

Resilient Cellular Polymers Comprising the Reaction Product
of an Amine Terminated Poly (Alkylene Oxide) and an Epoxy Resin

Background of the Invention

5 This invention concerns providing resilient cellular polymers
suitable for use in products for absorbing body fluids such
as sanitary napkins, catamenial tampons, diapers, bandages
and surgical dressings. Such materials, commonly referred
10 to as foams, have already been considered for use in such
products and various polymers and processes have been suggested
as suitable. For example, newly developed polyurethane foams
have been considered as well as polyester foams and cellulose
foam.

15 While, in the main, such prior suggested foams have been
capable of absorbing body fluids to varying degrees, the
properties of these prior materials have fallen short of
those preferred for products such as are considered
20 herein. Ideally, for a product such as a diaper,
sanitary napkin or catamenial tampon, a foam material
should provide substantial capacity for absorbing body
fluids. The foam should be resilient and soft so as to
provide user comfort and conform to the body as the user
25 exerts stress on the product when worn. The foam should
be able to efficiently carry fluid deposited on its
surface into the body of the foam, i.e. the foam should
exhibit efficient wicking. Needless to say, the foam
should consist solely of biologically acceptable material.

30 Prior suggested foams have, in one respect or another,
fallen short of these ideal properties. For example,
cellulose and polyvinyl alcohol foams are stiff and
uncomfortable. Polyurethane and polyvinyl chloride foams
35 are soft and resilient and may be modified to be absorbent

to a degree, but inherently lack the property of efficient wicking. Accordingly, there is a need for a cellular polymeric material, i.e. a foam, which more closely approaches ideal properties.

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Summary of the Invention

10 In accordance with this invention, a cellular polymeric material is provided which combines the desired properties of absorbency, softness, resiliency, efficient wicking and biological compatability to a degree not found in any prior material. Specifically, it has been discovered that such an absorbent, flexible, resilient cellular foam may be provided from a polymeric material which comprises the
15 reaction product of at least one epoxy resin and an amine terminated poly (alkylene oxide) being:

a) a mixture of an amine terminated (polyethylene oxide) and an amine terminated (polypropylene oxide);

20 b) an amine terminated copolymer of ethylene oxide and propylene oxide; or

c) a mixture of b) and at least one of an amine terminated (polyethylene oxide) and an amine terminated (polypropylene oxide),

25 the ratio of ethylene oxide groups to propylene oxide groups in the amine terminated poly (alkylene oxide) being from 1 to 15, and

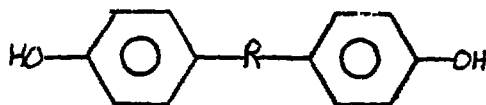
the ratio of epoxy groups to amine groups in the reaction mixture being from 1 to 3.

30 Preferably, the ratio of ethylene oxide groups to propylene oxide groups is from 3.0 to 10.0. For convenience, it is preferred that copolymers of the alkylene oxides are employed.

35 A wide variety of epoxy monomers and polymers are suitable for use and are well known in the art. It is preferred that the epoxy resin be supplied to the reaction mix such that in the aggregate, the reaction mixture comprises from 1.2 to 1.8 epoxy groups per amine group. The epoxy resins

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of choice are the di- and polyglycidyl ethers of bisphenols, the bisphenols having the formula



wherein R is a bivalent radical containing 1 to 8 atoms of C, O, S, and/or N and more preferably, an alkylene or alkylidene groups containing 1 to 8 carbon atoms or still more preferably 1 to 6 carbon atoms.

The foam is prepared by combining the reactants at room temperature or more preferably at an elevated temperature to form an intermediate reaction product which is preferably at the point in the reaction just prior to gelation. A blowing agent then is introduced to create the cells of the foam. A preferable blowing agent is one which releases CO₂ gas upon activation and, when this is used in combination with the teachings of this invention, the resulting foam advantageously exhibits a snow-white appearance.

Detailed Description of the Invention

25 The invention provides a foam which is the reaction product of amine terminated poly(alkylene oxide) and epoxy resin.

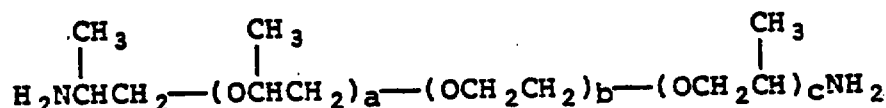
30 The amine terminated poly(alkylene oxide) may be in the form of mixtures of amine terminated poly(alkylene oxides), copolymers of alkylene oxides such as random copolymers or block copolymers, or even mixtures of the above. It is important however, that such reaction mixture be provided with a sufficiently high enough ratio of ethylene oxide groups to propylene oxide groups so that the resulting reaction product has the desired degree of hydrophilicity. On the other hand, this ratio of ethylene

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oxide to propylene oxide groups must be low enough to produce a reaction product with the desired resiliency. The range for this ratio which produces a suitably hydrophilic, resilient foam is from 1 to 15 ethylene oxide groups per propylene oxide group and preferably from 3 to 10 ethylene oxide groups per propylene oxide group.

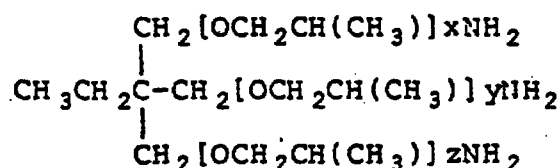
Amine terminated poly(alkylene oxide)s are commercially available, one such source being the series of polymers sold by the Texaco Chemical Company of Bellaire Texas, under the trademark "Jeffamine". A particularly useful series of Jeffamine compounds are designated by Texaco as Jeffamine ED compounds and have the structure:



These block copolymers are derived from propylene oxide-capped polyethylene glycol and are available from Texaco as compounds wherein the a, b, and c values are in the following ratios:

<u>Jeffamine Compound</u>	<u>Approximate Value of</u>	
	<u>b</u>	<u>a + c</u>
ED-600	13.5	3.5
ED-900	20.5	3.5
ED 2001	45.5	3.5

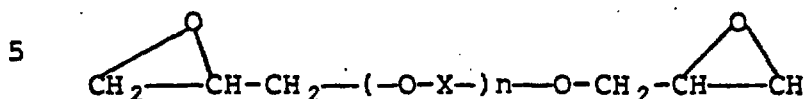
Suitable foams have also been prepared by combining these amine terminated poly(alkylene oxides) with a polyoxypropylene amine sold by the Texaco Chemical Company under the name JEFFAMINE T-403 and having the following chemical structure:



wherein the sum of $x + y + z$ is equal to about 8.3.

Many epoxy monomers and polymers are suitable for use. Such epoxy resins have already been suggested for use in providing hydrophobic foams from amine-terminated liquid polymers and are described in a European Patent Application number 80107479.0, of the B. F. Goodrich Company, claiming priority to a United States application filed on December 3, 1979, and published June 24, 1981. The epoxy resins described therein and usable in producing the resilient, absorbent, hydrophilic foams of this invention contain at least an average of 1.7 epoxy groups per molecule, more preferably from 1.7 to 4 epoxy groups per molecule, and even more preferably from 1.7 to 2.3 epoxy groups per molecule. The epoxy resins may be liquids or low-melting solids but are preferably liquids having a bulk viscosity from 200 centipoises to 2,000,000 centipoises, measured using a Brookfield RVT viscometer at 25°C. The epoxy resins can have an epoxy equivalent weight, i.e. gram molecular weight per epoxy group, from 70 to 6,000, more preferably from 70 to 2,000. Examples of suitable polyglycidyl esters of polycarboxylic acids include the diglycidyl ester of linoleic dimer acid and the triglycidyl ester of linoleic trimer acid. Suitable glycidyl ether resins include polyallyl glycidyl ether, the diglycidyl ether of chlorendic diol, the diglycidyl ether of dioxanediol, the diglycidyl ether of endomethylene cyclohexanediol, epoxy novolac resins, alkanediol diglycidyl ethers and alkanetriol triglycidyl ethers.

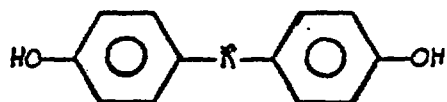
More preferred glycidyl ether resins include alkanediol diglycidyl ethers having the formula



wherein X is an alkylene or alkylidene group containing from 1 to 10 carbon atoms, more preferably from 2 to 6 carbon atoms, and n is from 1 to 25, more preferably from 1 to 15. Suitable alkanediol diglycidyl ethers include ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether and butanediol diglycidyl ether.

Other more preferred glycidyl ether resins include alkanetriol triglycidyl ethers wherein the alkane group contains from 2 to 10 carbon atoms, more preferably from 3 to 6 carbon atoms, such as glyceryl triglycidyl ether or the triglycidyl ether of trimethylolpropane.

This class of glycidyl ether resins produces a foam, in accordance with the teachings of this invention, which is soft, absorbent and resilient. Unfortunately, this group reacts disadvantageously slowly. A most preferred class of glycidyl ether resins is the di- and polyglycidyl ethers of bisphenols, the bisphenols having the formula



wherein R is a bivalent radical containing 1 to 8 atoms of C, O, S and/or N, more preferably an alkylene or alkylidene groups containing 1 to 8 carbon atoms, and even more preferably an alkylene or alkylidene groups containing 1 to 6 carbon atoms. Examples of suitable bisphenols include methylene bisphenol, isopropylidene bisphenol, butylidene bisphenol, octylidene bisphenol, bisphenol

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sulfide, bisphenol ether and bisphenol amine
Excellent results were obtained using isopropylidene
bisphenol. The latter epoxy resin not only produces a
foam with the desired properties but also is quite
5 reactive and is most suitable for use in connection with
the teachings of this invention.

The proportions of epoxy resin to amine terminated
poly(alkylene oxide) in the reaction mixture may vary over
10 a substantial range. The ratio of active
epoxy groups to amine groups ranges from 1 to 3.
Preferably this ratio varies from 1.2
to 1.8 epoxy groups per amine group.

15 The production of the foams of this invention is best
carried out using a two step process consisting of first
performing an intermediate reaction step and then foaming
the reaction mixture as polymerization continues.

20 The intermediate reaction step is carried out by first
mixing the epoxy resin and amine terminated poly(alkylene
oxide) in the proportions taught herein. The reaction
mixture is then heated and maintained at a reaction
temperature which may range from 25°C to

25 130°C. In practise, temperatures much below 50°C will
require a disadvantageously long reaction time whereas
temperatures above 110°C will result in a reaction time
which is too short and hence difficult to control.

Accordingly, a preferable temperature range is between
30 50°C and 110°C with a range of 65°C to
110°C being most preferable. As the reaction
proceeds and polymerization occurs between the epoxy resin
and the amine terminated poly(alkylene oxide), the viscosity of
the reaction mixture rises. The degree of intermediate
35 reaction may be monitored and controlled by a continuous
or incremental measurement of the reaction mixture

viscosity. Alternatively, other properties could be measured which indicate the progress of the reaction e.g. density, refractive index or mechanical or electrical properties.

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Irrespective of what properties are used to measure the progress of the reaction, as the reaction proceeds, the mixture passes from the liquid state to that of a relatively inelastic solid. The transition state between
10 liquid and solid is generally referred to as the gelation state and, ideally, it is just prior to this point in the reaction process that a blowing agent should be introduced to produce a stable foam having uniform cells. Too early an introduction of blowing agent results in the gas
15 diffusing through the relatively liquid reaction mixture and hence failing to form stable cells. Too late an introduction will result in the now substantially solidified reaction mixture being too inelastic to allow the gas to form cells.

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It has been discovered that advantageously a foaming agent is introduced when the reaction mixture reaches a viscosity of from 1000 cps to 12,000 cps (measured at 25°C). Depending primarily on the temperature at which
25 the reaction is run, typically such viscosity range can be reached in a time period of as short as 10 minutes or as long as two hours.

A wide variety of foaming agents may be employed. For
30 example, certain compounds may be introduced which release gases upon heating. Examples of this type of foaming agent are azo bis(isobutyronitrile) and benzene sulfonyl hydrazide which release nitrogen gas when heated.

35 A preferred method of foaming is to mix into the reaction mixture a compound or mixture of compounds such as sodium

carbonate or sodium bicarbonate. Upon the addition of a suitable acid or acidic salt, these compounds react to release carbon dioxide gas to perform the foaming.

Suitable acids or acid compounds include

- 5 hydrochloric acid; phosphoric acid, organic acids such as acetic, lactic and citric, sodium bisulfite, and potassium dihydrogen phosphate.

10 The foaming agents may be added to the initial copolymerization reaction mixture when such mixture is at a temperature of from 30°C to 110°C. Preferably, to have a controlled release of carbon dioxide, the reaction mixture should be at a temperature ranging from 40°C to 80°C. Accordingly, it may be
15 necessary to first reduce the temperature of the initial copolymerization reaction mix prior to adding the foaming agents. After foaming is initiated, the foaming is completed by heating, preferably in an oven for five to twenty minutes at an elevated temperature ranging
20 from 120°C to 140°C.

Examples 1-6

25 A series of foams are prepared by reacting various combinations of Jeffamine amine terminated poly(alkylene oxide) polymers with epoxy resins in an intermediate reaction step, cooling the reaction mixture, in some cases, and then combining the reaction mixture with blowing agents by mixing the blowing agents into the reaction mixture for
30 about 30 seconds. The reaction mixture is then foamed and cured by heating in an oven at various temperatures over various time intervals. Table 1 below sets out the starting reactants (in parts by weight) and conditions under which these reactants were combined in the initial
35 copolymerization step:

Table 1 - Intermediate Reaction

Sample	Jeffamine Polymer			Epoxy Resin		Intermediate Reaction Conditions				
	ED-600		ED-900	ED-2001	EPON 828*	A508**	Reaction Temp (°C)	Reaction Time (Min)	Cooling Temp (°C)	Cooling Time (Min)
	T-403									
1	7.7	42.0	--	--	39.3	--	95	15	95	--
2	12.8	8.3	--	27.7	41.6	--	110	15	80	10
3	12.3	--	--	40.4	35.2	--	125	--	70	30
4	2.8	--	36.6	--	33.8	--	130	10	70	10
5	4.7	18.4	--	--	17.3	38.6	135	10	100	10
6	--	20.0	31.1	--	44.4	--	110	10	70	15

* EPON 828 is a diglycidylether of bisphenol A sold under the tradename EPON 828 by the Shell Oil Co.

**A-508 is diglycidylether of bisphenol A diluted with an epoxidized polyol and sold under this tradename by Ciba-Geigy, Inc.

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Table 2 below sets out the foaming agents in parts per weight and the foaming and curing conditions:

Table 2 - Foaming and Curing

Sample	Foaming Agent		Foam and Cure Conditions	
	50% By Weight NaHCO ₃ in Water	50% Aqueous H ₃ PO ₄	ABIN* Mixing Temp (°C)	Curing Temp (°C) Temp (Min)
1	4.0	7.0	95	125 10
2	4.0	5.6	80	120 15
3	5.7	6.4	70	125 20
4	11.2	15.6	70	135 15
5	15.3	5.7	60	135 30
6	--	--	70	130 10

*ABIN is azo bis (isobutyronitril)

Samples 1-6 are tested to determine their various properties. Absorbency, expressed as weight of water absorbed per unit weight of dry foam, is determined by weighing a sample of the foam dry and then totally immersing the foam sample in a container of water. The sample is removed from the container and weighed without the application of external pressure. The results are reported below in units of grams of water per gram of dry foam.

Resiliency is tested by applying pressure to compress a sample of the foam to 50% of its original height and maintaining the foam in the compressed state for one minute. The pressure is then released and the foam is allowed to recover. The percent recovery, based on the original height of the uncompressed foam, after one minute of recovery is reported in Table 3 below.

The density of the foam is determined by measuring the dimension of a sample of foam, weighing the sample and reporting the density in Table 3 below as the weight, in grams, per unit volume, in cubic centimeters.

Vertical wicking is determined by immersing the tip of a foam strip measuring 6.35 X 6.35 X 50.8mm (0.25 X 0.25 X 2 inch) into a beaker of water while the strip is held vertically (i.e. the longitudinal direction is vertical) above the beaker. The time required for the water to climb 38.1 mm (1.5 inches) is recorded in Table 3 below.

Table 3 - Properties of Foam

<u>Sample</u>	<u>Absorption</u> <u>gm./gm.</u>	<u>Resiliency</u> <u>% Recovery</u>	<u>Vertical Wicking</u> <u>... secs.</u>	<u>Density</u> <u>gm./cm³</u>
1	10	99.5	76 sec.	0.14
2	--	----	-----	----
3	8	92.0	60 sec.	0.22
4	12	99.5	-----	0.67
5	8	100.0	100 sec.	0.2
6	15	98.0	-----	0.08

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Samples 7-14 (Not according to the Invention).

A series of samples are produced by using the procedure of examples 1-6 with the exception that no foaming agents are introduced, thereby resulting in reaction products in the form of films. This is done to illustrate the effects of varying the ratio of epoxy groups to amine groups (E/A) in the initial reaction mix as well as the ratio of ethylene oxide groups to propylene oxide groups (EO/PO) in the amine terminated poly(alkylene oxide) polymer. The foaming step is eliminated to avoid the variables of foam cell structure and density in illustrating how the properties vary with varying EO/PO and E/A ratios. The properties reported below in Table 4 are Young's Modulus and the Glass Transition temperature which relate to rigidity and elasticity of the reaction products. Water absorption is likewise recorded and is measured by weighing a sample of the film, and then immersing the film in water for fourteen days. The weight of water absorbed expressed as a percentage of the dry weight of the film, is reported in Table 4 below.

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Table 4

Sample	E/A	EO/PO	Young's Mod. (PSI) (MPa)	Glass Trans. Temp.: (°C)	Water Absorption %
7	1.00	3.85	160 (1.10)	-17	58
8	1.00	5.85	126 (0.85)	-35	115
9	1.17	3.85	337 (2.32)	-12	41
10	1.17	5.85	293 (2.02)	-35	85
11	1.66	3.85	600 (4.14)	+4	23
12	1.66	5.85	485 (3.34)	-22	75
13	2.03	3.85	796 (5.49)	+21	7.7
14	2.03	5.85	664 (4.57)	-15	28.8

Referring now to Table 4 and specifically to samples 7, 9, 11, and 13, it can be seen that at a constant EO/PO ratio of 3.85, as the E/A ratio increases from 1.00 to 2.03, the Young's Modulus increases from 160 to 796 and the glass transition temperature increases from -17°C to +21°C. This indicates an increasing rigidity and inelasticity with increasing E/A ratio.

Further, it can be seen that as the E/A ratio increases through the range of 1.0 to 2.03, the water absorbency decreases from 58% to 7.7%.

Similarly, when referring to samples 8, 10, 12, and 14, at a second constant value of EO/PO ratio of 5.35, the above described relationships pertain.

The above data is consistent with the discovery that the E/A ratio must be carefully balanced to produce a foamed polymer suitable for use in accordance with the teachings of this invention. At high E/A ratios the polymer is too rigid and inelastic, and concomitantly the resulting foam will be inflexible. Further, the foam will be relatively non-absorbent. At low E/A ratios the polymer is weak, extremely elastic and in some instances disadvantageously tacky. Accordingly, cell walls will collapse during foaming and curing. By operating within the range of E/A ratios prescribed herein suitable foams may be provided.

Again referring to Table 4, reference is made to the set of paired samples 7 and 8, 9 and 10, 11 and 12, 13 and 14. Each pair illustrates two samples at a constant E/A ratio, with one sample at a low EO/PO ratio and a second sample at a high EO/PO ratio. It shall be noted that as the EO/PO ratio is increased the sample becomes less rigid, more elastic and more absorbent. Again, by operating within the teachings set out herein with respect to EO/PO ratio a suitable foam may be obtained.



CLAIMS

1. An absorbent, resilient, flexible, cellular, polymeric material comprising the reaction product of at least one epoxy resin and an amine terminated poly (alkylene oxide), the amine terminated poly (alkylene oxide) being:

5 a) a mixture of an amine terminated (polyethylene oxide) and an amine terminated (polypropylene oxide);

10 b) an amine terminated copolymer of ethylene oxide and propylene oxide; or

c) a mixture of b) and at least one of an amine terminated (polyethylene oxide) and an amine terminated (polypropylene oxide),

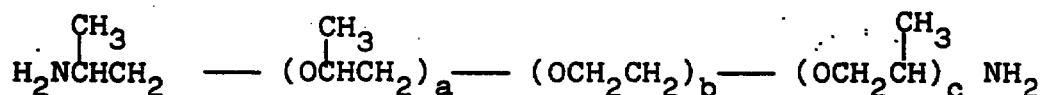
15 the ratio of ethylene oxide groups to propylene oxide groups in the amine terminated poly (alkylene oxide) being from 1 to 15, and

the ratio of epoxy groups to amine groups in the reaction mixture being from 1 to 3.

20 2. The cellular polymeric material of claim 1, wherein the ratio of ethylene oxide groups to propylene oxide groups is from 3 to 10.

25 3. The cellular polymeric material of claim 1 or claim 2, wherein the ratio of epoxy groups to amine groups is from 1.2 to 1.8.

30 4. The cellular polymeric material of any one of claims 1 to 3, wherein said amine terminated poly (alkylene oxide) comprises a compound having the empirical formula

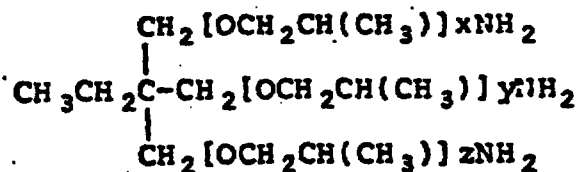


35 wherein b has an empirical value of from 10 to 50, and the sum of a and c has an empirical value of from 1 to 5.

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5. The cellular polymeric material of Claim 4,
wherein said amine terminated poly (alkylene oxide) further
comprises a compound having the empirical formula:



wherein the sum of $x + y + z$ is equal to from 7 to 10.

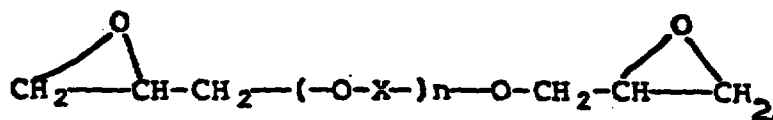
6. The cellular polymeric material of any one of claims
1 to 5, wherein said epoxy resin has an average ratio of
epoxy groups per molecule of epoxy resin of at least 1.7.

7. The cellular polymeric material of claim 7, wherein
said epoxy resin has an average ratio of epoxy groups per
molecule of epoxy resin of from 1.7 to 4.

8. The cellular polymeric material of any one of claims
1 to 7, wherein said epoxy resin comprises a polyglycidyl
ester of a polycarboxylic acid.

9. The cellular polymeric material of any one of claims
1 to 7, wherein said epoxy resin comprises a glycidyl ether
resin.

10. The cellular polymeric material of claim 9, wherein
said epoxy resin comprises an alkanediol diglycidyl ether
having the formula:



wherein x is an alkylene or alkylidene group containing
from 1 to 10 carbon atoms, and n has a value of from 1 to
25.



11. The cellular polymeric material of claim 9, wherein said epoxy resin is a di- or polyglycidyl ether of a bisphenol, said bisphenol having the formula:



wherein R is a bivalent radical containing 1 to 8 C, O, S, or N atoms.

10 12. The cellular polymeric material of claim 11, wherein R is an alkylene or alkylidene radical containing from 1 to 8 carbon atoms.

15 13. The cellular polymeric material of claim 12, wherein said epoxy resin comprises isopropylidene bisphenol.

20 14. A product for absorbing body fluids comprising as an absorbent element therein, a cellular polymeric material according to any one of claims 1 to 13.

25 15. The product of claim 14, wherein said product is a sanitary napkin, a catamenial tampon, a disposable diaper or a wound dressing.

16. An absorbent, resilient, flexible, cellular polymeric material, substantially as hereinbefore described with reference to any one of Examples 1 to 6.

30 17. A product for absorbing body fluids, containing a cellular polymeric material substantially as hereinbefore described with reference to any one of Examples 1 to 6.