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HEAT STERILIZABLE ELASTIC FILM BACKED BANDAGE

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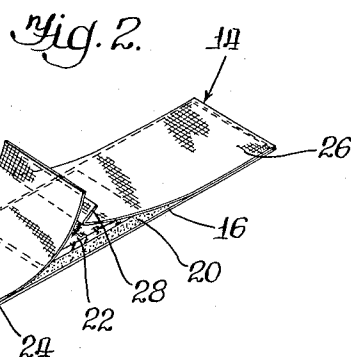
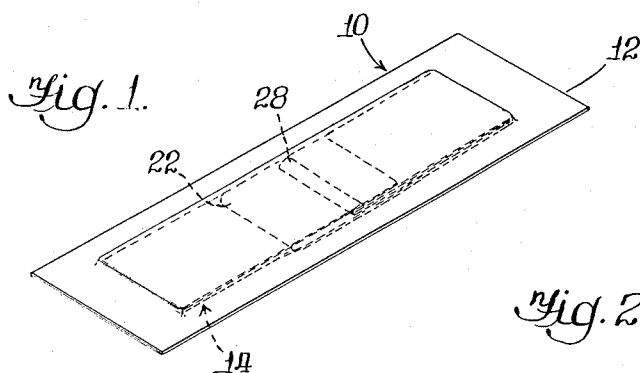


Fig. 3.

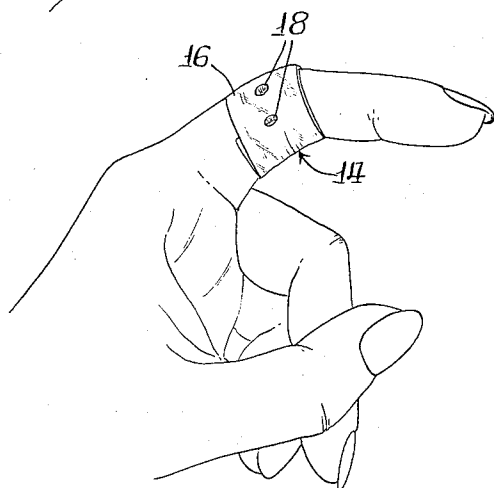
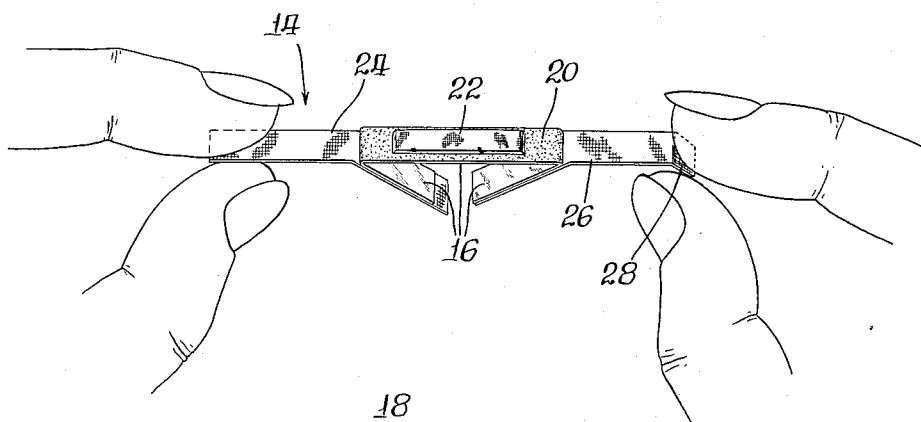


Fig. 4.

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HEAT-STERILIZABLE ELASTIC FILM BACKED BANDAGE

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12 Claims. (Cl. 128—156)

This invention is concerned with sterilizable, and sterilized, adhesive ready-to-apply bandages of the type comprising a pad dressing and an adhesive backing strip. The invention is concerned particularly with such bandages having relatively unstretched but easily stretchable polymeric elastic film backings.

Elastic bandages of the woven elastic thread type and of the over-twist thread type have been utilized from time to time to provide bandages having elasticity of a sort but these bandages have been unsatisfactory because of their bulkiness and because they soon became dirty, wet and stained. The provision of a comparatively non-porous bandage not easily soiled or stained which has an elastic character with sufficiently low modulus as to be almost like a second skin has long been a goal of the ready-to-apply bandage industry. Bandages with elastic plastic film backings would appear to provide the answer which the industry was seeking. Unfortunately, hitherto, there have been serious difficulties in using such films in adhesive bandages.

In the United States, ready-to-apply adhesive bandages are required by the Food and Drug Administration to be individually wrapped and sterile. Because heat is the means universally used for positive after-packaging sterilization, it is desirable, if possible, that such positive means be utilized in sterilizing elastic plastic ready-to-apply bandages. Up until bandages made in accordance with this invention were introduced, however, no such sterilized bandages were commercially available because of no practical solution of inherent difficulties which cause unsightly distortion and deleterious physico-chemical changes in such bandages during and following exposure to sterilization temperatures.

It is the object of this invention to provide bandages comprising dressing material adhered to elastically conformable but substantially undistorted polymeric film backed adhesive tapes having low modulus (within the range of from 1000 to 2400 pounds per square inch of cross sectional area) at 100% elongation, which after manufacture may be subjected to ordinary heat-sterilization temperatures without appreciable distortion or change in dimensions and without substantial physico-chemical deterioration.

The invention is illustrated in the accompanying drawings, in which:

Figure 1 is a plan view in perspective of a sterilized bandage in an envelope,

Figure 2 is a plan view in perspective of a bandage after removal of the wrapper,

Figure 3 is a perspective view showing the adhesive protective covering being removed, and

Figure 4 is a perspective view showing the bandage applied over a knuckle.

Referring to Figures 1, 2, 3 and 4, the wrapped sterilized bandage 10 indicates the condition of the bandage when received by a purchaser. After removal of the wrapper or envelope 12 the bandage 14 is seen to consist of a polymeric elastic backing 16 pierced by ventilation holes 18,

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an adherent pressure-sensitive adhesive 20, a superimposed adherent pad dressing 22 and adhesive protective strips 24 and 26. A turned back portion 28 of strip 26 facilitates removal of the strips.

Ready-to-apply bandages have as a common feature protective coverings for the pressure-sensitive adhesive such as 24 and 26. These coverings which are generally of crinoline, or some other flexible sheet material relatively easily separated from the adhesive, are usually applied as a final step prior to cutting individual bandages from a web.

As has been indicated, one of the difficulties which has confronted elastic plastic bandage entrepreneurs has been unsightly distortion of bandages by sterilization. I have discovered that the distortion in bandages brought about during heat-sterilization is due to shrinkage of the film in one dimension (with accompanying slight expansion thereof in another dimension) while the film is adherent to the protective covering which latter shrinks either none at all or in a different degree or direction. I have further discovered that such heat-initiated alterations in dimension are largely reversions approaching in degree the changes from the original dimensions caused by stretching the film in the machine direction during processing. I have found that by adhering only substantially unstretched or relaxed adhesive tape to the protective covering, the distortion due to shrinkage may be eliminated for all practical purposes.

A second difficulty which has confronted those who would provide heat-sterilized bandages having low modulus at 100% elongation, has been the practical attainment of sufficiently low tensile-stress in backings capable of physically withstanding sterilization temperatures. I have discovered that there exist three possibilities for such backings, having melting points above sterilization temperatures, namely: high molecular weight internally-plasticized polymeric films; high molecular weight polymer films plasticized with low molecular weight polymers of the same monomer; and high molecular weight polymer films plasticized with polymers of other monomers. The employment of non-polymeric plasticizers (examples of which are given in column 4, lines 13 to 21) universally used to reduce the modulus of elasticity in ordinary films must be carefully limited, as hereinafter explained, when adhesives are used with films intended for bandages which are to undergo heat-sterilization.

Of the internally plasticized group of possible backings I have found the following to be satisfactory to produce the elastic plastic film bandages having low modulus at 100% elongation, of this invention:

N-alkyl polyamides
Chlorinated and chlorosulfonated polyethylene
Polyamides containing oxo and thioxo linkages

Of the group consisting of high molecular weight polymers plasticized with low molecular weight polymers of the same monomer, films of polymerized tetrafluoroethylene and polymerized trifluoromonochloroethylene are examples of those suitable for the bandages of this invention.

The third group, which I consider most suitable for bandage backing materials of this invention, consists of high molecular weight polymers and copolymers plasticized with polymeric plasticizers of different monomers than the polymer plasticized. In this group are:

Polymerized vinyl chloride
Polymerized vinylidene chloride
Polymerized vinyl fluoride
Polymerized vinylidene fluoride
Vinyl chloride-acrylonitrile copolymers
Chlorinated polymerized ethylene
Vinyl chloride-vinyl acetate copolymers

Vinyl chloride-vinylidene chloride copolymers
Vinyl chloride-vinyl acetate and vinylidene chloride ter-
polymers

Vinylidene chloride-vinyl acetate copolymers
Polyvinyl alcohol cross-linked with hexamethylene di-
isocyanate or other cross-linking agents
Polyurethanes such as that obtained by interaction of
polyethylene glycols and hexamethyl diisocyanate and
Elastic cellulose ethers

In polymers of monomers including vinyl acetate, the
latter should not be used in excess of 15% of the total
monomer weight.

A third difficulty, which has not been fully appreciated
by some manufacturers of plastic adhesive tapes having
higher modulus characteristics in plastic backings, has
been the possibility of physico-chemical instability
brought about by interdiffusion and migration of plasti-
cizers from and between the film and the pressure-sensi-
tive adhesive. This problem has been known to exist
even under ordinary storage conditions. Solutions have
been proposed in the past but the severe effects of heat-
sterilization upon physico-chemical stability have not been
encountered by any of the plastic tapes which heretofore
have been available such as those for plastic sealing, for
anticorrosion wrappings and for electrical resistance wrap-
pings. The Oace Patent No. 2,559,990 has proposed
certain plasticizers for polymeric-backed tapes contain-
ing predominately vinyl chloride but the proposed pro-
portions of polymeric and non-polymeric plasticizers uti-
lized are not satisfactory for tapes having low modulus
at 100% elongation which are to be subjected to steriliza-
tion temperatures. I have found that it is not enough to
consider the plasticizer associated with the backing alone;
the plasticizer in the pressure-sensitive adhesive must
be considered as well.

In accordance with this invention I have discovered
that those tapes having the greatest degree of physico-
chemical stability are those in which both the backing
and the adhesive are completely free of non-polymeric
type plasticizers. Backings of the third group indicated
above may be effectively plasticized to low modulus at
100% elongation solely with from 25 to 40% based on
the weight of the backing of one of the modified or un-
modified polymerized condensation products of a poly-
hydric alcohol and a polybasic acid or with acrylonitrile
rubbers. Examples of the former are the viscous alkyl
resins which are mixtures of oil-modified polyesters of
sebacic acid and other polybasic acids sold under the de-
signation, Paraplex Resins, by the Resinous Products and
Chemical Company, Philadelphia, Pa. These resins may
presently be purchased in four molecular species by the
designations G-25, G-40, G-50 and G-60. Other plasti-
cizers in this general group are the polyglycol azelates
sold under the trade name Plastolein 9715 and X-960-R
by Emery Industries Inc., Cincinnati, Ohio, the polyethyl-
ene sebacate-azelates sold under the trade name Harflex
500 by the Hardesty Chemical Co. Inc., New York, N. Y.,
and the polyesters sold by The General Electric Com-
pany of Pittsfield, Mass., under the designations 2557
and 2559.

Of the group of acrylonitrile rubbers suitable as plasti-
cizers, examples are the butadiene-acrylonitrile copoly-
mers sold under the trade name, Hycar, by the B. F.
Goodrich Chemical Co., Cleveland, Ohio, and under
the trade name Paracril by the Naugatuck Division of the
U. S. Rubber Company, New York, N. Y.

While plastic elastic adhesive tapes preferred for the
bandages of this invention attain the greatest degree of
physico-chemical stability when only polymeric plasti-
cizers are used in both the adhesive and the backing, I
have obtained acceptable results when an amount of
non-polymeric plasticizer not more than of the order of
3% of the total weight of the backing and adhesive is
utilized where the ratio between adhesive weight to the
total weight varies from 20 to 40%. Such small amounts

of non-polymeric plasticizer appear insufficient to ma-
terially change the optimum characteristics of the tape
during or after heat-sterilization. It is immaterial also
whether this amount of non-polymeric plasticizer be uti-
lized all in the plastic back, all in the adhesive or divided.
Very probably such non-polymeric plasticizers seek a bal-
ance eventually regardless of where they are initially
placed.

Of the non-polymeric type plasticizers suitable for the
tapes of the bandages of this invention to the extent of
the order of 3% of the weight of the backing and adhe-
sive, the following are examples:

Diocetyl phthalate
Butyl benzoyl benzyl phthalate
Diocetyl sebacate
Di-2-ethylhexyl adipate
Ethylene diacetate
Octyl diphenyl phosphate
Methyl Cellosolve ricinoleate
Triocetyl phosphate

Opaque or filled film backings are preferred for the
bandages of this invention but transparent unfilled films
with transparent or opaque adhesives are entirely satis-
factory.

In general, fillers useful in rubber compounding may
be used in the backings of this invention with the possible
exception of certain amphoteric and alkaline earth oxides,
especially zinc oxide, which appears to have some detri-
mental effect especially upon the vinyl chloride and vinyl-
idene chloride backings of this invention. The preferred
filler for the backings in products of this invention is
titanium dioxide. Other recommended fillers are hy-
drated silica, precipitated silica, alumina hydrate, calcium
silicate, magnesium silicate, whiting and carbon black.

All of the vinyl chloride and vinylidene chloride poly-
mers useful in the products of this invention should be
stabilized by methods well known in the vinyl film in-
dustry. Stabilizers which are useful for protection
against the deteriorating effects of heat and light are
barium ricinoleate, cadmium ricinoleate, barium 2-
ethylhexoate, cadmium 2-ethylhexoate, dibutyl tin di-
laurate, dibutyl tin maleate, dibutyl tin oxide, dibutyl di-
phenyl tin, bisglycidyl tin dilaurate, strontium ureate,
strontium naphthenate, dioctyl pyrophosphate, poly-
merized alkyl phenoxy epoxides, and glycidyl phenyl
ether.

FILMS

A preferred example of the films suitable for the prod-
ucts of this invention was prepared from a white poly-
vinyl chloride organosol material in accordance with the
following formula:

Example I

	Parts by weight
55 An emulsion copolymer of vinyl chloride and vinyl acetate containing 93-95% vinyl chloride and having a particle size of approximately 5-10 microns.....	100
A modified polymerized condensation product of a dibasic acid and polyhydric alcohol.....	45
60 Di-2 ethylhexyl phthalate.....	3
Titanium dioxide.....	10
Light and heat stabilizers.....	4.0
Calcium stearate (release agent).....	0.5
65 Dispersing agent.....	0.35
Solvent blend comprising: xylol-75%; methyl isobutyl ketone-25%.....	125

The formula was ground in a water-jacketed pebble
mill for 48 hours to a point of adequate dispersion with-
out substantial increase in viscosity.

Following deaeration and screening to remove undis-
persed pigment or resin particles, the organosol was
metered in suitable wet thickness onto a heavy super-
calendered paper by means of an adjustable floating knife

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of the type well known in the coating and spreading industry. Thereafter it was passed through a multiple zoned oven increasing in temperature from approximately 125° F. to approximately 525° F. or to such temperature as would permit adequate fusing of the polyvinyl chloride resin. After fusing, the film was one which at room temperature exhibited adequate physical characteristics of tensile, elongation, modulus of elasticity, elastic recovery and tear resistance.

Another example of a preferred type of film was prepared from a flesh-colored organosol of polyvinyl chloride material in the same manner as was used in preparing Example I but according to the following formula:

Example II

	Parts by weight
An emulsion copolymer of vinyl chloride and vinylidene chloride where the vinyl chloride content is in the range of 85-90%.....	100
Polyethylene sebacate.....	40
Octyl diphenyl phosphate.....	4
TiO ₂	10
Red organic pigment.....	0.05
Carbon black.....	0.001
Heat and light stabilizers.....	3.5
Mixed solvents.....	150.0

A further example of a preferred type of film was prepared from a white organosol from a polymer predominately vinylidene chloride in the same manner as was used in preparing Example I from the following formula:

Example III

	Parts by weight
An emulsion copolymer of vinylidene chloride and vinyl chloride containing less than 25% vinyl chloride.....	100
Polyethylene azelate-sebacate.....	35
Diocetyl adipate.....	1.5
Methyl Cellosolve ricinoleate.....	1.0
N-ethyl toluene sulfonamide.....	0.5
TiO ₂	10
Heat and light stabilizers.....	3
Calcium stearate (release agent).....	.5
Mixed solvents.....	150

PRIMERS

Because of the relatively poor anchorage which hydrocarbon adhesives achieve with some of the suitable backings, particularly the vinyl chloride and vinylidene chloride polymer backings, I prefer to utilize a primer to be applied to the backing prior to application of the adhesive. As my preferred primer I utilize the following:

Example I

	Parts by weight
Latex (55% solids) of 60-65 parts monomeric vinyl chloride polymerized with 40-35 parts butadiene acrylonitrile copolymer in 75:25 ratio.....	100
Latex (60% solids) of polymer of 2-chloro-butadiene.....	100
Dispersion of condensation products of heptaldehyde and polyamines (10% solids).....	10
Methyl cellulose ether (1200 cps.).....	1

Other primers satisfactory for use with vinyl chloride and vinylidene chloride backings and hydrocarbon adhesives are:

Example II

	Parts by weight
Latex (55% solids) of 60-65 parts monomeric vinyl chloride polymerized with 40-35 parts butadiene-acrylonitrile copolymer in 75:25 ratio.....	100
Natural rubber latex (centrifuged).....	100
Ammonium caseinate (added as solution).....	1.7

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Example III

	Parts by weight
Latex (50% solids) of a copolymerization of vinyl chloride and vinylidene chloride.....	50
Latex (55% solids) of a copolymerization of butadiene and acrylonitrile.....	50
Latex (60% solids) of a polymerized 2-chloro-butadiene.....	45
Sodium salt of polyacrylic acid (as 13% solution).....	.4

Example IV

	Parts by weight
Latex (55% solids) of a polymerized vinyl acetate.....	25
Latex (50% solids) of a polymerized vinyl chloride.....	50
Latex (60% solids) of a polymerized 2-chloro-butadiene.....	25
Morpholino abietate (10% aqueous solution).....	5.0
Carboxymethyl cellulose.....	.5

Example V

	Parts by weight
Latex (50% solids) of a copolymerization of methacrylate and butylacrylate in 1:1 ratio.....	100
Hydroxyethyl cellulose.....	.5

Example VI

Latex (50% solids) of a copolymerization in equal parts of vinyl chloride, acrylonitrile and ethyl acrylate

In addition to the above primers, that illustrated in Example I of the Oace patent above mentioned or the primer claimed in claim 1 of the Hopkins Patent No. 2,555,745 may be utilized.

ADHESIVES

As examples of adhesives preferred for the adhesive films of this invention, the following are given:

Example I

	Parts by weight
#1 pale crepe natural rubber.....	35
Dihydro abietic acid (tackifying resin).....	15
Heat treated wood rosin (tackifying resin).....	15
Zinc oxide.....	28
Polyisobutylene.....	2
Age resistors.....	3.5
Solvents, blended hydrocarbons.....	150

Example II

	Parts by weight
Polyisobutylene (high molecular weight).....	15
#1 thin pale crepe natural rubber.....	12
Factice (white).....	5
Glycerol ester of dihydroabietic acid (tackifying resin).....	15
Polyterpene resin (tackifying resin).....	10
Dihydroabietic acid (tackifying resin).....	5
Zinc oxide.....	25
Precipitated silica.....	3
Polyisobutylene (low molecular weight).....	6
Age resistors.....	3.0
White lanolin.....	1
Solvents, blended hydrocarbons.....	150

Example III

	Parts by weight
GR-S rubber-X496-SP.....	56
Pale crepe rubber.....	16
Precipitated hydrated silica.....	11
Age resistors.....	4.5
Synthetic beeswax.....	1.5
Titanium dioxide.....	8
Rosin, 40% polymerized.....	34.2
Hydrogenated rosin.....	34.2
Solvents, blended hydrocarbon.....	250

An example of a pressure-sensitive adhesive which may be applied directly to backings of vinyl chloride and vinylidene chloride is as follows:

	Parts by weight
Copolymer of methyl acrylate-ethyl acrylate-----	50
Aryl toluene sulfonamide-formaldehyde polymer (tackifying resin)-----	15
Terpene - modified phenol - formaldehyde polymer (tackifying resin)-----	10
Polyhydric alcohol ester of maleic modified heat- isomerized wood rosin (tackifying resin)-----	10
Benzoylbenzyl phthalate-----	3
Modified polymerized condensation polymer of dicar- boxylic acid and polyhydric alcohol-----	12
Precipitated silica-----	8
Alkylated polyhydroxyphenol-----	3
Mixed solvents: (xylol—80%; propanol—10%; methylisobutyl ketone—10%)-----	150

The above adhesives are prepared by milling the elastomers on a chilled mill for fifteen minutes, adding the tackifying resins while heating to 220°–225° F. The mix is then transferred to a suitable internal mixing device such as the Baker-Perkins mixer where the remaining ingredients, with the exception of the solvent, are added and the whole mixed for fifteen minutes at 220°–225° F. Thereafter cooling water is circulated through the mixer jacket. The solvent blend is added slowly so as to avoid excessive loss by evaporation. When the solvent addition has been completed, the adhesive is ready for spreading.

The pad dressings of this invention may be of any conventional type or material capable of withstanding sterilization temperatures. They may be absorbent or non-absorbent, woven or non-woven, fibrous or non-fibrous. Such diverse materials as cotton gauze, synthetic fiber gauzes, felts of cotton, wool and synthetic fibers, sponges such as rubber and synthetic polymer sponges, and alginate sponges, felts and fibrous pads are representative and suitable.

The following general procedure may be employed in producing the novel bandages of this invention:

The plastic film-forming material is spread either in the form of a solution, a plastisol, an organosol or a latex onto a heavy super-calendered paper of the type generally used for preparing cast films. The film is then dried and fused (if necessary) while adherent to the paper. If a primer anchor-coat is desired, the film is run through a reverse roll spreader where it is coated with a skim coating of a suitable primer. The primer is dried either by passage through a short oven or by other conventional means. An adhesive, as previously described, is then applied to the backing in proper thickness by a suitable knife or reverse roll spreader. The combination then passes through an oven wherein the adhesive is dried. Upon emerging from this oven, the tape and the adherent paper are slit, as a unit, into widths corresponding to the lengths of the finished bandages. Each of the narrow widths is then led to a machine similar to that described in the Eustis Patent No. 2,029,260 wherein dressing materials are spotted onto the adhesive surface and the divided crinoline or other covering strips are applied with the fold-over running lengthwise. At this point the paper carrier-surface is separated from the bandage material, the paper carrier being used to intermittently pull project-

ing portions of the bandage material out beneath a cut-off knife which severs the bandage strip into successive individual bandages by cutting through the entire bandage strip including the crinoline coverings. The bandages are then wrapped and packaged after which they are heat-sterilized.

I claim:

1. A stable heat-resistant ready-to-apply bandage comprising a substantially unstretched, relaxed, polymeric film backing having a low modulus at 100% elongation, a layer of pressure-sensitive adhesive and an adherent pad dressing, said backing and adhesive together containing a total of not more than the order of 3% by weight of non-polymeric plasticizer for said backing.

2. A bandage as claimed in claim 1 wherein the bandage is heat-sterilizable.

3. A bandage as claimed in claim 1 wherein the adhesive is a hydrocarbon-elastomer pressure-sensitive adhesive.

4. A bandage as claimed in claim 1 wherein the adhesive is a polymeric acrylic elastomer pressure-sensitive adhesive.

5. A bandage as claimed in claim 1 wherein the polymeric film backing includes an internally plasticized polymer.

6. A bandage as claimed in claim 1 wherein the polymeric film backing includes a polymer plasticized by a polymer of different monomeric origin.

7. A bandage as claimed in claim 1 wherein the polymeric film backing includes a polymer plasticized by a lower molecular weight polymer of the same monomeric origin.

8. A bandage as claimed in claim 1 wherein the polymeric film backing includes a polymer plasticized by a polymer of different monomeric origin derived from a condensation product of a polyhydric alcohol and a polybasic acid.

9. A bandage as claimed in claim 1 wherein the polymeric film backing includes a polymer of monomers including a major proportion of vinyl chloride plasticized by a polymer of different monomeric origin.

10. A bandage as claimed in claim 1 wherein the polymeric film backing includes a polymer of monomers including a major proportion of vinylidene chloride, plasticized by a polymer of different monomeric origin.

11. A bandage as claimed in claim 1 wherein the polymeric film backing and the layer of pressure-sensitive adhesive constitute a transparency.

12. A bandage as claimed in claim 1 wherein the polymeric film backing includes a polymer of monomers including a major proportion of vinyl chloride plasticized with 25 to 40% of the total weight of the backing of a polymeric plasticizer derived from a condensation product of a polyhydric alcohol and a polybasic acid.

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