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(12) (19) (CA) **Demande-Application**

(21) (A1) **2,219,628**
(86) 1996/05/04
(87) 1996/11/21

(72) BABEL, Wilfried, DE
(72) PÖRSCHKE, Ralf, DE
(72) BRÄUMER, Klaus, DE
(72) MEHNERT, Reiner, DE
(72) SCHERZER, Tom, DE
(72) HINTERWALDNER, Rudolf, DE
(71) Deutsche Gelatine-Fabriken Stoess AG, DE

(51) Int.Cl.[6] C08L 101/02, C09D 101/00, C08L 1/00, C09D 189/00, C08L 3/00, C09D 201/02, C08J 3/24, C08L 89/00, C08L 101/12, C08J 3/28, C09D 103/00
(30) 1995/05/18 (195 18 247.2) DE

(54) **MATERIAU D'ARRET RESISTANT A L'EAU**
(54) **WATER-RESISTANT BARRIER MATERIAL**

(57) L'invention a pour objet un nouveau type de matériau d'arrêt résistant à l'eau, destiné en particulier à être utilisé pour le garnissage, le formage ou la structure de couches ou de films de protection, adhésifs ou intermédiaires ou pour la production de feuilles sans supports, doté de remarquables propriétés d'arrêt vis-à-vis de milieux ambiants gazeux et/ou liquides, en particulier oxygène, air, vapeur d'eau et analogue. Une simple couche d'un tel matériau présente des degrés de perméabilité à l'oxygène et à l'eau extrêmement faibles.

(57) A new type of water-resistant barrier material is proposed. The barrier material in question is intended for use in particular for finishing, forming or building up protective, adhesive and intermediate layers or films or in the production of unsupported films with excellent barrier characteristics against gaseous and/or liquid ambient media, in particular oxygen, air, water vapour and the like. Even a single layer of the proposed material has extremely low oxygen- and water-permeability values.

PCT WELTORGANISATION FÜR GEISTIGES EIGENTUM
Internationales Büro

INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

(51) Internationale Patentklassifikation 6 :		(11) Internationale Veröffentlichungsnummer: WO 96/36653
C08F 290/06, 290/14, 299/02, C09K 3/00	A3	(43) Internationales Veröffentlichungsdatum: 21. November 1996 (21.11.96)

(21) Internationales Aktenzeichen: PCT/EP96/01862

(22) Internationales Anmeldedatum: 4. Mai 1996 (04.05.96)

(30) Prioritätsdaten:
195 18 247.2 18. Mai 1995 (18.05.95) DE

(71) Anmelder *(für alle Bestimmungsstaaten ausser US)*: DEUTSCHE GELATINE-FABRIKEN STOESS AG [DE/DE]; Gammelsbacher Strasse 2, D-69412 Eberbach (DE).

(72) Erfinder; und
(75) Erfinder/Anmelder *(nur für US)*: BABEL, Wilfried [DE/DE]; Am Linkbrunnen 39, D-69412 Eberbach (DE). PÖRSCHKE, Ralf [DE/DE]; Adalbert-Seifriz-Strasse 19, D-69151 Neckargemünd (DE). BRÄUMER, Klaus [DE/DE]; Allensteiner Strasse 6, D-69412 Eberbach (DE). MEHNERT, Reiner [DE/DE]; Mittelstrasse 8, D-04416 Leipzig (DE). SCHERZER, Tom [DE/DE]; Bernburger Strasse 15, D-04129 Leipzig (DE). HINTERWALDNER, Rudolf [DE/DE]; Kastanienstrasse 13, D-81547 München (DE).

(74) Anwälte: WÖSSNER, Gottfried usw.; Hoeger, Stellrecht & Partner, Uhlandstrasse 14c, D-70182 Stuttgart (DE).

(81) Bestimmungsstaaten: AU, CA, JP, US, europäisches Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Veröffentlicht
Mit internationalem Recherchenbericht.
Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist. Veröffentlichung wird wiederholt falls Änderungen eintreffen.

(88) Veröffentlichungsdatum des internationalen Recherchenberichts: 9. Januar 1997 (09.01.97)

(54) Title: WATER-RESISTANT BARRIER MATERIAL

(54) Bezeichnung: WASSERRESISTENTES BARRIEREMATERIAL

(57) Abstract

A new type of water-resistant barrier material is proposed. The barrier material in question is intended for use in particular for finishing, forming or building up protective, adhesive and intermediate layers or films or in the production of unsupported films with excellent barrier characteristics against gaseous and/or liquid ambient media, in particular oxygen, air, water vapour and the like. Even a single layer of the proposed material has extremely low oxygen- and water-permeability values.

(57) Zusammenfassung

Es wird ein neuartiges wasserresistentes Barrierematerial, welches im besonderen zum Ausrüsten, Ausbilden bzw. Aufbau von Schutz-, Kleb- und Zwischenschichten bzw. -filmen oder zur Herstellung von trägerlosen Folien mit hervorragenden Sperreigenschaften gegenüber gasförmigen und/oder flüssigen Umgebungsmedien, insbesondere Sauerstoff, Luft, Wasserdampf und dergleichen, geeignet ist, vorgeschlagen, welches bei nur einer Schicht geringste Sauerstoff- und Wasserdurchlässigkeitswerte aufweist.

Water-Resistant Barrier Material

The invention relates to a water-resistant barrier material that is suitable in particular for the finishing, formation or synthesis of protective, adhesive and intermediate layers or films or for the production of unsupported foils having outstanding sealing properties in relation to gaseous and/or liquid ambient media, in particular oxygen, air, water vapour and the like.

The main fields of application of the planar substrates and moulded articles or of the unsupported films that are finished or coated with such material are to be found, inter alia, in the following areas

- planar, optionally flexible packaging substrates for foodstuffs and pharmaceutical products,

- automotive engineering, aviation industry and shipbuilding

- construction engineering

- lacquering and painting sector.

With the barrier material according to the invention, both planar substrates and moulded articles consisting of metal, plastic, cellulose material and/or inorganic materials can be finished or coated and also adhesion-bonded.

In engineering the finishing of planar substrates, the coating of moulded articles with sealing layers or the formation of sealing layers in connection with the synthesis of composite materials or laminates by adhesion is a known necessity, conditioned by the material, in order that objects are protected against environmental influences and in order that their lifespan is prolonged. Protection in

relation to environmental influences has a prominent status in the national economy. In the case of packagings, in particular for the foodstuff and pharmaceutical sector but also for other high-quality goods, particularly high demands are made of the barrier-medium finishes. Particularly in the case of fillings stemming from the foodstuff and pharmaceutical sector the barrier materials have to be chemically and physically inert and must not give off any toxic substances that influence taste or odour, or undergo sensory changes as a result of such substances. Furthermore, in the case of direct or indirect contacts with fillings they must not trigger any so-called 'scalping' effects. In order to be able to achieve this objective with good sealing properties, particularly in relation to oxygen and/or water vapour, using means pertaining to the state of the art, predominantly use still has to be made of barrier materials containing solvent, water and/or monomer, such as coating compositions, lacquers. With these product groups the solvents are important auxiliary substances, in order for example to obtain barrier materials in liquid, processable states of aggregation from solid polymers and/or resins, in order thereby to be able to wet the surfaces of the material to be coated with a view to the development of adhesion.

The solvents that are necessary for this purpose are, unless it is a question of water or monomers (reactive diluents), of aliphatic and aromatic type, such as, for example, esters, ketones, toluene, xylene and the like, and have to be removed from the barrier materials after the applications. According to emission legislation and German technical regulations on clean air (TA-Luft), the released solvents have to be disposed of or recycled by means of cost-intensive techniques.

In the case of the so-called 'aqueous' barrier materials there are added, moreover, to the solvent 'water' up to 20 %

of organic solvents, which according to German technical regulations on clean air also have to be disposed of after removal.

One of the biggest disadvantages with the use by way of barrier material of polymer solutions and resin solutions that contain solvent arises from the fact that with a view to the development of sealing layers the solvent has to be removed from said material by evaporation. The evaporation or expulsion of the solvents is effected in this connection almost exclusively via the pores which form in the process. Since these pores are partly responsible for causing the permeability in respect of oxygen and water vapour, in practice, for this reason alone, several sealing layers have to be laid on top of one another in order to achieve good barrier properties. But such a processing technique for the purpose of achieving sealing layers that have a low number of pores or are non-porous is consequently exceptionally cost-intensive.

Recently solvent-free coating compositions or barrier compositions have also become known. Such compositions contain, instead of inert solvents, so-called reactive diluents or monomers that are integrated into the polymer matrix in the course of curing or crosslinking. Since in this connection it is a question of relatively low-molecular compounds, they are not only physiologically questionable but they also present characteristic, intense, negative taste and odour difficulties. The degree of crosslinking that can be achieved with them often amounts only to $\leq$ 90 %, so they are not suitable, inter alia, for the finishing of packing materials for foodstuffs and pharmaceuticals. But also in technical fields a degree of crosslinking that is too low can result in problems, above all in the resistance to environmental influences. Altogether the reactive diluents have the disadvantage that if residues thereof, also in the ppm range, are not incorporated by crosslinkage,

they have a negative influence on the adhesion at the boundary surface because they may wander like inert solvents.

Now, in order to accelerate polymerising or curing at high rates of production, several years ago polymerisable barrier materials also became known that are capable of being cured by means of ionising radiation, in particular by means of electron beams and UV rays.

To the UV-curable barrier compositions there are added photoinitiators and possibly so-called synergists, in order that they polymerise under UV rays. However, these photosensitive additives remain in the barrier layers after the curing and contaminate the environment both in the course of stacking and also upon contact with fillings and for this reason alone are also unsuitable for foodstuff and pharmaceutical packing materials, since physiologically they are to be regarded as questionable. In the case of curing or crosslinking with ionising beams or rays, such contamination problems do not exist.

However, the radiation-curable barrier compositions that are known in the current state of the art have the disadvantage overall that for processing reasons they have to contain a relatively high proportion of monomers containing (meth)acrylic groups by way of reactive diluents. These (meth)acrylic monomers may be physiologically questionable to a greater or lesser extent. Some of them are also regarded as toxic. One of the biggest disadvantages, however, is the taste- and odour-influencing component in relation to the environment, the fillings, particularly in the foodstuff and pharmaceutical sector, which is caused by contents of residual monomer, also in the case of very low ppm values.

The barrier materials described above will, either from an economic or from a technical point of view, make it difficult in future for the person skilled in the art to produce sealing-layer finishes under environmentally friendly conditions that are optimal as regards industrial hygiene, because the state of the art offers no overall solutions that comply with all requirements. Considerable demands are made precisely in the field of packagings for foodstuffs and pharmaceuticals, as can be gathered just from the recommendations of the German Federal Public Health Department (Bundesgesundheitsamt, BGA) entitled "Kunststoffe im Lebensmittelverkehr" or from the legal regulations of the Food and Drug Administration (FDA) and also from the individual laws on the environment. The additives that are necessary in conventional anti-corrosion agents may also represent an additional problem, as is described in Gächter/Müller, "Kunststoff-Additive", 2nd Edition, Hanser-Verlag, München, 1983, in Chapter 18 "Gewerbe- und lebensmittelhygienische Aspekte von Kunststoff-Additiven". These problems are made clear in particular by the article by Piringer et al on the topic "Der Einfluß von Restlösemitteln und monomeren Acrylaten aus Verpackungen auf die sensorischen Eigenschaften von Lebensmitteln", Verpackungsrundschau, Issue 8/1986, pages 53-58, since precisely the residual solvents and the acrylic monomers have a particular influence on foodstuff fillings in sensory respects. On the basis of the relative threshold values of inert solvents, acrylates and methacrylates with respect to odour and taste that are presented, it is made abundantly clear that in the case where use is made of such low-molecular compounds the latter remain beset by problems. For instance, the relative odour threshold value amounts in the case of n-butyl acrylate, for example, to around 0.002 and in the case of 2-ethylhexyl methacrylate to around 0.02 mg/kg.

Furthermore it may be said that evaluation of the legal measures and directives as regards the environment, industrial and food hygiene and the like in the European Community and also in the North-American market and Japan are very largely identical, if certain nuances in the regulations to be implemented are disregarded. Synoptic and comparative accounts have been published, inter alia, by Keener R.L., Plamondon J.E. and West A.S.: "Recent Developments in the Regulation of Industrial Chemicals in the United States and Europe", lecture RADCURE EUROPE '85, Basel/Switzerland, Organiser: AFP/SME, Dearborn, Mich. 48121, USA, and in the book by Ronald Brickman et al entitled "Controlling Chemicals: The Politics of Regulation in Europe and the United States", Cornell University Press, Ithaca, N.Y., 1985.

Conventional barrier materials which are based on various polymers and dissolved in solvent are described very extensively in the literature, such as, for example, H Kittel, "Lehrbuch der Lacke und Beschichtungen", Vols. 4, 5 and 7, Verlag W A Colomb Verlagsgesellschaft mbH, Berlin und Oberschwandorf, and therefore this state of the art need not be especially appraised.

The finishing with sealing layers of planar substrates and/or moulded articles, in particular of metals and cellulose materials, using coating agents that are free from inert solvents is likewise sufficiently well-known in industrial practice. For this purpose use has been made of coating agents in which the backbone polymers are present dissolved in reactive diluents or the base products are present in such a liquid state of aggregation that they are capable of being applied. Even if these reactive diluents and/or other liquid coreactants are integrated into the polymer matrix by curing or crosslinking, free residues are still left over, depending on the degree of crosslinking. In many cases these unincorporated residues cannot be

removed or reduced to such an extent that they conform to the legal regulations, not even by means of additional purification processes that add to the cost of the product. Since they may in addition be physiologically questionable, such barrier materials are only usable to a limited extent, in which connection the foodstuff and pharmaceutical sector has to be totally ruled out. This is necessary, in addition, purely for the reason that the filling is influenced in sensory respects - that is to say, as regards taste and odour. Although qualitative improvements can likewise be achieved by means of baking and/or post-curing in the case of substrates that are not thermosensitive, these improvements are often not sufficient to achieve the required minimum standard. Besides, a further factor is the additional cost burdens for end products as a result of such aftertreatment measures. Therefore efforts have been made to work out, with the aid of curing by beams or rays, better technical solutions which at the same time also ensure economic efficiency. On account of the minimum degree of crosslinking which cannot be achieved under economic conditions - as already mentioned above - the breakthrough that was hoped for could not be achieved with these radiation-curable coating agents.

In another European Patent Application, EP 0 184 345, (illegible), radiation-curable, thermoplastic coating compositions for wood and other substrates are described that consist of copolymerisable ethylenically unsaturated polyesters and thermoplastic polymers. In order to be able to process them as coating compositions, monomers or reactive diluents and/or inert organic solvents are necessary. Hence coating agents are presented which, although able to produce good final properties, are beset with the problems of the evaporation of the inert solvents and those associated with the contents of residual solvent and of monomers.

For the purpose of forming sealing layers, so-called hot melt coatings (Heißschmelzmassen) that are synthesised on the basis of inert resins, waxes, thermoplastics and/or elastomers have furthermore also become known. In German linguistic usage the use of the unconnected term 'heiß' ('hot') is advised against (see Römpps Chemie-Lexicon, 8th Edition, Volume 3 (1983, page 1763), therefore only the term 'melt coatings' (Schmelzmassen) will subsequently be used. Whereas the melt adhesives that are related to the melt coatings have attained considerable importance in many branches of industry, the melt coatings have remained relatively insignificant, if certain fields of application such as films for protection against corrosion are disregarded. These films for protection against corrosion are formed from a hot-dip coating consisting, inter alia, of cellulose ester, plasticiser mixtures and mineral-oil additives if, for example, tool parts, machine parts are immersed in the hot composition and are then allowed to cool. The film or coating that forms may later be pulled off without leaving any residue.

Irrespective of whether it is a question of melt coatings for coating purposes or for adhesive purposes, the thermoplastic basic raw materials, including the resins and plasticisers, are thermosensitive and subject to thermal oxidation, particularly in the presence of atmospheric oxygen. In this connection not only are the properties of the product changed but cracking products which are physiologically questionable are also formed. These associated thermal problems are paraphrased in the international jargon by the term 'heat history'. Whereas in the case of the melt adhesives it is possible to work with stabilisers and anti-oxidants, these can only be used in the case of the melt coatings when they find application in the technical field. Thermo-oxidative decomposition can also be reduced by means of a covering with protective gases such as nitrogen (N_2), for example. Another disadvantage of the

thermoplastic melt coating compositions is constituted by the relatively low softening-points, which preferably lie below +150° C, in particular below +120° C. Another disadvantage arises as a result of the fact that the backbone polymers are already present in their final state in the form of a macromolecule and therefore very high processing temperatures of +180° C to +270° C are necessary in order to achieve a sufficient wetting and hence adhesion on the different substrate surfaces. Certainly compositions do also exist that melt at lower temperature, (sic), but such compositions possess no resistance to thermal distortion and also their resistance to chemicals is not always adequate. Those melt coating compositions which are formulated on the basis of ethylene/vinyl-acetate copolymers are described, inter alia, in DE-OS 24 25 395. Other melt coatings are described in the monograph by R Jordan entitled "Schmelzklebstoffe", Volume 4a (1985) and Volume 4b (1986), HINTER-WALDNER-VERLAG, Munich. Listed among them are polyester melt coatings which are synthesised on the basis of linear copolyesters formed from terephthalic acid and/or isophthalic acid and which may range from amorphous to crystalline (DE-OS 24 14 287).

In DE-OS 19 17 788 and DE-OS 31 06 570 radiation-sensitive telomerised and acryloxy-terminated or methacryloxy-terminated polyesters are described which are preferably produced from aliphatic and cycloaliphatic polycarboxylic acids and only partially from aromatic polycarboxylic acids and multivalent aliphatic alcohols. They are markedly linear and may only be cured with beams or rays under aggravated conditions. Since in the case of linear molecules the relative spacings of the acrylic or methacrylic groups become greater with increasing molecular weights, the necessary energy demand that is needed for crosslinking or curing also increases. Despite this higher energy demand, a good thorough crosslinking, in order that a degree of crosslinking less (sic) than 90 % is achieved, is

not guaranteed. If, on the other hand, use is made of low-molecular polymers or monomers, although a relatively sufficient degree of crosslinking can be obtained, such coatings are exceptionally brittle and therefore sensitive to shocks and impacts and are not deformable. In addition, stresses may arise in the coatings in the event of loads, such stresses then resulting at least in the formation of fine hairline cracks.

The situation is analogous as regards resistances also in the case of high-molecular linear polyester, even though the cured coatings may be more viscoplastic. One of the essential main points of attack is constituted by the uncrosslinked reaction groups that are still free.

A still more significant disadvantage consists in the thermosensitivity and the rheological properties, above all when it is a question of high-molecular linear polyesters, for the latter decompose very strongly as a result of oxidation with increasing temperature.

In order to keep a tighter hold on the critical parameters associated with the 'heat history', on the one hand, and the improvement in the final properties such as, for example, resistance to thermal distortion, on the other hand, reactive melt coatings have also been proposed already. With these melt coatings it is preferably a question of adhesives and sealants which are in fact processed from a melt in analogous manner to a melt coating at temperatures $\leq 150°$ C, in particular $\leq 100°$ C, and as a result are functionally manageable at an early stage, but their crosslinking function is triggered only by the ambient moisture. In this connection it is preferably a question of polyurethane systems that cure through the action of moisture. Depending on the layer thickness and ambient moisture, curing requires between 1 and 96 hours. For industrial manufacture this is a curing phase that is out of

the question, quite apart from the fact that uncrosslinked portions of curing agent may migrate.

In European Patent EP 0 270 831 solvent-free, low-monomer or monomer-free, polymerisable melt coatings on the basis of (meth)acrylated cellulose esters and polyesters are described which may optionally, inter alia, be employed for the formation of sealing layers on planar substrates. However, in order now to be able to synthesise an effective sealing layer in relation to oxygen and water vapour, layer thicknesses of ≥ 50 µm, in particular ≥ 100 µm, are required. Despite these layer thicknesses the oxygen permeability, for example, falls only by a factor of 10 to 20 on substrates consisting of polyethylene and/or polypropylene. In the case of substrates consisting of polyesters (eg, Melinex), no improvement in the sealing properties arises. These melt coatings were also conceived for other tasks. Since these melt coatings are likewise processed at temperatures ≥ 80° C, in particular ≥ 140° C, they are likewise thermosensitive.

The reasons for the negative evaluation are certainly not to be sought solely in the so-called 'heat history' but rather in the lack of suitable raw materials on offer. In order to comply with the legal directives on improving the environment which have to be continually updated, to conform to food and industrial hygiene and to do justice to the sensory problems, more preventive measures are not sufficient on their own, since they are associated, on the one hand, with higher investment expenditure on installations, measuring instruments and the like and, on the other hand, with costly monitoring systems. Therefore, both for a better ecology and also with regard to industrial and food hygiene it is better to eliminate these existing stated problems, and those which are approaching, by removing the causes as far as possible and in the process also ensuring a high degree of economic efficiency.

Regardless of these numerous efforts it has not hitherto been possible to ascertain, from the extensive range of products and processes in accordance with the state of the art that are on offer, highly effective, foodstuff-resistant sealing layers for planar substrates or moulded articles, particularly in relation to oxygen and water vapour, that are also economic.

Independently of the barrier compositions pertaining to the state of the art which are described above and which are processed from solutions, aqueous dispersions and melts, a large number of additional barrier polymers are known in industrial practice. According to Römpps Chemie-Lexicon, 9th Edition, Volume 1, page 349, the barrier polymers can be classified as follows:

Barrier effect	Plastic
high (1st class)	.a. polyvinylidene chloride (PVDC), copolymers of acrylonitrile with styrene or acrylates
medium (2nd class)	polyamides, polyesters, polyvinyl chloride (PVC) and polyvinyl fluoride (PVF)
low (3rd class)	polystyrene and polyolefins

Processing of the barrier polymers is effected in accordance with diverse processing techniques such as, for example, by injection moulding, compression moulding, blow moulding, rotation moulding, thermoforming and the like. Since individual barrier polymers rarely possess multiple barrier properties, so-called 'composite foils' or 'composite laminates' have to be produced from different substrates by co-extrusion and/or adhesion.

The specific properties of the individual barrier polymers are adequately described in the relevant literature. A current overview of the barrier polymers is provided by William J. Korosin in "Barrier Polymers and Structures", ACS Symposium Series 423, Washington D.C., 1990, ISBN 0-8412-1762-9.

In EP-A1-0 547 551 edible films are described that consist of modified starches, gelatin, plasticiser, lipids and water. In the case of foodstuffs these films are intended to possess physical or microbial barrier properties in relation to water, dissolved substances, gas and water vapour. Depending on the type, content and film thickness, water-vapour permeabilities of ≥ 7 % are ascertained. In this connection the starch/gelatin mixture still possesses a value of 25 %. The gas-barrier properties are not substantiated by any values. A further point is that the basic materials for the films consist of multi-component mixtures which are complicated and relatively expensive to manufacture and apply. These barrier properties are unacceptable for the packing industry, particularly in the case of sensitive foodstuffs and pharmaceutical products.

For the keeping quality of perishable goods the permeability of the barrier polymers with respect to water vapour and gases is of particular importance. With this permeability it is a question not of imperfect seals in the classical sense of porosity and/or capillary holes but of so-called 'solution diffusion'. In this case the gas dissolves in the barrier polymer in a manner similar to dissolving in a liquid, migrates though it and emerges again on the other side in the form of gas. This diffusibility does not depend on the thickness of the barrier layer but exclusively on the barrier polymer. The thickness of the polymer sealing layer represents only a time factor.

In the case of barrier polymers that absorb moisture, such as, for example, polyamide, cellulose acetate, as a result of an increased degree of moisture easier diffusing of gases occurs, since the latter are also able to dissolve in the moisture itself. The barrier polymers are assessed, inter alia, in accordance with their permeability coefficients. In connection with the summary of the state of the art which has been partially described in brief, the person skilled in the art will note that the use of barrier polymers is a very complex field, both as regards processing and as regards application. In addition there are the ecological, environmental and recycling problems and the constant effort to reduce the requisite volumes of barrier polymers.

The tabulation below is a characteristic example, taken from the foodstuff and beverage sector, of the demands made of barrier materials against oxygen and water vapour in order to obtain a stability in storage of 1 year at 25° C (Plastics Engineering, May 1984, page 47).

Table 1

Foodstuff/Beverages	Estimated maximum decrease in weight Oxygen ppm	increase or Water wt-%
Canned milk, meat, baby food, beer*), wine	1 to 5	- 3
Instant coffee	1 to 5	+ 2
Canned vegetables, canned soups and canned spaghetti	1 to 5	- 3
Canned fruit	5 to 15	- 3
Nuts, snacks	5 to 15	+ 5
Dried foods	5 to 15	+ 1
Fruit juices	10 to 40	- 3
Oils	50 to 200	+ 10

*) less than 20 % loss of CO_2

The known barrier polymers possess very different sealing properties, particularly in relation to oxygen and water vapour. Only in a few applications do they provide the required sealing properties in the form of a single layer. Now in order to be able to satisfy the catalogue of requirements of the packing industry, amongst which not just the sealing properties alone are numbered, predominantly so-called multiple coatings, composite foils or laminates have to be produced from the barrier polymers and/or the surfaces of such coatings, foils or laminates have to be metallised. Only with the aid of these measures can sealing properties

be achieved that are comparable to those of aluminium foils. But technical and economic limits are laid down for such multilayer composites, because

- the weight of packaging and hence the requirement for barrier polymer rises
- disposal and/or recycling is made difficult and
- economic efficiency for the manufacturer and user is no longer ensured.

Further aspects in connection with the selection of barrier polymers, particularly for use by way of packing materials for consumer commodities which are everyday necessities, are the legal directives and/or self-restraints imposed on manufacturer and consumer in relation to the ecology and the environment. In some countries this fact has already resulted in polyvinyl halides such as PVC and PVDC, for example, no longer being permitted as barrier polymers in packing materials. Although the number of usable barrier polymers decreases by virtue of this measure, the range of requirements existing in practice cannot be covered by the remaining barrier materials. This is the case, above all, when very superior sealing properties - ie, very low oxygen and water-vapour permeability values, for example - are required. So in practice there are a great many needs where the requirements can no longer be satisfied - even by high-quality barrier polymers.

But efforts are also being made to improve the barrier properties of packing materials with the aid of transparent evaporated films consisting of oxides of Si, Al and Mg. However, not all the objectives that have been set by the packing industry can be achieved in this way. See, on this point, Coating, Volume No. 8, 1994, pages 274 to 280.

The state of the art described above concerning barrier finishes and reasons arising from ecology, environment and

industrial hygiene are sufficient cause for the industry that processes and uses barrier polymer, particularly in the foodstuff and pharmaceutical sector, to seek technically and economically simpler solutions having further improved sealing properties in order to be able to produce packaging substrates having very low area weights.

It is the object of the present invention to make available barrier materials that avoid the aforementioned disadvantages and satisfy the requirements defined in Table 1 with only a single layer.

In particular it is intended to provide remedies for problems in connection with sensory perception, ecology, disposal and/or recycling. In this regard the fields of application in the foodstuff and pharmaceutical sectors and in the sphere of industrial hygiene constitute, inter alia, a main focus.

In accordance with the invention this object is achieved by means of a water-resistant barrier material comprising natural, biologically degradable hydrocolloids that are substituted once or several times by ethylenically unsaturated residues and/or by residues bearing epoxide groups, the hydrocolloids being cured and/or crosslinked by means of a polyreaction that affects the residues.

Surprisingly it has now been found that high-quality barrier materials having superior, advantageous properties can be produced from hydrocolloids that are capable of being cured or crosslinked by means of a polyreaction, in particular a polymerisation and/or polyaddition, and are substituted with singly or multiply (sic) ethylenically unsaturated residues and/or residues bearing epoxide groups.

The adhesive primary materials according to the invention on the basis of natural, biologically degradable hydrocolloids

that are substituted once or several times by ethylenically unsaturated residues and/or by residues bearing epoxide groups include water-soluble, biologically degradable hydrocolloids or backbone polymers A which, inter alia, originate from the following polymer families:

- Proteins
  polypeptides, in particular those of collagenic origin, such as, for example, gelatin; animal glues; collagens; whey proteins, caseins; plant proteins, in particular soybean, rape and grain proteins and/or their hydrolysates.
- Polysaccharides
  cellulose and its derivatives such as methylcellulose, ethylcellulose, hydroxyethylcellulose, carboxymethylcellulose, etc, starch and starch derivatives, glycogen, alginic acid and derivatives including salts, agar-agar, heteropolysaccharides, heteroglycanes, hemicelluloses and their derivatives, chitin, gum arabic and the like.

In the case of the barrier materials according to the invention it is preferably a question of hydrocolloidal compounds corresponding to the general formula (I)

$$(R^1 - \overset{\overset{O}{\|}}{C} - X)_n - (R^2)_m - Y - A \qquad (I)$$

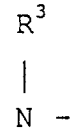
wherein A is a hydrocolloid having the above significance, preferably with a molecular weight from about 500 to about 2,000,000,

R^1 is the hydrocarbon residue of an ethylenically unsaturated, optionally hydroxy-, nitrile-, halogen- and/or C_1-C_4-alkyl-substituted carboxylic acid, preferably of an acrylic, methacrylic and/or crotonic

acid and/or with an α-, ß-epoxide group having 2 to 10 C atoms,

X = -O-, -N(R^2)-, -NH-C(O)- and/or the group R^1 -C(O)-X- stands for an ethylenically unsaturated residue of dicarboxylic imide, preferably a residue of maleic imide,

R^2 is an optionally hydroxy-, amino-, multiply R^1 -C(O)-X-, C_1-C_8-alkyl-, C_1-C_8-alkoxy- and/or oxyalkyl-substituted, saturated or unsaturated hydrocarbon residue, preferably an aliphatic hydrocarbon residue, and optionally comprises -C(O)-O-, -O-C(O)-O-, -O-C(O)-, -O-, -C(O)-, -NH-C(O)-NH-,



and/or -NH-C(O) bridge-type links,

R^3 may be = H, R-C(O)-, R^2 - Y - A and/or C_1-C_4 alkyl,
Y = -O-, -O-C(O)-, C(O)-O-, -NH-C(O)- or -C(O)NH-
n = 1 to 5 and
m = 0 to 10.

The barrier materials according to the invention are based on functionalised hydrocolloids. The primary materials are, inter alia, known and conventional hydrocolloids or their basic raw materials. The chemical modification of the primary materials is effected through the introduction of reactive and/or functional groups into the main molecular chains without changing or damaging the colloidochemical and water-soluble properties in the process.

The barrier materials according to the invention are reactive, biologically degradable hydrocolloids or backbone

polymers. They are substantially conversion products resulting from a non-radical reaction between polypeptides and/or polysaccharides, whereby their functional groups, for example hydroxyl, amino, imino, thiol and/or carboxyl groups, are at least partially subjected to derivatisation with a polymerised residue.

In the case of the barrier materials according to the invention it is consequently a question of derivatives of esters of unsaturated carboxylic acids and/or residues bearing epoxide groups with hydrocolloids from the aforementioned groups. Particularly preferred are those hydrocolloidal compounds corresponding to the above formula (I). In the hydrocolloidal compounds corresponding to formula (I) R^1 may be the hydrocarbon residue of, for example, methacrylic acid, chloroacrylic acid, cyanoacrylic acid and the like, the residues of acrylic and methacrylic acid being particularly preferred. Furthermore, R^1 may also be a hydrocarbon residue bearing epoxide groups and having 2 to 10 C atoms, the epoxy groups preferably being arranged in α or ß position.

Quite particularly preferred are compounds in which X is oxygen.

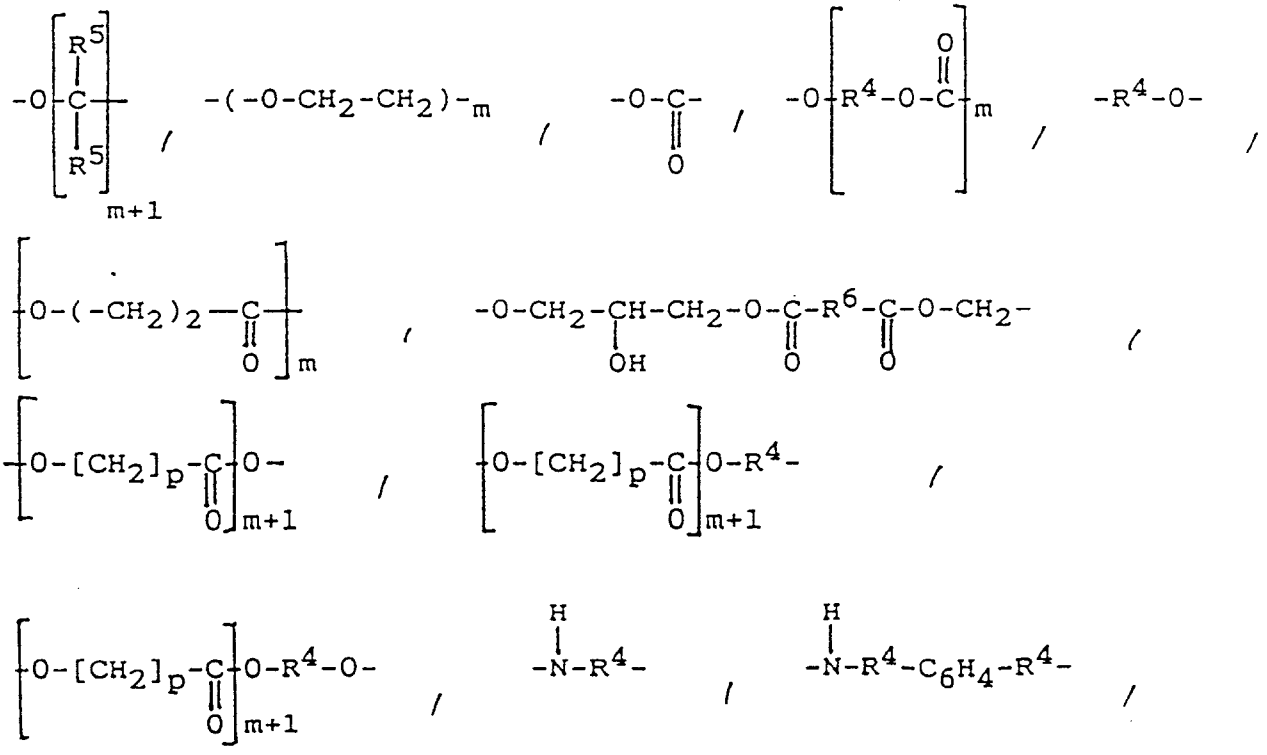
The residue R^2 contains at least one R^1-C(O)-X group, wherein R^1 and X may have the above significance and in the case of several R^1-(C)-X residues within one molecule the residues R^1 and X may in each case be the same or different. Bridge-type links of the residue R^2 which are optionally present may be arranged both within the residue, especially in the case of aliphatic residues R^2, and/or arranged terminally on one side or on both sides as bridge-type links of the residue R^2 in relation to X, Y or A. In a quite particularly preferred embodiment R^2 is an at least divalent, optionally substituted, glycol or polyol residue having 2 to 6 C atoms, the divalent residue of an aliphatic hydroxycarboxylic acid

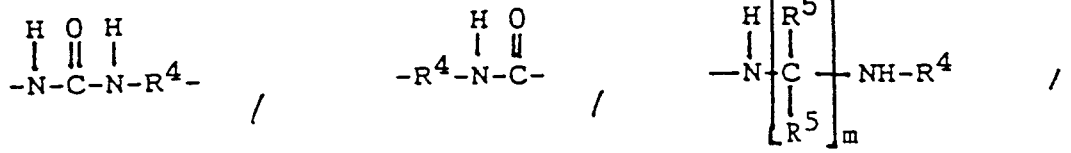
having 2 to 18 C atoms or the divalent residue of a carboxylic acid $-C_2-C_6$-glycol or C_6-C_{80} polyalkylene glycol ester. R^2 may also, for example, be a C_1-C_4 alkylene group which is optionally substituted with low alkyl groups. The residue R^2 is preferably linked to the residue Y or A via ether, ester and/or imino groups (Y = -O-, -OCO-, -COO- or NR^4-). A further group of usable, well suited compounds that are substituted in ethylenically unsaturated manner have the general formula (II):

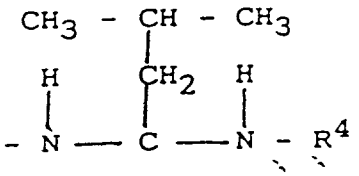
$$(R^1 - X)_n - (R^2)_m - Y - A \qquad (II)$$

wherein R^1 is an allyl or vinyl group and/or an α-, ß-epoxide group having 2 to 10 C atoms, X, R^2, Y, A, n and m have the same significance as before.

In particularly preferred manner use is made of compounds according to formula (I) in which - X - R^2 - may be $-(O-[CH_2]_p)_m-O-$, $-O-[CH_2]_p)_m-O-R^4-$ and also residues corresponding to the general formulae







and/or - $(CH_2)_m$,

R^4 may be the same or different and branched and unbranched as well as cyclic alkylene residues having 1 to 20, preferably 1 to 10, carbon atoms, arylene residues, aralkylene residues and/or acyl residues having 1 to 20 C atoms,

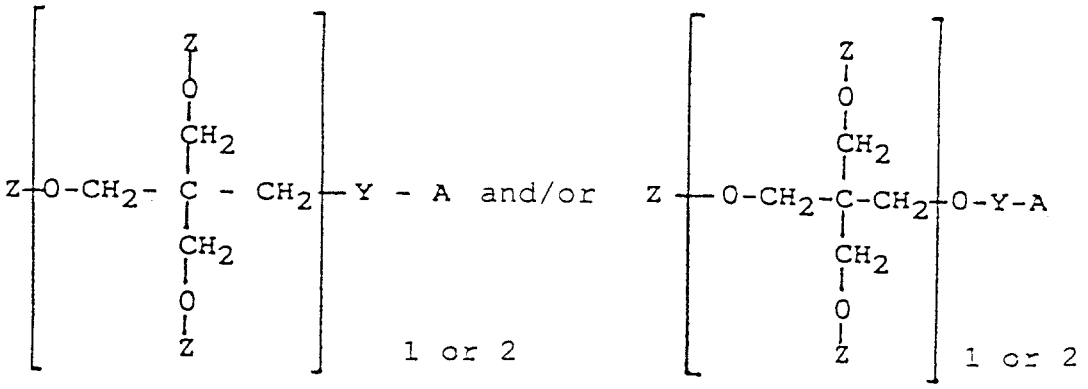
R^5 = H, Cl, CN, OH, C_1-C_4 alkyl,

R^6 = - CH = CH -, $-CH_2$ - CH_2-,

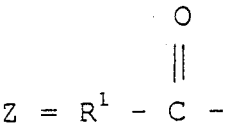
m = 0 to 50

p = 1 to 20.

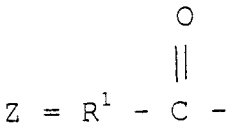
Another preferred group of compounds is constituted by those corresponding to the formulae



wherein



and/or - Y - A, but at least one of the residues



and A, Y and R^1 have the above significance.

The binding link Y between the residues from formula (I) and/or (II) and the main chain of the polymer results from the reaction of the functional groups of the hydrocolloid A with the corresponding reactive groups of the aforementioned polymerisable residue. In particular, Y has the same meanings as the heterogroups of R^2. Derivatisation may be effected by non-radical reaction or by graft reactions onto the backbone polymer.

The reactive groups that are introduced into the main molecular chains of the hydrocolloids A in accordance with

the present invention are ethylenically unsaturated residues and/or residues bearing epoxide groups. These may be linked to the hydrocolloids directly or via the residue R^2, for example a divalent, optionally substituted hydrocarbon residue or polyol residue. Curing or polymerisation is effected by means of the reaction initiators, curing agents that are conventional for compounds of this type, and/or by high-energy beams or rays. The barrier materials may additionally contain other known components such as accelerators, stabilisers, rheology-influencing agents, fillers, pigments and/or other polymerisable compounds or compounds that are capable of being copolymerised with the aforementioned ethylenically unsaturated hydrocolloids and/or hydrocolloids bearing epoxide groups, in particular water-soluble compounds and/or compounds bearing active hydrogen atoms and the like.

Preferred in accordance with the invention are, however, the functionalised backbone polymers or hydrocolloids in which the reactive groups have been introduced into the main molecular chains via a non-radical reaction. They make a significant contribution to a homogeneous barrier material, as has surprisingly been found. The production of these functionalised products is effected, inter alia, as described in DE-A-42 10 334.

Functionalisation of the hydrocolloids A with one or more reactive residues is effected in particular via their hydroxyl, amino, imino, thiol and/or carboxyl groups. The contents of functional residues in the hydrocolloid amount to $\geq$ 0.1 mass-% (m-%). The particularly preferred contents amount to between 1 and 50 m-%, in particular between 5 and 35 m-%. Those functionalised hydrocolloids which possess at least 10 curable or crosslinkable groups per 1,000 amino-acid or monosaccharide units prove to be particularly advantageous barrier materials.

According to the invention a large number of ethylenically unsaturated compounds and/or compounds bearing epoxide groups in accordance with the above formulae are suitable for the purpose of functionalising the hydrocolloids A. Particularly preferred are those reactive residues which, inter alia, are introduced into the hydrocolloid A from the groups of the

- ethylenically unsaturated compounds such as, for example, glycidyl acrylate, glycidyl methacrylate, glycidyl acryloxypropionate, glycidyl methacryloxypropionate, monomethylacryloxyethyl maleate, urethane methacrylate, allyl glycidyl carbonate, (meth)acrylamide, 2-acrylamido-2-methylpropanesulphonic acid, epoxydicyclopentenyloxyethyl methacrylate, vinylcyclohexane epoxide, allyl glycidyl ether and/or

- compounds bearing epoxide groups, such as, for example, epichlorohydrin, butyl diglycidyl ether, 1,6-hexanediol diglycidyl ether, neopentylglycol diglycidyl ether, polypropyleneglycol diglycidyl ether, vinylcyclohexene diepoxide.

Particularly preferred for the functionalising are those compounds which are water-soluble and/or capable of being easily dispersed in water.

The polymerisation required for the curing may be effected in the form of pure homopolymerisation of one of the derivatives containing the above residues, but it may also be effected by copolymerisation of a mixture of such derivatives. But the hydrocolloids according to the invention may also copolymerise with water-soluble or water-dispersible unsaturated monomers, oligomers and/or polymers or with monomers, oligomers and/or polymers bearing epoxide groups. In this connection these coreactants have, inter

alia, the function of a crosslinker. These crosslinking compounds may, for example, be those employed above for the purpose of functionalisation or may be other compounds. Suitable furthermore for the purpose of crosslinking hydrocolloids bearing epoxide groups are compounds that possess active H atoms in the molecule and that, for example, cure via polyaddition, unless a cationic polymerisation is preferred. Such compounds are, inter alia, polyamines, polyimines, polyamides, polyamidoamines, polysulphides, silane compounds and the like. Also suitable for the cationic polymerisation are polyols, in particular water-soluble polyols, that additionally provide a 'softening' or 'plasticising' component in a cured polymer matrix.

The curing or polymerisation of the barrier materials according to the invention themselves is effected

a) in the case of ethylenically unsaturated residues by free-radical polymerisation

   - in the presence of reaction initiators selected from

     1. inorganic peroxides such as, for example, alkali-metal peroxides and/or alkaline-earth metal peroxides, and also hydrogen peroxide;
     2. organic peroxides and/or hydroperoxides such as, for example, benzoyl peroxides, cumene hydroperoxides;
     3. peroxo acids and the salts thereof, such as, for example, peroxodisulphuric acid, sodium peroxodisulphate (persulphate);

   - actinic light, in particular UV rays in the wavelength range from 380 to 100 nm in the presence of photoinitiators such as, for example,

benzophenone, benzoin ether, Michler's ketone, methylthioxanthone, ketone acetals and optionally other synergists such as, for example, amines, tert. amino alcohols and/or

- by means of electron beams in the low-energy acceleration range from 50 to 300 keV and a preferred effective depth of penetration from 3 to 400 g/m^2 and also a dose distribution from 5 kGy to 100 kGy, in particular 10 to 70 kGy, and a dose variance of about ± 3 %.

b) in the case of residues bearing epoxide groups

- by means of polyaddition with compounds bearing active H atoms such as already mentioned above in connection with the crosslinkers, such as, for example, isophoronediamine, diethylenetriamine, 4,4-diaminodiphenylmethane

- by means of cationic polymerisation and actinic light in the presence of Lewis acids and Brønsted acids, carbonium ions and trialkyloxonium salts such as, for example, bis-[4-(diphenylsulphono)-phenyl]-sulphite-bis-hexafluorophosphate, η-2,4-(cyclopentadienyl)[1,2,3,4,5,6-η)-(methylethyl)-benzene]-iron(II) hexafluorophosphate.

Furthermore, the polymerisation and copolymerisation may be accelerated after addition of one or more reaction initiators by addition of an accelerator, above all if curing is effected at temperatures ≤ 25° C. Suitable for this purpose are accelerators on the basis, inter alia, of tertiary amines such as, for example, diethylaniline, diethyl-p-toluidine, triethyleneamine, salts of heavy metals, such as cobalt acetylacetonate, for example.

Particularly preferred are water-soluble or water-emulsifiable accelerators such as triethanolamine.

The curing or crosslinking of the ethylenically unsaturated residues in the barrier materials according to the invention by means of free-radical polymerisation has to be effected, particularly in the case of thin layers, in an inert protective-gas atmosphere consisting of nitrogen (N_2), carbon dioxide (CO_2) and/or noble gas with a view to forestalling the inhibition of oxygen. If, on the other hand, layers, coatings, films and foils or the like consisting of the aqueous barrier materials according to the invention are cured or crosslinked prior to the dehydration or drying, an inert protective-gas atmosphere can be dispensed with, as has surprisingly been found, for the content of water that is present creates its own self-sufficient protective zones in relation to molecular oxygen (O_2). Furthermore, this manner of proceeding also offers the additional advantage that the dehydration or drying that follows directly can be made technically simpler and hence more economical.

Independently of the above explanatory remarks, in addition other reactive groups can be crosslinked in the main molecular chains of the hydrocolloids. Suitable for this purpose are, inter alia, bifunctional and/or polyfunctional isocyanates and the like, but also aldehydes such as glutaraldehyde, for example. But dual curing and hybrid curing may also be carried out with the barrier materials according to the invention, provided that they have been functionalised for this purpose with the suitable residues and/or contain other reactive members in the main molecular chain.

Particularly suitable crosslinkers for the copolymerisation with the hydrocolloids according to the invention are, inter alia, monomeric and/or oligomeric monofunctional,

bifunctional, trifunctional and polyfunctional (meth)acrylic compounds, in particular those with molecular weights (M_w) ≥ 500. This group includes, inter alia, aliphatic and/or cycloaliphatic urethane (meth)acrylates, polyether (meth)acrylates, acrylamido-2-methylpropanesulphonic acid. If these compounds are not water-soluble, they are advantageously added to the barrier materials according to the invention in the form of aqueous dispersions. Additions of just ≤ 25.0 m-%, preferably ≤ 10.0 m-%, in particular ≤ 5.0 m-%, of urethane (meth)acrylates again result in significant reductions in permeation, particularly as regards oxygen, as has surprisingly been found.

The barrier materials according to the invention may optionally be modified by means of further additives. By way of known conventional additives, mention should firstly be made of pigments, in order to impart a coloured appearance to the barrier materials. The term 'pigments' is to be understood to encompass quite generally dyestuffs, colouring compounds, fillers and extenders of all types which supply additional solids to the barrier materials according to the invention and optionally also make them printable. At the same time they impart a number of specific properties to the barrier materials.

In connection with the use of the pigments in barrier materials that are later employed in the foodstuff and pharmaceutical sector said pigments have to conform to the respective legal regulations regarding foodstuffs and pharmaceuticals. The particular properties and functions are summarised in "Pigmente und Füllstoffe", 2nd Edition, 1980, M. and O. Lückert, Laatzen. The content of pigments and fillers may amount to between 0.5 and 80 wt-%, preferably between 1.0 and 70 wt-%.

Furthermore, the barrier materials may also contain plasticisers. Especially suitable by way of plasticisers

are water-soluble products such as polyols, such as, for example, diols, glycols, glycerin, sorbitol, inositol and other sugar alcohols which may optionally possess reactive groups according to the above formula.

For use in the technical field, further additives such as, for example, stabilisers, anti-oxidants, flow-control agents and wetting agents may be added to the barrier materials according to the invention. The additives are sufficiently described in the literature, so reference may be made to the aforementioned book by Gächter/Müller entitled "Kunststoff-Additive", 2nd Edition, Hanser-Verlag, Munich, 1983. If, on the other hand, additives that are used in the foodstuff and pharmaceutical sector are required for barrier materials, the legal regulations applying are to be observed. The supplemental amounts are generally between 0.1 and 5.0, preferably between 0.1 and 2.5 wt-% - relative to the solids content. Since the physical characteristic data are not altered by the derivatisation of the hydrocolloids, in connection with the processing and production of sealing layers and films the barrier materials according to the invention offer an additional advantage by virtue of the fact that they remain water-soluble or water-dispersible. Only as a result of the curing or crosslinking are these properties - depending on the content of reactive groups - partially or entirely eliminated. Consequently the person skilled in the art is provided with a barrier material, the processing of which is familiar to him and the properties of which he knows.

The barrier materials according to the invention are present in solid form as powders, granulates and the like or as aqueous gels, solutions and/or dispersions. With a view to processing they have to be

- in the case of solid forms, previously wetted with water, optionally swollen, then molten under heat and/or dissolved in water and

- in the case of aqueous gels, molten by means of heat and hence converted into the sol state.

Since processing is effected from aqueous solutions and/or dispersions, the hydrocolloids according to the invention are particularly environmentally friendly also from this point of view.

The addition and incorporation of the crosslinking coreactants, reaction initiators and optionally other adjuvants and/or additives is effected likewise in an aqueous, liquid phase in the case of the hydrocolloids according to the invention. To this end, simple mixing vessels with suitable mixing tools may be used which, where required, have to be equipped so as to be heatable for the purpose of melting the gels. Preparation and processing may also be effected continuously, for which purpose extruders, screw mixers are, inter alia, suitable.

If the barrier materials according to the invention contain trapped gases, for example air, prior to application they have to be degassed by means of a vacuum.

A further subject of the invention is the finishing of substrates with the polymerisable barrier materials according to the invention or the production of self-supporting barrier films. The polymerisable barrier materials according to the invention are suitable for the formation of coatings for planar substrates and moulded articles consisting, inter alia, of

- cellulose materials such as, for example, paper, cardboard and paperboard of all types,

- plastics such as, for example, foils and sheets consisting of, inter alia, polyvinyl alcohols, polyethylene, polypropylene, polycarbonate, polyester, polyvinyl ester, polyamides, polyvinyl halides and their copolymers, as well as fibrous composite materials formed from thermoplastics and thermosetting plastics, but also

- for other materials such as metals, inorganic materials such as, for example, glass and the like.

In particular they are suitable for porous substrates and/or substrates that are not diffusion-proof, in order to impart the necessary barrier properties to the latter. The barrier materials according to the invention are also quite particularly suitable, as has surprisingly been found, as so-called topcoats of substrate surfaces that are finished with evaporated films consisting of metals or oxides of silicon (Si), aluminium (Al) and/or magnesium (Mg), because they improve the gas and water-vapour permeability values thereof again by very high factors.

The sealing properties of the barrier materials according to the present invention may be varied within wide limits. In addition to the

- contents of reactive residues or groups - according to the above formula - and/or

- the respective layer thicknesses, optionally as a time-dependent influencing factor,

the barrier properties are essentially partly determined by the type of the hydrocolloids according to the invention and their dehydration behaviour, as has surprisingly been found. Particularly high reductions in permeation are produced by

those hydrocolloids which dehydrate or dry from their aqueous solutions and/or gels not via pores or capillary activities but via diffusion processes. These preferably include, inter alia, those hydrocolloids according to the invention which form gels or which in the uncrosslinked state are subject to a sol/gel transformation and have a content of reactive groups amounting to between 20 and 50 m-%. In particular, those hydrocolloids according to the invention are suitable which are of collagenic origin - for example, gelatin.

The sealing properties of the hydrocolloids according to the invention can optionally be further improved if

- in addition to the curing or crosslinking the aforementioned crosslinkers and/or other known crosslinkers are used concomitantly and/or

- dual curing and/or hybrid curing are carried out.

The dehydration and drying of the uncrosslinked and crosslinked layers, coatings, films, foils or the like also have an influence on the polymer-network formations and their sealing-layer properties. For this reason the dehydration and drying are performed under air-conditioned climates, predried air having a relative atmospheric moisture ≤ 40 % and low temperatures ≤ 100° C being particularly preferred.

The cured or crosslinked barrier materials, films and/or foils according to the invention possess differing barrier properties and functions, depending on

- their hydrocolloid base,
- the respective degrees of crosslinking and crosslink densities and
- the layer thicknesses chosen in each case.

Consequently they are able to form sealing layers having outstanding functionalities in relation to a large number of gases, vapours and/or liquids, in which connection gases and vapours containing oxygen, for example, but also water vapour and readily volatile vapours, constitute a main focus.

Furthermore, the barrier materials according to the invention also possess good resistances to organic solvents such as, for example, alcohols; oils and fats; and also a large number of weak acids and bases. In this connection the chemical resistance is essentially influenced by the base hydrocolloid, the degree of crosslinking and the crosslink density. In relation to water or liquids containing water, in the case of the cured or crosslinked barrier materials according to the invention considerably reduced reswelling capacities are obtained which in addition may optionally have a positive influence on the sealing properties, as has surprisingly been found.

With the barrier materials according to the present invention it is possible for innovative, high-quality sealing layers to be produced. These sealing layers according to the invention provide barrier factors which in comparison with their unmodified base hydrocolloids may be higher by a factor of up to 10^7. These potential improvements were already surprising, because the barrier factors of the unmodified hydrocolloids are generally $\leq 10^2$. Hence, depending on the supporting material, the pretreatment of the surface thereof and the barrier material according to the invention that is employed, inter alia permeation values can be achieved

- in the case of oxygen (O_2), amounting to $\leq$ 0.1 ml / (m^2 x 24 h x bar)
  (ASTM D 3985-81)

- in the case of water vapour, amounting to ≤ 0.3 g (m^2 x 24 hrs) (ASTM 372-78).

The barrier materials according to the invention adhere to a large number of substrate surfaces. With a view to improving the wetting and adhesion of the surfaces to be coated, a pretreatment of the surface may be necessary. This is particularly the case when these surfaces are non-polar, as in the case of polyolefinic substrates, for example.

Suitable for the pretreatment of the surface are, inter alia, singeing, corona discharges, low-pressure plasma and/or adhesive primer.

Self-supporting barrier films and foils can be produced from the barrier materials according to the invention by, inter alia, pouring onto an adhesive backing sheet, subsequent curing or crosslinking and dehydration. The processing conditions are analogous to those above.

As a result of the curing, crosslinking and/or polymerising, the hydrocolloids according to the invention lose their hydrocolloidal properties. That is to say, the layers, coatings, films, foils and the like produced with them are no longer water-soluble and/or water-dispersible but they produce, inter alia, network polymers that are resistant to boiling water and optionally resistant to sterilisation. Furthermore, the temperature-dependent reversible sol/gel transformation turns into an irreversible transformation. In water the polymer networks may still have a relatively weak charactersitic swelling.

The new polymer networks are, inter alia, resistant to water, media containing water, salt solutions, weak acids

and bases, sugar solutions, fruit juices, milk, alcoholic beverages, soft drinks, milk and milk products, oils, fats, organic solvents and are therefore particularly suitable for the finishing of packing materials and packagings consisting of different materials. Since they are diffusion-proof with respect to a large number of aromatic media, the barrier layers also offer outstanding protection to products that are sensitive in sensory respects, such as, for example, coffee, fruit powders and the like.

The cured barrier layers, coatings, films and foils are neutral in sensory respects and do not produce or have any so-called 'scalping effect' in relation to any fillings or the like.

The barrier materials according to the invention that are cured by means of UV rays and electron beams are, in addition, sterile.

The new polymeric networks that have formed as a result of curing, crosslinking and/or polymerising the barrier materials according to the invention have furthermore remained biologically degradable, as has surprisingly been found. By addition of enzymes the cured barrier materials can be degraded in acid or alkaline medium within a few days. When the materials are buried in the ground or composted, biological degradation requires a period from several days to a few weeks.

Such substrates and others having a barrier protective film are required in many sectors of the industrial economy and in many branches of industry. These include, inter alia, the packaging and wrapping industry, the vehicle industry, aviation and aerospace, construction engineering, etc.

Particular fields of application for additive-free, monomer-free, polymerisable barrier materials according to the

present invention are the packaging and wrapping sectors for foodstuff and pharmaceutical products. In order to be able to make packagings and wrappings available in future for these fields of application, said packagings and wrappings will have to be capable of being produced and processed not only under more severe legal directives but they will also have to satisfy in their physiological and sensory behaviour the higher requirements of foodstuff and pharmaceutical legislation. In order to achieve this objective, new barrier materials are needed in the form of coating compositions which are based on different, innovative, new technologies. According to the present invention this object can be achieved in technically and economically successful manner with the polymerisable barrier materials, which in particular are additive-free and monomer-free, because

- their primary hydrocolloids are natural polymers and predominantly foodstuffs and their properties and technical characteristic data are not modified as a result of derivatisation and

- only as a result of the curing, crosslinking and/or polymerising are new, polymeric networks formed having exceptionally high sealing properties in relation to gases, water vapour and a large number of other media,

as has surprisingly been found. These polymeric networks that form in accordance with the invention possess such sealing properties already in very thin layers or films, such as less than 10 µm for example, that they can be assigned to at least the 1st barrier class above. Furthermore it was totally surprising that the already outstanding sealing properties of the substrates that are finished with evaporated films consisting of metals and oxides of Si, Al and Mg can, after the application and

curing of the barrier materials according to the invention as topcoats, be improved again by factors $\geq 10^1$.

Furthermore, porous and/or absorptive substrates such as, for example, cellulose materials, in particular paper, cardboard, paperboard, wood, derived timber products and the like, can be impregnated with the barrier materials according to the present invention in order to impart highly functional sealing properties to said substrates.

According to the present invention new, innovative barrier materials are created which are not comparable to the known barrier polymers. As a result, not only can the described disadvantages and other known disadvantages be very largely eliminated but totally new barrier polymers and barrier materials are made available which are better able to cope with current and future aspects and requirements, particularly in the foodstuff and pharmaceutical sector. This new class of barrier polymers according to the present invention offers, inter alia, the following advantages:

- natural polymers which are available from national resources

- the primary hydrocolloids are preferably foodstuffs or permitted additives for foodstuffs

- may be processed like their base colloids

- biological degradability

- after curing, crosslinking and/or polymerising, monomer-free polymeric networks are formed which are resistant to boiling water and to sterilisation

- high economic efficiency, as layers ≤ 10 µm already possess high barrier functions in relation to gases and liquids

- improvement of the barrier factors by up to 10^7.

In comparison with the barrier polymers described at the outset and other barrier polymers according to the state of the art, the barrier materials according to the present invention are potentially superior and consequently make essential contributions to improving the ecology, the environment and the disposal of waste and are, physiologically and toxicologically, generally acknowledged to be many times safer.

The invention is elucidated in more detail by means of the following Examples, without, however, being restricted thereto.

Example 1

100 g derivatised high-bloom type A gelatin having a methacrylate proportion of 14 mmol/100 g 20-% aqueous gel were mixed at 50° C with 0.5 ml 50-% aqueous triethanolamine and 5 ml 10-% $Na_2S_2O_8$ solution. The formulation polymerised after 40 seconds to form a gel that was resistant to boiling water. An increase in temperature (60, 70° C) resulted in short reaction-times (10-20 seconds) - formulations without addition of amine polymerised more slowly.

Example 2

Derivatised high-bloom type A gelatin having a methacrylate proportion of 28 mmol/100 g 20-% aqueous gel was mixed at 50° C with 0.5 ml 50-% aqueous triethanolamine and 5 ml 10-% $Na_2S_2O_8$ solution. The formulation polymerised for an additional

25 seconds. As in Example 1, an increase in temperature resulted in shorter reaction-times, whereas formulations without addition of amine polymerised more slowly.

Example 3

Derivatised high-bloom type A gelatin having a methacrylate proportion of 45 mmol/100 g 20-% aqueous gel was mixed with a photoinitiator (Igracure 184 = 1-hydroxy-cyclohexyl-phenyl-ketone). The concentration of photoinitiator amounted to 0.5 wt-%. The mixture was applied onto paper with a manual doctor blade and irradiated by means of a high-pressure Hg lamp (power 120 W/cm^2). At a throughput speed of 13 m/min, solid layers that were resistant to boiling water were produced.

Example 4

Derivatised high-bloom type A gelatin gels (sic) (20 % W/W) of the types specified in Table 2 was applied onto 210 g/m^2 cardboard by the manual doctor blade and irradiated with 180 keV electrons. The radiation dose amounted to 40 kGy. The O_2 permeability and N_2 permeability of the cardboard coated with crosslinked gelatin were determined. By way of barrier factor for O_2 the ratio

$$\frac{O_2 \text{ permeability of the substrate}}{O_2 \text{ permeability of the coated substrate}}$$

is specified.

Table 2

Methacrylate content mmol/100 g 20-% gel.	Dry layer thickness µm	Barrier factor O_2 O_2	Permeability (ml/m^2.h.bar)	Permeability N_2
Cardboard	250 (cardboard)	-	$30.3 \cdot 10^6$	
20	6	$2.5 \cdot 10^6$	12	10
14	8	$8.8 \cdot 10^5$	34	34
45	18	$1.2 \cdot 10^6$	25	27
28	24	$4.1 \cdot 10^5$	73	-

Example 5

Derivatised high-bloom type A gelatin of the types specified in Table 3 was applied by manual doctor blade onto polypropylene (PP) foils with a thickness of 25 µm and irradiated with 180 keV electrons. The radiation dose amounted to 40 kGy. Permeabilities and barrier factors were measured.

Table 3

Methacrylate content mmol/100 g 20-% gel.	Dry layer thickness µm	Barrier factor O_2 O_2	Permeability (ml/m^2.h.bar)	Permeability N_2
PP foil	25 (foil)	-	74	21
20	7	264	0.28	0.18
20	7	62	1.2	0.25
20	7	93	0.8	0.25
45	7	123	0.8	-

Example 6

Derivatised high-bloom type A gelatin of the type specified in Table 4 was applied by manual doctor blade onto polyester foil that had been precoated with SiOx and was irradiated with 180 keV electrons. The radiation dose amounted to 40 kGy. The oxygen permeability of the gelatin-coated foil was measured.

Table 4

Methacrylate content mmol/100 g 20-% gel.	Dry layer thickness µm	Barrier factor O_2 O_2	Permeability (ml/m^2.h.bar)
PET SiOx foil	11.5 (foil)		2.5
45	6		< 0.1

Example 7

Derivatised type A gelatin of the types specified in Table 5 was mixed with aqueous dispersions of various monomeric and oligomeric acrylates such as TMPTA, polyether acrylates and polyester acrylates. The acrylate concentration amounted to between 1 and 10 wt-%. The mixtures were applied by manual doctor blade onto 60 g/m^2 paper and irradiated with 180 keV electrons. The radiation dose amounted to 40 kGy. In Table 5 barrier factors and O_2 permeabilities of the coated substrates are stated and compared with measured values for pure gelatin coatings.

Table 5

Methacrylate content of derivatised gelatin mmol/100 g 20-% gel.	Acrylate addition %	Layer thickness µm	Barrier factor O_2 O_2	Permeability (ml/m^2.h.bar)
Base paper	-	61		$2.4 \cdot 10^8$
45	-	13.6	$6 \cdot 10^3$	420
45	10[1)]	15.8	$6.7 \cdot 10^5$	3.6
45	10[1)]	16.4	$1.3 \cdot 10^6$	1.8
45	5[2)]	18.1	$1.6 \cdot 10^4$	150

[1)] urethane acrylates

[2)] polyether diacrylate

Example 8

The biological degradability of the irradiated - that is to say, crosslinked - coating material was investigated by means of tests in vivo and in vitro.

The in-vitro test includes the treatment of the coating material in the form of foils having a thickness of 20 µm with the protease pepsin at 37° C over a period of 7 days. Depending on the radiation intensity employed for the crosslinking, different changes in mass result after the enzymatic hydrolysis, relative to the initial mass.

	Intensity of Irradiation		
	20 kGy	40 kGy	60 kGy
Relative change in mass after 7 days	15 %	32 %	45 %

In a modification of the burial trial from DIN 53739, according to process D, use was made of a soil-burial test under anaerobic conditions for the in-vivo investigation.

This test enables qualitative and semi-quantitative determination of the biological degradability by soil bacteria and soil moulds of test samples consisting of biological or synthetic polymers.

Incubation period days	Rel. change in mass of foils irradiated with different intensities			Gelatin type
	20 kGy	40 kGy	60 kGy	
3	100 %	100 %	100 %	B
3 6	100 %	100 %	60 % 100 %	A

CLAIMS

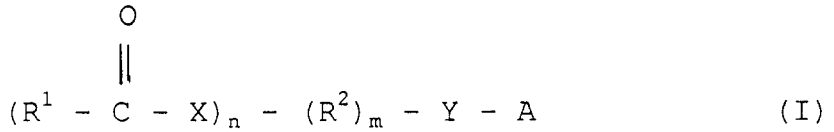
1. Use of a water-resistant barrier material comprising natural, biologically degradable hydrocolloids as coating and/or impregnation of a packaging for fillings with a view to the long-term stabilisation of said fillings, whereby the barrier material, which (sic) are substituted once or several times by ethylenically unsaturated residues and/or residues bearing epoxide groups, and whereby the substituted hydrocolloids are cured and/or crosslinked by means of a polyreaction involving the residues.

2. Use according to Claim 1, characterised in that the hydrocolloids are polypeptides of collagenic origin, in particular gelatin, animal glues, collagen and also caseins, whey proteins and/or their hydrolysates.

3. Use according to Claim 1, characterised in that the hydrocolloids are polypeptides of plant origin, in particular soybean proteins or rape proteins.

4. Use according to Claim 1, characterised in that the hydrocolloids are polysaccharides, in particular cellulose, starch or derivatives hereof.

5. Use according to one of Claims 1 to 4, characterised in that the substituted hydrocolloids are compounds corresponding to the general formula (I):



$$(R^1 - C(=O) - X)_n - (R^2)_m - Y - A \qquad (I)$$

wherein A is a polysaccharide or polypeptide, preferably with a molecular weight in the range between 500 and 2,000,000,

R^1 is a hydrocarbon residue of an ethylenically unsaturated, optionally hydroxy-, nitrile-, halogen- and/or C_1-C_4-alkyl-substituted carboxylic acid, preferably of an acrylic, methacrylic and/or crotonic acid and/or a ß-epoxide group,

X = -O-, $-N(R^2)-$, -NH-C(O)- and/or

the group R^1-C(O)-X- represents an ethylenically unsaturated residue of dicarboxylic imide, preferably a residue of maleic imide;

R^2 represents an optionally hydroxy-, amino-, multiply R^1 -C(O)-X-, C_1-C_8-alkyl-, C_1-C_8-alkoxy- and/or oxyalkyl-substituted, saturated or unsaturated hydrocarbon residue, preferably an aliphatic hydrocarbon residue and optionally comprises -C(O)-O-, -O-C(O)-O-, -O-C(O)-, -O-, -C(O)-, -NH-C(O)-NH-, $-N(R^3)-$ and/or -NH-C(O)- bridge-type links,

R^3 represents hydrogen, R^2-C(O)-, R^2-Y-A and/or a C_1-C_4 alkyl group,

Y represents an -O-, -O-C(O)-, -C(O)-O-, -NH-C(O)- or -C(O)NH- group,

n = 1 to 5 and

m = 0 to 10.

6. Use according to one of Claims 1 to 4, characterised in that the substituted hydrocolloids comprise compounds corresponding to formula (II):

$(R1 - X)_n - (R^2)_m - Y - A$ (II)

wherein R^1 is an allyl or vinyl group and/or an α-, ß-epoxide group having 2 to 10 C atoms and wherein X, R^2, Y, A, n and m have the same significance as in Claim 5.

7. Use according to one of Claims 5 or 6, characterised in that X signifies $-(O-[CH_2]_p)_m-$, R^2-O- or $-O-R^4-$ or represents residues corresponding to the general formulae

$-O\left[C(R^5)(R^5)\right]_{m+1}$, $-(-O-CH_2-CH_2-)_m$,

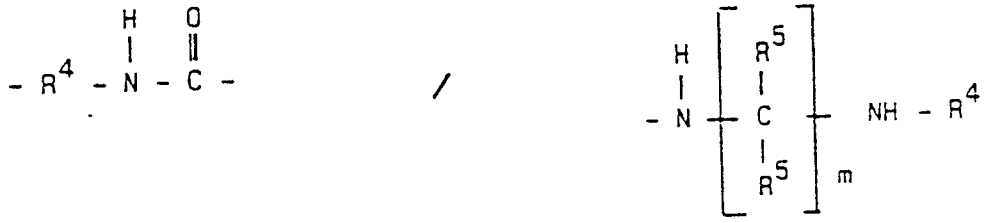
$-O-C(=O)-$, $-O\left(R^4-O-C(=O)-O\right)_m$,

$\left[O-(-CH_2)_2-C(=O)\right]_m$, $O-CH_2-CH(OH)-CH_2-O-C(=O)-R^6-C(=O)-O-CH_2-$,

$\left(O-[CH_2]_p-C(=O)\right)_{m+1}O$, $\left(O-[CH_2]_p-C(=O)-\right)_{m+1}O-R^4-$,

$\left(O-[CH_2]_p-C(=O)-\right)_{m+1}O-R^4-O-$, $-N(H)-R^4-$,

$-N(H)-R^4-C_6H_4-R^4-$, $-N(H)-C(=O)-N(H)-R^4-$,



and/or may be $-(CH_2)_m$,

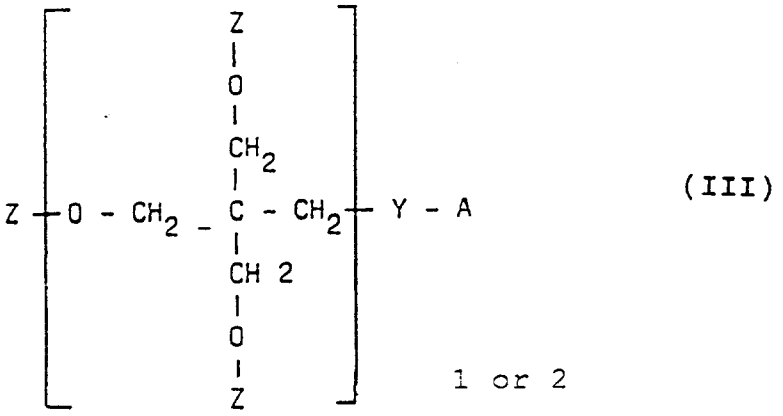
R^4 independently of one another may be the same or different and represents branched and unbranched as well as cyclic alkylene residues having 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms, arylene residues, aralkylene residues and/or acyl residues having 1 to 20 C atoms,

R^5 represents hydrogen, chlorine, CN, OH or C_1-C_4 alkyl,

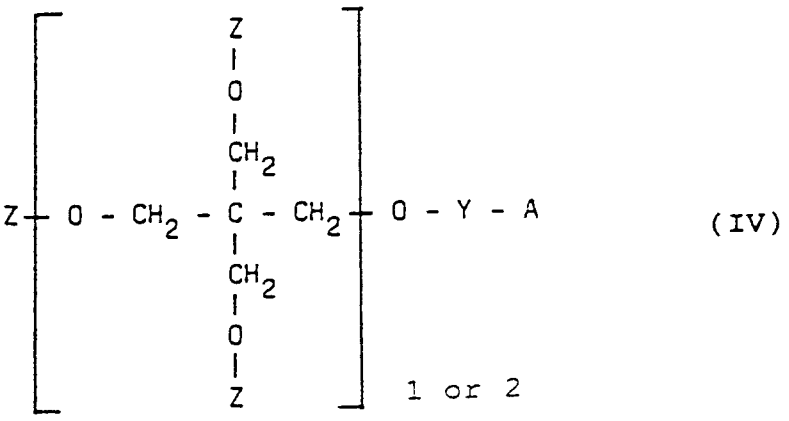
R^6 represents -CH=CH- or $-CH_2-CH_2-$,

m represents 0 to 50 and p may be equal to between 1 and 20.

8. Use according to one of Claims 1 to 4, characterised in that the substituted hydrocolloids comprise compounds corresponding to the general formulae (III) and/or (IV):



(III)



(IV)

wherein Z signifies R^1-C(OH)- and/or represents -Y-A, whereby, however, at least one of the residues has the former significance and whereby A, Y and R^1 have the significance as in Claim 5.

9. Use according to one of the preceding claims, characterised in that the substituted hydrocolloids contain at least 10 crosslinkable groups per 1,000 amino acids or monosaccharide units.

10. Use according to one of the preceding claims, characterised in that the substituted hydrocolloids are cured by the use of crosslinkers.

11. Use according to Claim 10, characterised in that the crosslinkers are ethylenically unsaturated compounds and/or compounds bearing epoxide and having a molecular weight ($\overline{M}_w$) $\geq$ 500.

12. Use according to one of Claims 1 to 11, characterised in that the substituted hydrocolloids are cured by means of high-energy beams or rays, in particular electron beams.

13. Use according to Claim 11, characterised in that the substituted hydrocolloids are cured by means of high-energy beams or rays in an environment that is free from protective gas.

14. Use according to one of Claims 12 or 13, characterised in that it has been subjected to dual curing or crosslinking.

15. Use according to Claim 14, characterised in that for the purpose of dual curing use has been made of compounds containing isocyanate groups.

16. Use according to one of the preceding claims, characterised in that the barrier material is post-cured and dried, dehydration having taken place under conditioned air with a relative atmospheric moisture ≤ 50 % and at temperatures between 20 and 100° C.