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(54) AQUEOUS COATING AGENTS, IMPREGNATING AGENTS AND ADHESIVES CONTAINING CATIONIC BINDER SYSTEMS.

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pay that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:-

The present invention relates to aqueous coating agents, impregnating agents and adhesives which contain a cationic binder system, and to their use for cathodic electrocoating.

Cationic binders have numerous potential applications as adhesives and impregnating agents, since on certain substrates, e.g. paper fibres, they are absorbed more rapidly from a dilute liquor than are anionic or neutral binders.

In surface coating technology, cationic binders have, with the introduction of cathodic electrocoating, aroused increased interest since they provide improved corrosion protection, above all on non-phosphatized types of tinplate.

The fact that cationic binders are as yet employed to a relatively small extent in practice is above all attributable to the high curing temperatures required to convert them to solvent-resistant end products.

The present invention seeks to provide a new, modified cationic binder system for aqueous coating agents, impregnating agents and adhesives, which system, exhibits good stability in dispersion, may be cured fully at lower temperatures (below 180-190°) and is in particular suitable for cathodic electrocoating.

According to the present invention, there is provided an aqueous coating agent, impregnating agent or adhesive in which the binder comprises a mixture of

(A) from 20 to 97% by weight of a cationic water-dispersible resin and
(B) from 3 to 80% by weight of a polydiene resin which per se is not water-dispersible.

The invention also provides a cathodic electrocoating process in which such an aqueous coating agent, impregnating agent or adhesive is used.

The mixtures according to the invention can in general be cured at substantially lower temperatures than conventional cationic binders and they offer special advantages in specific fields of use, e.g. electro-coating.

For cathodic electro-coating they generally offer, for example, improvements in respect of the following properties: they give a higher electrochemical deposition equivalent, require lower baking temperatures and have a broader baking range, have better throwing power, are less sensitive to water droplets, and offer better corrosion protection.

Furthermore, they generally exhibit less redispersion of the freshly deposited coating when the current is switched off.

The following may be noted in respect of the individual components of which the binder is composed:

(A) Examples of cationic water-dispersible resins (by which is meant cationic resins which are in themselves water-dispersible without the need for a dispersing agent) are:

(i) copolymers of aminoalkyl ester salts of acrylic acid or methacrylic acid, as described, for example, in British Patent Specification 1,132,267, Netherlands Patent 70/17,172, British Patent Specification 1,331,859, German Laid-Open Application DOS 2,325,117 and U.S. Patents 3,883,483 and 3,853,803;

(ii) copolymers of salts of vinylated heterocyclic compounds containing a basic nitrogen, as disclosed, for example, in British Patent Specification 1,139,837 and U.S. Patent 3,853,803;

(iii) copolymers of salts of polymerizable aminoalkylamides (cf., for example, British Patent Specification 1,159,812);

(iv) salts of epoxy resin derivatives possessing basic groups, such as are described, for example, in Belgian Patent 693,753; German Published Application DAS 1,814,072, U.S. Patent 3,640,926, British Patent Specification 1,307,585, French Patent 2,051,662, British Patent Specification 1,235,975, U.S. Patent 3,719,626, German Laid-Open Applications DOS 2,033,770, DOS2,003,123 and DOS 2,163,143, German Published Application DAS 2,237,114 and U.S. Patent 3,925,180;

(v) salts of Mannich bases derived from phenols, such as are disclosed, for example, in German Published Application DAS 1,644,839 and British Patent Specification 1,302,328;

(vi) solubilized polyamides (cf., for example, British Patent Specification 1,302,328);

(vii) polymers possessing quaternary ammonium groups, such as are described, for example, in German Laid-Open Applications DOS 2,339,398, DOS 2,163,143 and DOS 2,237,114;

(viii) polymers possessing sulfonium groups, such as are described, for example, in German Laid-Open Applications DOS 25 57 562 (British Patent Application 52730/76 Serial No.1564717) and DOS 25 48 394 (British Patent Application 44803/76 - Serial No. 1556224), Netherlands Patent 7,205,851, U.S. Patent 2,166,214, German Laid-Open Application DOS 2,261,804, U.S. Patents 3,873,488 and 3,793,278 and British Patent Specification 1,370,966;

(ix) polymers possessing phosphonium groups (cf., for example, German Laid-Open Application DOS 2,261,804) and

(x) urethane polymers possessing ammonium groups, such as are disclosed in Japanese published Patent Applications 8101-430 and 8101-431 and U.S. Patent 3,891,527.

The cationic water-dispersible resins (A) can be cross-linked, or co-crosslinked, by heating. The crosslinking takes place via reactive groups contained in the resin molecule, e.g. hydroxyl, amide, N-methylolamide, N-methylolamide-ether, ester, epoxide or blocked isocyanate groups or reactive double bonds.

Instead of a particular individual cationic resin, a mixture of two or more cationic resins, e.g. of a resin possessing quaternary ammonium groups and a resin possessing ternary sulfonium groups, may be employed. The result is virtually the same whether the pH of the aqueous dispersions in which the resins are processed is acid, neutral or alkaline.

(B) Among the Polydiene resins,

relatively short-chain polymers or mixtures of relatively short-chain polymers, which have a linear and/or cyclic structure and contain reactive double bonds distributed over the chain and in the terminal positions are particularly suitable. The polydiene resins (B) may be dried or cured either oxidatively or by a temperature-dependent crosslinking polymerization reaction, by themselves or in combination with other unsaturated compounds or systems.

The mean molecular weight of the polydiene resins (B) to be used is generally from 300 to 6,000. For most applications, a mean molecular weight of about 1,000 is advantageous. The acid number is generally at most 25, preferably at most 1 and the saponification number is generally at most 20, preferably at most 1. The iodine number is generally from 100 to 480. These polydiene resins may be synthesized from butadiene, isoprene, cyclopentadiene or distillation cuts of unsaturated hydrocarbons, which may also contain aromatic components, e.g. styrene and/or indene, but preferably contain aliphatic unsaturated hydrocarbons.

The polydiene resin content of the binder mixture (A) +(B) is from 3 to 80, preferably from 5 to 40, % by weight.

The binder mixtures (A) + (B) are usually manufactured by starting from a concentrated solution of a basic resin in an organic solvent, into which the polydiene resin (B) is stirred. If the latter resin is of low molecular weight and low viscosity, the mixture can be prepared readily. If the polydiene resin to be stirred in is of high molecular weight, it is best admixed, to the cationic resin, in the form of a solution in a water-miscible or water-insoluble solvent.

Another method of manufacture of the binder mixture (A) + (B) is to introduce the polydiene resin, if appropriate in the form of an organic solution, into an aqueous solution of the cationic resin and to stir the mixture (in a ball mill or simple stirred equipment) until a dispersion of the desired fineness has been produced.

Suitable counter-ions for the cationic resin are the radicals of inorganic or, preferably, organic acids, e.g. of acetic acid, propionic acid, butyric acid, formic acid, lactic acid and boric acid. The cationic binder may be completely or partially neutralized. In some cases, especially in the case of most binders containing basic nitrogen, adequate dispersibility is achieved even by mere neutralization with CO_2. In the majority of cases, especially in the case of starting resins containing basic nitrogen, equivalent neutralization is not needed in order to achieve a stable dispersion on dilution with water.

To facilitate dispersion, improve levelling and substrate wetting and improve pigment wettability and the like, the effect of the neutralizing agent can be assisted by the use of special solvents, plasticizers, autoxidation stabilizers, curing accelerators and other conventional assistants.

In addition, the aqueous dispersions may contain up to 40% of other binders, preferably low molecular weight compounds or oligomeric compounds which undergo a co-crosslinking reaction with the reactive groups of the cationic resin. Examples include amine-formaldehyde resins, e.g. melamine-formaldehyde and benzo-guanamine-formaldehyde resins, phenol-formaldehyde resins, epoxy resins, blocked polyisocyanates, e.g. polyisocyanates which are blocked by CH-active, NH-active or OH-active compounds which can be split off at below 180°C, e.g. malonate esters, ε-caprolactam or oximes, such as methyl ethyl ketonoxime, and mixtures of these and other resins.

For various applications, especially for use as finishes, pigmenting of the binder mixture is desirable. Pigments, e.g. titanium dioxide and carbon black, fillers, e.g. talc and china clay, dyes, curing catalysts, e.g. acids or compounds which eliminate acids, leveling agents, e.g. high-boiling organic solvents, and the like, may be incorporated either into the organic phase before dilution with water or into the diluted aqueous dispersion. The conventional milling or grinding equipment may be used, since the binder mixtures are stable to shear.

The preferred use of the binder mixtures is the cathodic electrocoating of electrically conductive surfaces, for example of metal articles, e.g. sheets of brass, copper, aluminium, iron and steel, which may have been chemically pretreated, e.g. phosphatized.

The binder solids content of the aqueous compositions is in general from 35 to 75% by weight for conventional processing methods; where the binders are used as electrocoating finishes, the solids content of the aqueous finishes is as a rule from 8 to 15% by weight. The temperature of the electrocoating finish should be from about 20 to 40°C, The deposition voltage, whether direct voltage or asymmetrical alternating voltage, is preferably from 100 to 450 V. The high breakdown strength and low residual current density of these binders and of the electrocoating finishes manufactured therefrom deserve particular mention. A further advantage is the low current required for deposition (the low electrical deposition equivalent in Coulomb/g).

The films deposited by electrocoating have an excellent insulating action, even whilst still wet and in the form of a relatively thin layer of about 20μm, and exhibit a high electrical breakdown strength, which results in very good throwing power of the finish.

In the Examples, parts and percentages are by weight.

EXAMPLE 1

Cationic electrocoating finish using a water-dispersible resin (A) containing ammonium groups.

1a Comparative finish (Finish 1): a cationic finish without polydiene resin. A heat-durable condensation product based on bisphenol A, formaldehyde and a secondary amine which has been obtained under the conventional conditions of manufacture of Mannich bases is partially neutralized with acetic acid and diluted with water to a solids content of 10% by weight.

1b. Finish 2: the condensation product from 1a is mixed in the weight ratio of 70:30 with a polydiene resin which is based on a cationically polymerized C_5-cut and has a mean molecular weight of 300, an acid number of <1, a saponification number of <1 and an iodine number of 380; the mixture is partially neutralized with acetic acid as under 1a and diluted with water to a total solids content of 10% by weight.

1a Finish 3: a 70:30 mixture is prepared similarly to 1b, using a polydiene resin which is based on a cationically polymerized mixture of cylclopentadiene, isoprene, butadiene and other C_5-cut constituents and has a mean molecular weight of 430, an iodine number of 210, an acid number of <0.1. After partial neutralization as described under 1a, the material is diluted with water to a total solids content of 10% by weight.

The three finishes are deposited cathodically under identical conditions in a DC voltage deposition cell. The coating time is 2 minutes in each case, and the deposition voltages are shown in Table 1.

TABLE 1

		Finish 1	Finish 2	Finish 3
I	Deposition equivalent	56 Cb/g	39 Cb/g	34 Cb/g
II	Final current density at 250 V (m A/cm^2)	0.36	0.32	0.26
III	Deposition voltage for a film which is 23μm thick when dry (V)			
	untreated iron sheet	80	170	180
	zinc-phosphatized iron sheet	200	200	210
	iron-phosphatized iron sheet	200	200	210
IV	Throwing power (depth of penetration in cm into a gap 2 mm wide)	11.4	13.6	15.7
V	Required baking temperature (to give an acetone-resistant finish)	190°	180°	150°

The finishes 2 and 3, which are based on a binder mixture proposed according to the invention, show the following advantages over the comparative finish 1:

A lower deposition equivalent and a lower final current density which mean lower current consumption for depositing the finish (I and II).

Substantially less variation in deposition voltage, in the case of the new binder mixtures proposed according to the invention, between untreated iron sheet and phosphatized iron sheets (III).

Better throwing power of the mixtures proposed according to the invention binder (IV).

A substantial lowering of the baking temperature, dependent on the hydrocarbon resin used.

EXAMPLE 2

Cathodic electrocoating using a binder based on a polymer containing sulfonium groups.

2a Comparative finish (Finish 1): 135 parts of a 60% strength solution, in ethylglycol, of a sulfonium acetate based on a di-glycidyl ether of molecular weight about 1,800, described for example in DOS 2,548,394, are mixed with 40 parts of a plasticized urea-formaldehyde resin in butanol (Plastopal BT from BASF) and the mixture is diluted with water to a total solids content of 10% by weight.

2b Finish 2: Finish 2 consists of 70 parts of the binder described in 2a and 30 parts of the polydiene resin described in Example 1b. 93.5 parts of the 60% strength sulfonium acetate solution (cf. 2a), 26 parts of a 50% strength solution of a urea resin (as described in 2a) and 30 parts of a water-insoluble polydiene resin (mean molecular weight 400, Gardner-Holdt viscosity Z1-Z3, iodine number 180, acid number 0, saponification number 0) are mixed homogeneously and the mixture is diluted with water to a total solids content of 10% by weight.

The cathodic finishes are deposited onto zinc-phosphatized sheet iron slabs in an electrocoating installation, using a deposition voltage of 210 V, with a coating time of 2 minutes. Some results are compared in Table 2. It is found that the binder mixture proposed according to the invention (Finish 2) gives greater hardness and greater solvent resistance even at a baking temperature which is lower by 10°. The throwing power and deposition equivalent are also more advantageous in the case of the finish according to the invention.

TABLE 2

	Finish 1	Finish 2
baking temperature (duration 30 minutes)	180°	170°
throwing power (2 mm gap) in cm	6.4	9.5
deposition equivalent (Cb/g)	39	30
Konig pendulum hardness, sec.	160	180
acetone resistance	almost resistant	resistant

EXAMPLE 3

40 parts of a heat-curable condensation product based on bisphenol A, formaldehyde and a secondary amine (cf. German Laid-Open Application DOS 2,320,301), 60 parts of a polydiene resin based on a cationically polymerized C$_5$-cut and 1 part of acetic acid were mixed and slowly stirred into 173 parts of water.

A stable dispersion is obtained.

0.6 part of the above dispersion is added to a paper fibre pulp of 12 parts of soda cellulose and 3,000 parts of water, and the mixture is converted in the conventional manner, at pH 7, to give a paper weighing 75 g/m^2. In a flotation test, this paper shows no water penetration after

2 weeks.

WHAT WE CLAIM IS:-

1. An aqueous coating agent, impregnating agent or adhesive, in which the binder comprises a mixture of
(A) from 20 to 97% by weight of a cationic water-dispersible resin and
(B) from 3 to 80% by weight of a polydiene resin which per se is not water-dispersible.

2. An aqueous coating agent, impregnating agent or adhesive as claimed in Claim 1, in which the component (A) is selected from copolymers of aminoalkyl ester salts of acrylic acid or methacrylic acid, salts of epoxy resin derivatives possessing basic groups, salts of Mannich bases derived from phenols, polymers possessing quaternary ammonium groups, polymers possessing sulfonium groups and urethane polymers possessing ammonium groups.

3. An aqueous coating agent, impregnating agent or adhesive as claimed in Claim 1 or 2, in which component (B) has a mean molecular weight of from 300 to 6,000.

4. An aqueous coating agent, impregnating agent or adhesive as claimed in any of Claims 1 to 3, in which component (B) has an iodine number of from 100 to 480.

5. An aqueous coating agent, impregnating agent or adhesive as claimed in any of Claims 1 to 4 in which the binder mixture (A) + (B) contains from 5 to 40 per cent by weight of component (B).

6. An aqueous coating agent, impregnating agent or adhesive as claimed in any of Claims 1 to 5, which has a binder solids content of from 35 to 75% by weight.

7. An aqueous coating agent as claimed in any of Claims 1 to 5, for use in electrocoating, in which the solids content is from 8 to 15% by weight.

8. An aqueous coating agent, impregnating agent or adhesive as claimed in any of Claims 1 to 7, in which component (B) has an acid number of less than 25 and a saponification number of less than 20.

9. An aqueous coating agent, impregnating agent or adhesive as claimed in any of Claims 1 to 8, to which has been added up to 40% by weight, based on the binder mixture (A) + (B), of a cross-linkable resin selected from amine-formaldehyde resins, phenol-formaldehyde resins and blocked polyisocyanates.

10. An aqueous coating agent, impregnating agent or adhesive as claimed in Claim 1 and substantially as described in any of the foregoing Examples.

11. A cathodic electrocoating process in which a coating agent as claimed in any of Claims 1 to 5 or 7 to 10 is used.

12. An article which has been coated by the use of an aqueous coating agent as claimed in any of Claims 1 to 10 or by a process as claimed in Claim 11.

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