer layer is continuous and has raised areas.

21. A body contacting article which comprises a first layer of rubber and thereupon a layer of polymer comprising repeating units of the formula:

\[ \text{[-CH}_2\text{-CH(OR)-]} \text{ and [-CH(CO}_2\text{H)}\text{-CH(CO}_2\text{R}^1\text{-]} \text{ (I)} \]

wherein \( R \) is a lower alkyl group and \( R^1 \) is a lower
alkyl group.

22. A surgeon's glove which comprises a rubber glove which has on the hand contacting surface thereof a layer of polymer comprising repeating units of the formula:

\([-\text{CH}_2\text{-CH(OCH}_3\text{-)}\] and \([-\text{CH(CO}_2\text{H)}\text{-CH(CO}_2\text{R}^2\text{-)}\]) (II)

23. A method for production of a body contacting article which article comprises a first layer of rubber which method comprises forming a layer of a polymer comprising repeating units of the formula:

\([-\text{CH}_2\text{-CH(OR)-)}\] and \([\text{CH(CO}_2\text{H)}\text{-CH(CO}_2\text{R}^1\text{-)}\]) (I)

wherein \(R\) is a lower alkyl group and \(R^1\) is lower alkyl group, upon said first layer of rubber.

24. A body contacting article as claimed in any one of claims 1 to 6, 21,22 or 23 which comprises a surgeon's glove.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC(5) :B32B 25/04, 25/12
US CL :428/492, 494; 526/319, 329.6
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
U.S. : 428/492, 494; 526/319, 329.6

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>US, A, 4,879,348 (HENTON) 07 November 1989</td>
<td>1-5,7-9,11-15,21-23</td>
</tr>
<tr>
<td>A</td>
<td>US, A, 3,879,496 (PAXTON) 22 April 1975</td>
<td>1-5,7-9,11-15,21-23</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C. See patent family annex.

*A* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be part of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
27 NOVEMBER 1992

Date of mailing of the international search report
09 FEB 1993

Name and mailing address of the ISA/Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. NOT APPLICABLE

Authorized officer
DUC TRUONG
Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet)(July 1992)*
# INTERNATIONAL SEARCH REPORT

**International application No.**
PCT/US92/08575

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  
   - **Claims Nos.:**  
     - because they relate to subject matter not required to be searched by this Authority, namely:

2.  
   - **Claims Nos.:**  
     - because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3.  
   - **Claims Nos.:** 6, 10, 16-20, 24  
     - because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1.  
   - **As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.**

2.  
   - **As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.**

3.  
   - **As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:**

4.  
   - **No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:**

**Remark on Protest**

- **The additional search fees were accompanied by the applicant’s protest.**
- **No protest accompanied the payment of additional search fees.**

Form PCT/ISA/210 (continuation of first sheet(1))(July 1992)*
B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

CAS
APS: s vinyl methyl ether and (maleic ester? or maleate?) and copolymer? and polymer? and layer? and solution? and cetyl pyridinium chloride? and lauric acid? and surfactant? and water and polyethylene glycol?