(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 November 2012 (01.11.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/145857 A1

(51) International Patent Classification:
*C09D 133/04* (2006.01) *C08L 33/10* (2006.01)
*C08L 33/04* (2006.01) *C08L 33/14* (2006.01)
*C08L 33/08* (2006.01)

(21) International Application Number:
PCT/CN2011/000720

(22) International Filing Date:
25 April 2011 (25.04.2011)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant *(for all designated States except US)*: **EVONIK RÖHM GMBH** [DE/DE]; Kirschenallee, 64293 Darmstadt (DE).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **ZHANG, Zhengfeng** [DE/CN]; Room 1601, 96#, 2nd Branch Lane, 1028 Xiu Yan Road, Pudong New District, Shanghai 201315 (CN). **XUE, Lina** [CN/CN]; Room 402, 940 Luochunanzhong Road, Zhabei District, Shanghai 200072 (CN). **SCHMITT, Gerold** [DE/DE]; Rotäckerstr. 82, 63743 Aschaffenburg (DE). **KLESSE, Wolfgang** [DE/DE]; Tucholskyweg 26, 55127 Mainz (DE).

(74) Agent: **CCPIT PATENT AND TRADEMARK LAW OFFICE**; 8th Floor, Vantone New World Plaza, 2 Fuchengmenwai Street, Beijing 100037 (CN).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published**:

— *with international search report (Art. 21(3))*

WO 2012/145857 A1

(54) **Title**: AQUEOUS DISPERSION OF PREFERABLY BENZOPHENONE-CONTAINING (METH)ACRYLATE POLYMERS FOR LEATHER COATING

(57) **Abstract**: An aqueous dispersion of preferably benzophenone-containing (meth)acrylate polymers and its application in leather coating are disclosed. The advantages of the present invention include no additional photoinitiators required for UV curing and no release of formaldehyde during the UV curing.

# Aqueous dispersion of preferably benzophenone-containing (meth)acrylate polymers for leather coating

## Field of the invention

The present invention relates to an aqueous dispersion of preferably benzophenone-containing (meth)acrylate polymers and its application in leather coating.

## Background

Leather coating is a very special application field for water based polymer systems. There are a lot of requirements for such dispersions and their resultant films. Among others, the most important requirements include good adhesion, good low temperature flexibility, non-tackiness and good mechanical properties (rub fastness). It is difficult to fulfill all needs together. Crosslinking mechanism currently used (since many years ago) is the aziridine crosslinking but it is highly toxic. Therefore, since many years there is the target for substitution, but without success so far.

Polyacrylate dispersions are known in principle. Dispersions of this type have long been used for coating various substrates to seal and protect them. One exemplary application relates to the sealing of mineral substrates, such as brick, concrete, concrete roof tiles, conventional tiles and the like (cf. US patent 4,511,699 and also GB patent 1 411 268).

EP 0 355 028 A1 discloses a process wherein substrates are coated on their surfaces with aqueous polyacrylate dispersions and the coatings are subsequently dried at elevated temperature. The coating utilizes a mixture of A) a 20% to 65% by weight aqueous dispersion of a copolymer of a) 20% to 70%, based on the weight of the copolymer, of (meth)acrylic esters of alkanols which contain 3 to 20 carbon atoms and have a tertiary CH group, b) 30% to 60%, based on the weight of the copolymer, of styrene, alphamethylstyrene, methyl methacrylate, tert-butyl (meth)acrylate and/or (meth)acrylonitrile, and c) 0.2% to 7%, based

on the weight of the copolymer, of mono- and/or dicarboxylic acids of 3 to 5 carbon atoms and/or their amides which may optionally be substituted at the nitrogen atom by alkyl of 1 to 4 carbon atoms, said dispersion having a minimum film-forming temperature of -30 to +30°C, and B) 0.1% to 5% by weight, based on the amount of the copolymer present in component (A), of an aromatic ketone. The mixture is then cured by exposing it to ultraviolet light before or after drying.

Useful aromatic ketones according to EP 0 355 028 A1 include, for example, benzophenone and benzophenone derivatives such as 3,3'-dimethyl-4-methoxybenzophenone, 3- and 4-hydroxybenzophenone, benzophenone-2-carboxylic acid, benzophenone-3-carboxylic acid, benzophenone-4-carboxylic acid and the like and also 2-, 3- and 4-phenylbenzophenone, 2-, 3- and 4-alkylbenzophenones having 1 to 10 carbon atoms in the alkyl radicals, such as 2-, 3- and 4-methylbenzophenone, 2-, 3-, 4-nonylbenzophenone, dialkylbenzophenones and also olefinically unsaturated as well as water-soluble benzophenone derivatives.

Although the coatings of EP 0 355 028 A1 already reveal a satisfactory durability for the coating film, the coatings are nonetheless further in need of improvement, particularly with regard to properties such as film tackiness the like. Owing to these properties, the dispersions described are unsuitable for leather application.

Benzophenone and low molecular weight benzophenone derivatives are customary photoinitiators. Irradiation leads to the formation of free radicals which can effectuate the polymerization or crosslinking of ethylenically unsaturated monomers.

Carlini et al. in Polymer, 1983, Vol. 24, May, page 599 et seq., report polymers containing side-chain benzophenone chromophores and their use as highly efficient photoinitiators. Copolymers of acryloyloxybenzophenone with menthyl acrylate, methyl acrylate or 1-acryloyloxy-2-ethoxyethane are disclosed. The copolymers described include about 10 to 90 mol% of acryloyloxybenzophenone units and are

useful for photoinitiating the polymerization. The molecular weight of the photoinitiators described is not precisely specified in the paper in question.

US 5,900,472 A describes copolymerizable benzophenone photoinitiators. Disclosed are benzophenone derivatives having 2 to 4 (meth)acrylate groups and also UV-curable coatings, obtainable by reacting the polyfunctional benzophenone derivatives with (meth)acrylate under the action of radiation. According to US 5,900,472 A, the coatings obtainable using the polyfunctional benzophenones are superior to existing coatings involving known photoinitiators in that they display a reduced tendency to leach, bleed or migrate. Unconsumed photoinitiator hitherto tended to be prone to this phenomenon, which limited its use to a few possibilities, which did not include use for leather application.

WO 2002100912 describes UV-curable aqueous dispersions for coating cellulose, particularly adapted to hygiene articles. The purpose here is to improve the resistance to water. This system is not applicable to leather because the material requirements are completely different and the purpose of the coating is completely different.

WO2010108752 describes a benzophenone-containing (meth)acrylate polymer and its use as polymer-bonded UV initiators or additive to UV-curable resins. The possibility for leather application is not explored.

Aqueous dispersions for leather coating shall have good adhesion, good low temperature flexibility, non-tackiness at room temperature, and good mechanical properties. It is difficult to fulfill all the needs together.

An ideal aqueous dispersion itself shall be very simple to use. In this regard, the aqueous dispersion shall fully comply with workplace regulations and, more particularly, also be recognized as very safe to health. In addition, the coatings shall be very quick to cure and/or dry very fully and the leather materials processed shall have a comparatively long service life. For this, curing shall bring about very effective, i.e.

complete and intensive, crosslinking of the coating.

**Summary of the invention**

In view of the prior art cited and discussed above, the present inventor developed an aqueous dispersion and explored its possibility for leather coating, which finally leads to the present invention.

The present invention provides an aqueous dispersion of preferably benzophenone-containing (meth)acrylate polymers which can be used for leather coating.

The present invention also provides the use of the aqueous dispersion of the present invention for leather coating.

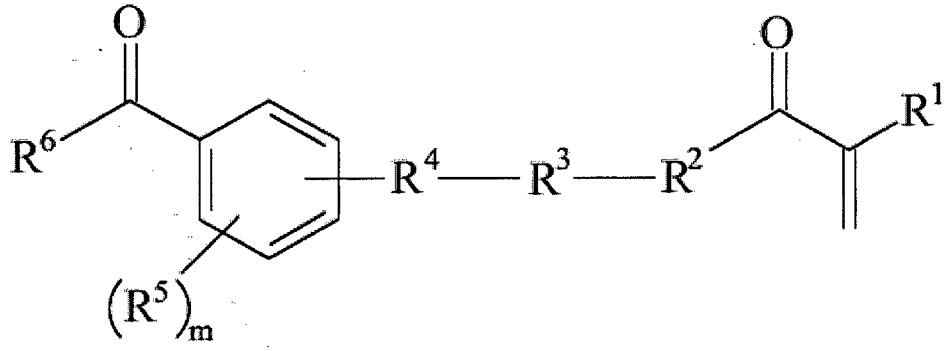
The present invention further provides a process for coating leather with the aqueous dispersion of the present invention.

The present invention further provides a leather material obtained by the process of the present invention.

**Detailed description of the invention**

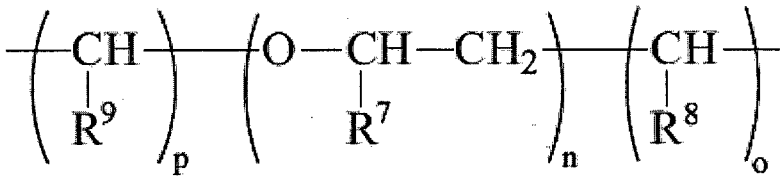
The aqueous dispersion of the present invention contains one or more (meth)acrylate polymers containing one or more compounds of the general formula (I) in polymerized form and obtainable by emulsion polymerization of a monomer composition comprising

a) 0.1% to 25.0% by weight of at least one compound of the general formula (I)



(I)

where $R^1$ is hydrogen or methyl,
$R^2$ is oxygen or NH,
$R^3$ is a radical of the general formula II



(II)

where
$R^7$, $R^8$ and $R^9$ are each independently hydrogen or methyl,
n is an integer from zero to two hundred,
o and p are each independently an integer from zero to two, subject to the proviso that $R^3$ is a bond when the sum total of n and o and p is zero,
$R^4$ is a bond, oxygen or O-CO-O,
$R^5$ is hydrogen, halogen or a radical which contains one to twenty carbon atoms and is optionally substituted with oxygen, nitrogen and/or sulphur, where m is an integer from one to five, and
$R^6$ is an aryl or heterocyclyl radical, substituted or unsubstituted

and

b) a mixture of further compounds comprising
40.0% to 99.9% by weight of one or more acrylates other than a),

0% to 59.9% by weight of one or more methacrylates other than a),
0% to 10% by weight of acrylic acid and/or methacrylic acid,
0% to 10% by weight of one or more acrylamides and/or methacrylamides and/or acrylonitrile and/or methacrylonitrile and/or hydroxyalkyl acrylates and/or hydroxyalkyl methacrylates,

wherein the components a) and b) together amount to 100% by weight of the polymerizable constituents of the monomer composition .

In one embodiment of the present invention, $R^1$ is methyl.

In one embodiment of the present invention, $R^2$ is oxygen.

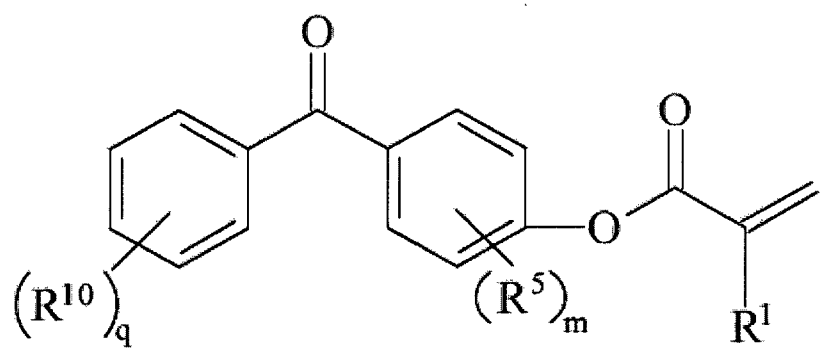
In one embodiment of the present invention, $R^4$ is a bond.

In one embodiment of the present invention, p = o = n = zero.

In one embodiment of the present invention, $R^6$ is phenyl.

In one embodiment of the present invention, $R^5$ is hydrogen.

A particularly preferred embodiment of the invention is directed to such aqueous dispersion wherein component a) used is one or compounds conforming to the general formula (J). In this case, component a) comprises at least one benzophenone (meth)acrylate of the general formula (J):



(J)

where $R^1$ and $R^5$ and also m are each as defined above for the formulae (I). The meanings of $R^{10}$ are analogous to those of $R^5$ and those of q are analogous to those of m. It is very particularly advantageous to use benzophenone methacrylate as component a) to produce the polymer for aqueous dispersion according to the invention.

The compounds of formulae (I) and (J) are either commercially available or obtainable by literature methods. Possible methods of preparation include for example the transesterification of (meth)acrylates with the corresponding alcohols.

Preferably, component a) represents 0.1% to 10.0% by weight, more preferably 0.1% to 5% by weight, more preferably 0.5% to 1.0% by weight of the polymerizable constituents of the monomer composition.

For component b) of the monomer composition of the aqueous dispersion of the present invention, it preferably comprises:
60.0% to 80.0% by weight of one or more acrylates other than a),
0% to 40.0% by weight of one or more methacrylates other than a),
0% to 5.0% by weight of acrylic acid and/or methacrylic acid,
0% to 5.0% by weight of one or more acrylamides and/or methacrylamides and/or acrylonitrile and/or methacrylonitrile and/or hydroxyalkyl acrylates and/or hydroxyalkyl methacrylates.

Acrylates herein are all functionalized or non functionalized acrylates other than a). Preference is given to ethyl acrylate, propyl acrylate, butyl acrylate, ethylhexyl acrylate or mixtures thereof.

Methacrylates herein are all functionalized or nonfunctionalized methacrylates other than a). Preference is given to methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, ethylhexyl methacrylate or mixtures thereof.

Preferably, the acrylamides and/or methacrylamides of component b) comprise acrylamide, N-methylol acrylamide, methacrylamide, N-

methylol methacrylamide or mixtures thereof.

More preferably, component b) of the monomer composition of the aqueous dispersion of the present invention comprises:
10.0% to 30.0% by weight of butyl acrylate,
40.0% to 80.0% by weight of ethyl acrylate,
0% to 40.0% by weight of methyl methacrylate,
0% to 3.0% by weight of methacrylic acid,
0% to 3.0% by weight of methacrylamide.

Preferably, component b) of the monomer composition of the aqueous dispersion of the present invention is preferably chosen such that the (meth)acrylate polymers used according to the invention have a glass transition temperature below 15°C, preferably below 5°C and more preferably below -5°C.

Preferably, the pH of the dispersion of the present invention is 6.0 to 9.0.

The polymers in the dispersions used according to the invention are generally obtained through free-radical polymerization. The customary free-radical polymerization is exhaustively described in Ullmanns' Encyclopaedia of Industrial Chemistry, Sixth Edition, as well as elsewhere.

In the present invention, the polymerization can be started using at least one polymerization initiator for free radical polymerization. This includes redox systems widely known among those skilled in the art. A preferably redox system consists of ammonium peroxodisulphate, sodium hydroxymethanefulinate and $FeSO_4$.

The polymerization to obtain the polymers of the invention can be carried out at atmospheric pressure, subatmospheric pressure or superatmospheric pressure. Polymerization temperature is similarly uncritical. Generally, however, it is in the range form -20 to 200°C, preferably in the range of 0-180°C, more preferably in the range of 50-180°C, even more preferably in the range of 50-130°C and yet even more

preferably in the range of 60-120°C.

Such an aqueous dispersion permits in a not readily foreseeable manner the creation of coatings on leather with advantageous properties through incorporation of polymer-attached UV curable (meth)acrylate polymers in conventional dispersions.

One advantage of the system in relation to the coating of leather with the aqueous dispersion of the invention resides in that no additional photoinitiators are required for the UV curing and no migration of the UV-active species is likely, since the UV active substance is incorporated as a copolymerized monomer in the corresponding coating.

A very particular advantage particularly for applications relating to leather is the curing without release of a low molecular weight compound such as, formaldehyde in the prior art. Hence the process of the invention is of immense advantageousness compared with the prior art in respect of ecological and toxicological aspects.

Processing the dispersions of the invention for coating leather takes the form of applying the aqueous dispersion to the leather sheet material, then drying and a subsequent UV cure which is usually carried out continuously in a belt apparatus. Preferably, a delay period is inserted between the drying step and the UV-curing step to complete the filming of the coating. This generally takes within a few minutes or even within a few seconds. The applying comprises spread coating, roll coating, printing, spraying, saturating or padding.

In relation to the processing of leather, the process of the invention, which involves a UV-curing step, is advantageous over the prior art thermal curing, in several respects. First, the energy requirements are distinctly lower; secondly, the equipment needed for the padding and subsequent curing can be made distinctly more space-saving and technically less complex. A distinctly more long-winded thermal cure naturally requires more space than a short unit for UV curing.

In addition, in the practice of the process of the invention, the dispersions of the invention are observed to be distinctly less prone to coagulate than the prior art dispersions. In addition, the materials display better shear stability and hence better and potentially also faster processibility.

It is further notable that the preferably benzophenone-containing compounds in the composition of the present invention comprise monomers which effectuate a cure via UV crosslinking, instead of polymeric photoinitiators. This constitutes a significant difference from prior art.

**Embodiments**

The examples which follow further elucidate the invention without restricting it in any way. The examples show in particular that the aqueous dispersions and the process of the invention at least meet the requirements for leather coating in respect of the material properties of the end product. Especially the equipment advantages of UV crosslinking and also the ecological advantages of the present invention were comprehensively described above.

**Apparatus**

1) 1L four-neck flask, reflux condenser, saber agitator, motor-driven agitator, metering pump, thermometer, PH meter, contact thermometer in the oil bath, oil bath with motor-driven agitator for homogenization, nitrogen flask with feed line and flow meter, high speed disperser.
2) UV curing lamp: Philips TL20W/05* 2
3) UV curing machine: GY UV 2kw/2, WANGYI

**Chemicals**

Ethyl Acrylate (EA),
Butyl Acrylate (BA),
Methyl Methacrylate (MMA),
Methacrylamide (MAA),
Methyacrylic Acid (GMAA),
4-(Methacryloyloxy)benzophenone (BPMA),
Ammonium peroxodisulphate (APS),

Sodium Hydroxymethanefulinate,
$FeSO_4 \cdot 7H_2O$,
Sodium Lauyl Sulphate (SLS),
Deionized Water.

**Preparing the aqueous dispersions**

**Example 1**

2.63 g of SLS (emulsifier), 145.08 g of EA, 70.47 g of BA, 10.57 g of MAA, 7.0 g of GMAA, 5.83 g of BPMA, 35.233 g of MMA and 497 g of deionized water were mixed and emulsified using Ultra-Turrax at 10000 rpm for 2.5 minutes. The mixture was charged to a reactor. The agitator speed was adjusted to 110 rpm and the temperature of the mixture was kept at about 35 °C.

Under nitrogen atmosphere, 1 g of APS in 10 g of deionized water was added to the reactor. After 30 seconds, 0.0052 g of $FeSO_4 \cdot 7H_2O$ in 4 g of deionized water was added. After another 30 seconds, 0.52 g of hydroxymethanefulinate in 8 g of deionized water was added to start the polymerization. The temperature went up to about 90 °C in about 6 minutes. 0.06 g of APS in 6 g of deionized water was added immediately thereafter. Then 78.12 g of EA was added dropwise over 15 minutes.

The temperature of the mixture was cooled to and maintained at 70 °C for 2 hours. Then 0.06 g of APS in 6 g of deionized water was added. The temperature of the mixture was maintained at 70 °C another 3 hours. The temperature of the mixture was then cooled to room temperature and the result mixture was filtered to remove any coagulum.

The total amount of the raw material used was 888 g. The content of all the monomers was 40 % by weight.

**Example 2-13**

Another 12 batches of aqueous dispersions were prepared. For each batch, the total amount of the raw material used was also 888 g and the content of all the monomers was also 40 % by weight.

The process for preparing these aqueous dispersions was the same as Example 1 except the ratio of monomers which is reported in Table 1. Percentages in the table are all by weight unless otherwise indicated.

The original pH of the dispersion is around 2-3. For Examples 10-13, a portion of the dispersion was taken out and their pH value was adjusted to 8-9 with aqueous ammonia.

Tg, coagulum weight, viscosity, pH, solid content and particle size of Examples 1-13 were calculated or measured. The results are reported in Table 1.

**Performance test of the resultant films**

**Film preparation**

The dispersions of Examples 1-13 were put in open containers and dried at 60 °C overnight. The dried films were further exposed to a weak UV source (Philips TL20W/05 *2 ) for a fixed time of 0h, 0.5h, 1h, 2h and 3h or to a stronger UV source (GY UV 2kW/2, WANGYI) for a fixed time of 2s, 5s and 10s.

**Elongation at break test**

The preparation of film samples and the tests for elongation at break was conducted according to QB/T 2223-96 (Chinese Industry Standard).

**Brittleness test**

The brittleness test of the film samples was conducted according to QB/T 2223-96 with the focus that whether the film is still flexible at -18 °C after long time storage at that temperature (8 hours or 16 hours - two cycles).

**Tackiness test**

The prepared film was kept at least for 24 hours at room temperature. Then the film was tested with finger. The tackiness was judged by the feeling.

The above performance of the films is reported in Table 2.

Table 1 shows that BPMA contributes to gel weight reduction. More BPMA in the recipe, less coagulum could be formed. Table 2 shows BPMA also contributes film tackiness reduction. More BPMA, less tacky the resultant film could be.

Leather coatings should meet many requirements. For example, the emulsion should not contain much coagulum, preferably less than 1 wt.%, or even less than 0.5 wt.%. The resultant film should be non-tacky at room temperature. But on the other hand, it should be flexible enough, that means, even at very low temperature (-18°C) it is not brittle and without any fold remained. Ideally, it would be better if the elongation at break is within 300% to 500% at room temperature while keeping enough tensile strength.

It can be seen from the results in the tables that the properties of the dispersions and the performance of the resultant inventive films generally meet the requirements of leather coating industry. Furthermore, the tensile strength of the resultant films is all above 2.0 MPa which is also advantageous for leather coatings.

## Table 1 Emulsion composition and property of examples

| Example | BA (%) | EA (%) | MAA (%) | GMAA (%) | BPMA (%) | MMA (%) | Tg (℃) | Coagulum (g) | Viscosity cp (RT) | pH | Solid content (wt. %) | Particle size (nm) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 20 | 63.35 | 3 | 2 | 1.65 | 10 | -13.7 | 3.5 | 22 | 2.85 | 38.8% | |
| 2 | 19.7 | 62.48 | 2.96 | 2 | 3 | 9.86 | -12.6 | 2.28 | 24.6 | 2.88 | 39.3% | 94 |
| 3 | 19.32 | 61.19 | 2.9 | 1.93 | 5 | 9.66 | -11 | 1.05 | 25.2 | 2.96 | 39.4% | 90 |
| 4 | 22.3 | 70.52 | 3.34 | 2.2 | 1.65 | 0 | -22.6 | 8.51 | 19.5 | 3.9 | 40.3% | 110 |
| 5 | 21.9 | 69.55 | 3.29 | 2.2 | 3 | 0 | -21.4 | 4.05 | 23.1 | 3.55 | 39.6% | 103 |
| 6 | 21.25 | 67.44 | 3.2 | 2.11 | 1 | 5 | -18.2 | 2 | 26.7 | 3.24 | 39.1% | 95 |
| 7 | 20.1 | 63.78 | 3.02 | 2 | 1 | 10.06 | -14.2 | 1.65 | 24.3 | 3.02 | 39.0% | 95 |
| 8 | 21.1 | 66.97 | 3.18 | 2.1 | 1.65 | 5 | -18.2 | 5.7 | 20.4 | 3.18 | 38.2% | 94 |
| 9 | 21.07 | 66.74 | 0 | 0 | 1.65 | 10.54 | -20 | 8.7 | 20.4 | 2.24 | 39.3% | 90 |
| 10 | 20.78 | 65.83 | 1.5 | 1 | 0.5 | 10.39 | -17.9 | 5 | 25.8 | 2.4/8.6 | 38.8% | 76 |
| 11 | 19.66 | 62.34 | 1.5 | 1 | 0.5 | 15 | -13.4 | 0.8 | 27.4 | 2.5/8.6 | 39.0% | 80 |
| 12 | 16.54 | 52.41 | 1.5 | 1 | 0.5 | 28 | 0.4 | 5.35 | 25.6 | 2.49/8.7 | 39.2% | 80 |
| 13 | 14.5 | 46 | 1.5 | 1 | 0.5 | 36.5 | 10.2 | 3.06 | 27.8 | 2.49/8.7 | 39.2% | 80 |

## Table 2 Film performance of the examples

| Example | Elongation at break (%) | | | | | Tackiness | | | | | Brittleness (-18 °C) | | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Before | 0.5h* | 1h* | 2h* | 3h* | Before | 0.5h* | 1h* | 2h* | 3h* | 8 h | 16h | |
| 1 | 622 | 300 | 275 | 225 | 225 | ++ | ++ | ++ | ++ | ++ | ++ | ++ | 3~4 |
| 2 | 650 | 250 | 225 | 200 | 200 | ++ | ++ | ++ | ++ | ++ | ++ | ++ | 3~4 |
| 3 | 600 | 500 | 150 | 125 | 100 | ++ | ++ | ++ | ++ | ++ | ++ | ++ | 3~4 |
| 4 | 700 | 350 | 250 | 200 | 200 | + | + | + | ++ | ++ | ++ | ++ | 3~4 |
| 5 | 800 | 250 | 205 | 200 | 150 | + | + | + | ++ | ++ | ++ | ++ | 3~4 |
| 6 | 700 | 400 | 350 | 300 | 300 | ++ | ++ | ++ | ++ | ++ | ++ | ++ | 3~4 |
| 7 | 610 | 525 | 375 | 300 | 300 | ++ | ++ | ++ | ++ | ++ | ++ | ++ | 3~4 |
| 8 | 650 | 400 | 300 | 250 | 250 | ++ | ++ | ++ | ++ | ++ | ++ | ++ | 3~4 |
| 9 | 1200 | 400 | 300 | 250 | 200 | + | + | + | + | + | ++ | ++ | 2.2 |
| 10 | 1025 | 550 | 425 | 400 | 400 | + | + | + | + | + | ++ | ++ | 2.4 |
| 10 | 1400 | 650 | 500 | 400 | 425 | + | + | ++ | ++ | ++ | ++ | ++ | 8.6 |
| 11 | 800 | 700 | 425 | 425 | 425 | + | ++ | ++ | ++ | ++ | ++ | ++ | 8.6 |
| 12 | 535 | 400 | 300 | 250 | 250 | ++ | ++ | ++ | ++ | ++ | / | / | 8.7 |
| 13 | 600 | 450 | 524 | 400 | 350 | ++ | ++ | ++ | ++ | ++ | / | / | 8.7 |
| | | | | | | | | | | | | | |
| | Before | 2s** | 5s** | 10s** | | Before | 2s** | 5s** | 10s** | | | | |
| 11 | 800 | 500 | 450 | 430 | | ++ | ++ | ++ | ++ | | ++ | ++ | 8.6 |
| 13 | 600 | 440 | 400 | 400 | | ++ | ++ | ++ | ++ | | ++ | ++ | 8.7 |

* UV curing time, using Philips TL 20W/05, ca 5.5cm between lamp and sample.

** UV curing time, using GY UV 2kw/2, WANGYI

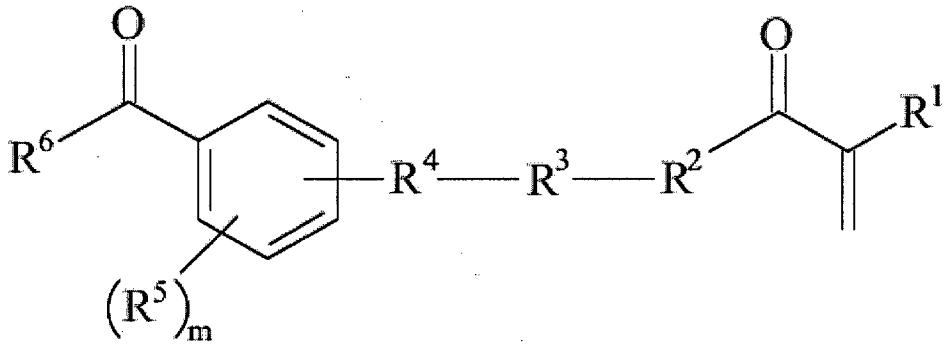
++ good;

\+ a little bit.

## Claims

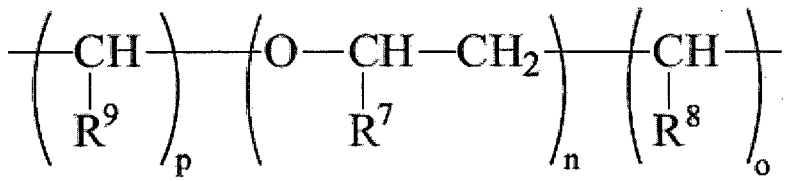
1. An aqueous dispersion, characterized in that the dispersion contains one or more (meth)acrylate polymers containing one or more compounds of the general formula (I) in polymerized form and obtainable by emulsion polymerization of a monomer composition comprising

a) 0.1% to 25.0% by weight of at least one compound of the general formula (I)



(I)

where $R^1$ is hydrogen or methyl,
$R^2$ is oxygen or NH,
$R^3$ is a radical of the general formula II



(II)

where
$R^7$, $R^8$ and $R^9$ are each independently hydrogen or methyl,
n is an integer from zero to two hundred,
o and p are each independently an integer from zero to two, subject to the proviso that $R^3$ is a bond when the sum total of n and o and p is zero,
$R^4$ is a bond, oxygen or O-CO-O,

$R^5$ is hydrogen, halogen or a radical which contains one to twenty carbon atoms and is optionally substituted with oxygen, nitrogen and/or sulphur, where m is an integer from one to five, and
$R^6$ is an aryl or heterocyclyl radical, substituted or unsubstituted,

and

b) a mixture of further compounds comprising
40.0% to 99.9% by weight of one or more acrylates other than a),
0% to 59.9% by weight of one or more methacrylates other than a),
0% to 10% by weight of acrylic acid and/or methacrylic acid,
0% to 10% by weight of one or more acrylamides and/or methacrylamides and/or acrylonitrile and/or methacrylonitrile and/or hydroxyalkyl acrylates and/or hydroxyalkyl methacrylates,

wherein the components a) and b) together amount to 100% by weight of the polymerizable constituents of the monomer composition .

2. The dispersion according to Claim 1, characterized in that $R^1$ is methyl.

3. The dispersion according to Claim 1 or 2, characterized in that $R^2$ is oxygen.

4. The dispersion according to any of the preceding claims, characterized in that $R^4$ is a bond.

5. The dispersion according to any of the preceding claims, characterized in that p = o = n = zero.

6. The dispersion according to any of the preceding claims, characterized in that $R^6$ is phenyl.

7. The dispersion according to any of the preceding claims, characterized in that each $R^5$ is hydrogen.

8. The dispersion according to any of the preceding claims, characterized

in that component a) is 4-(methacryloyloxy)benzophenone.

9. The dispersion according to any of the preceding claims, characterized in that component a) represents 0.1% to 10.0% by weight, preferably 0.1% to 5% by weight, more preferably 0.5% to 1.0% by weight of the polymerizable constituents of the monomer composition.

10. The dispersion according to any of the preceding claims, characterized in that component b) comprises:
60.0% to 80.0% by weight of one or more acrylates other than a),
0% to 40.0% by weight of one or more methacrylates other than a),
0% to 5.0% by weight of acrylic acid and/or methacrylic acid and
0% to 5.0% by weight of one or more acrylamides and/or methacrylamides and/or acrylonitrile and/or methacrylonitrile and/or hydroxyalkyl acrylates and/or hydroxyalkyl methacrylates.

11. The dispersion according to any of the preceding claims, characterized in that the acrylates of component b) comprise ethyl acrylate, propyl acrylate, butyl acrylate or ethylhexyl acrylate or mixtures thereof.

12. The dispersion according to any of the preceding claims, characterized in that the methacrylates of component b) comprise methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, ethylhexyl methacrylate or mixtures thereof.

13. The dispersion according to any of the preceding claims, characterized in that the acrylamides and/or methacrylamides of component b) comprise acrylamide, N-methylol acrylamide, methacrylamide, N-methylol methacrylamide or mixtures thereof.

14. The dispersion according to any of the preceding claims, characterized in that component b) comprises:
10.0% to 30.0% by weight of butyl acrylate,
40.0% to 80.0% by weight of ethyl acrylate,
0% to 40.0% by weight of methyl methacrylate,

0% to 3.0% by weight of methacrylic acid,
0% to 3.0% by weight of methacrylamide.

15. The dispersion according to any of the preceding claims, characterized in that the (meth)acrylate polymers have a glass transition temperature below 15°C, preferably below 5°C and more preferably below -5°C.

16. The dispersion according to any of the preceding claims, characterized in that the pH of the dispersion is 6.0 to 9.0.

17. Use of the dispersion according to any of the preceding claims for coating leather.

18. A process for coating leather, characterized in that the coating includes applying the dispersion according to any of Claims 1-16, then drying and subsequent curing by means of UV radiation.

19. The process according to Claim 18, characterized in that the applying comprises spread coating, roll coating, printing, spraying, saturating or padding, preferably padding.

20. Leather material obtained by the process according to Claim 18 or 19.

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2011/000720

**A. CLASSIFICATION OF SUBJECT MATTER**

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C08L 33/-, C09D 133/-

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI; EPODOC; CNKI; CNPAT; STN: aqueous dispersion; polymer+; +acrylate+; benzophenone; 4-(methacryloyloxy)benzophenone; leather coating

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | WO2010/108762A1(EVONIK ROEHM GMBH) 30 Sep. 2010(30.09.2010) page 5 line 15 to page 7 line 4; page 28 lines 9-16; page 21 lines 1-15 | 1-16 |
| X | TW201105758A (EVONIK ROEHM GMBH) 16 Feb. 2011(16.02.2011) Claims 14-20; page 56 line 23 to page 57 line 6 | 1-16 |
| A | CN1796421A(NAT STARCH & CHEM INVESTMENT HOLDING COR) 05 Jul. 2006 (05.07.2006) the whole document | 1-20 |
| A | WO2010/108752A1(EVONIK ROEHM GMBH) 30 Sep. 2010(30.09.2010) the whole document | 1-20 |

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

* Special categories of cited documents:

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

"E" earlier application or patent but published on or after the international filing date

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

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

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

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

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

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

"&"document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 19 Aug. 2011 (19.08.2011) | **22 Sep. 2011 (22.09.2011)** |
| Name and mailing address of the ISA/CN<br>The State Intellectual Property Office, the P.R.China<br>6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088<br>Facsimile No. 86-10-62019451 | Authorized officer<br>LI, Chen<br>Telephone No. (86-10)62084450 |

Form PCT/ISA /210 (second sheet) (July 2009)

# INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2011/000720

| Patent Documents referred in the Report | Publication Date | Patent Family | Publication Date |
|---|---|---|---|
| WO2010/108762A1 | 30-09-2010 | TW201105730A | 16-02-2011 |
| | | DE102009001776A1 | 30-09-2011 |
| TW201105758A | 16-02-2011 | WO2010112474A1 | 07-10-2010 |
| | | DE102009001966A1 | 07-10-2010 |
| CN1796421A | 05-07-2006 | TW200640955A | 01-12-2006 |
| | | KR20060076218A | 04-07-2006 |
| | | US2006142408A1 | 29-06-2006 |
| | | AU2005244547A1 | 13-07-2006 |
| | | JP2006188687A | 20-07-2006 |
| | | EP1676870A1 | 05-07-2006 |
| | | CN1796421B | 09-06-2010 |
| | | US7745505B2 | 29-06-2010 |
| WO2010/108752A1 | 30-09-2010 | DE102009001775A1 | 30-09-2011 |
| | | TW201105685A | 16-02-2011 |

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2011/000720

Continuation of second sheet:

A. CLASSIFICATION OF SUBJECT MATTER

C09D 133/04 (2006.01) i

C08L 33/04 (2006.01) i

C08L 33/08 (2006.01) i

C08L 33/10 (2006.01) i

C08L 33/14 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC