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(54) SELF-ADHESIVE DIAZOTYPE MATERIAL

- (71) We, HOECHST AKTIENGESSELLSCHAFT, a Body Corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention, for which we pray 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:- 5
- The present invention relates to a self-adhesive diazotype material comprising a film having a pressure-sensitive adhesive on one surface.
- Self-adhesive diazotype materials have been known for a long time, and are used whenever recurrent patterns, shapes, component drawings and the like are to be duplicated rapidly and simply. the commercially available types, however, have the following undesirable disadvantages which, in most cases, result from the base materials used for their manufacture. 10
- Self-adhesive diazotype material, for the manufacture of which self-adhesive commercially available films are used, lacks, for example, the requisite optical properties, since the light transmission in the visible region and in the near UV is inadequate. Furthermore, yellowing is frequently observed in use, caused by multiple exposure and/or by aging. An explanation for this behaviour is that adhesive tapes or insulating tapes do not have to meet stringent optical requirements and the film material used for their manufacture is therefore not suitable for the manufacture of self-adhesive diazotype materials. 15
- If, however, commercially available photoprinting materials having good optical properties are coated with a commercially available pressure-sensitive adhesive, the resulting material does not possess the necessary properties with respect to the mechanics of adhesion. Whilst the adhesive power is usually adequate, the adhesive is in most cases so soft that, under the action of pressure and/or heat, it emerges at the edges, either during storage or during copying. It is also frequently observed that when a sample cemented onto a mounting film is detached adhesive residues are left. If a photoprinting material is used as the mounting film, the commercially available adhesive can, especially if it has been applied from an aqueous dispersion, interact with the light-sensitive layer of the photoprinting material and thus discolour the background of the print. Furthermore, the dye in the dye print lines already formed, may be incipiently dissolved by the adhesive and the lines unintentionally broadened. The use of harder adhesives which have a lower tackiness is no solution since they make it more difficult to detach stuck-on patterns without residue, especially if they have been bonded for a considerable period or stored under unfavourable conditions. If they are forcibly detached, this can easily result in damage to the self-adhesive diazotype material. If, however, residues of adhesive remain on the original, an expensive cleaning of the latter with suitable solvents becomes necessary, and the user understandably resents this. 20 25 30 35
- A composite consisting of two layers of stencil material, held together by an adhesive layer, in which at least one of the layers of stencil material carries a light-sensitive layer, has been disclosed in German Offenlegungsschrift 2,316,958. The purpose of the adhesive layer 40

- described there differs from the present invention in that the adhesive used has to hold the layers of stencil material together only temporarily so that they do not slide against one another during cutting to size. For this purpose it does not require to possess self-adhesive bonding properties (that is to say it does not need to stick) and it does not in fact have these properties. An individual detached stencil thus does not adhere to a given base when it is simply pressed onto it.
- The present invention provides a diazotype material comprising a film, at least substantially transparent to ultraviolet radiation, having a diazo compound in the region of one surface thereof and a pressure-sensitive adhesive on the opposite surface, the adhesive comprising
- (A) from 35% to 90%, advantageously 40% to 80%, by weight of, a poly-(butyl acrylate), a 25% by weight solution of which either in gasoline/acetone (weight ratio of 3 : 1) or in ethyl acetate has a viscosity of at least 10 P at 25°C;
- (B) from 0 to 60%, advantageously 0 to 40%, by weight of a synthetic resin a 25% by weight solution of which either in gasoline/acetone (weight ratio of 3 : 1) or in ethyl acetate has a viscosity of less than 10 P at 25°C; and
- (C) from 0 to 50%, advantageously 0 to 25%, by weight of a natural resin or a derivative of a natural resin.
- Preferably, the diazo compound is present in a layer on the said one surface of the film.
- The percentages by weight of the components of the adhesive are their percentages of the solids content, and are based on the total weight of A, B and C.
- Preferably, the pressure-sensitive adhesive layer is covered by a protective layer to protect it against dust and mechanical damage.
- The self-adhesive diazotype material may be made by spreading on the back of a preformed photoprinting film which has the desired optical properties a pressure-sensitive adhesive layer, matched to the intended use.
- Elastomers based on poly-(butyl acrylate) (polymer A) which are commercially available from many manufacturers have proved suitable as the main component for the formula of the pressure-sensitive adhesive; those elastomers are preferred which possess a sufficiently high molecular weight and thus show high viscosities of ≥ 10 P in the solutions defined above. As a result of this, they contribute the requisite cohesion in use so that the adhesive layer will not tear apart when a sample, once stuck on, is detached.
- They have the purpose of providing a support structure which is required for the internal strength of the pressure-sensitive layer. The properties required, with respect to the mechanics of adhesion, may be obtained by mixing in additional components B, and/or C compatible therewith.
- The poly-(butyl acrylates) are inert or show an indifferent behaviour towards the top coatings which may have been applied to the surfaces, for example towards the diazo layers present on the photoprinting films, to which layers they are made to adhere if the latter is used as a mounting film. Poly-(butyl acrylates) are also very particularly suitable for the reason that they are light-stable and do not yellow if they are subjected to multiple exposure, as is often the practice.
- Whilst it is sometimes sufficient to add only component B to the poly-(butyl acrylates), the preferred embodiment contains both component B and component C.
- As component B there may be used, for example, a poly-(butyl acrylate) of low molecular weight or a copolymer of an acrylate (especially butyl acrylate) and vinyl ether or vinyl acetate.
- Component C may be used to increase the adhesive strength relative to the adhesive strength in the absence of component C. Examples of substances suitable for use as component C are tackifying resins, for example the rosin derivatives or terpene resins or alkylphenol resins listed below, amongst which the hydrogenated derivatives are in turn advantageous because of their better optical properties: polymerised rosin, hydrogenated rosin, methyl, pentaerythritol, glycol and polyether-alcohol esters of optionally hydrogenated rosin, abietyl alcohol, esters of abietyl alcohol, terpene/phenol resins having a melting point of 64°C - 130°C and a viscosity of 20 - 120 cP at 20°C in toluene (66.6% strength solution) or alkylphenol resins having a melting point of 50°C - 60°C and a viscosity of 15 - 30 cP at 20°C in toluene (50% strength solution).
- Their proportion in the total solids content is 0 - 50%, preferably 0 - 25%.
- To obtain a good pressure-sensitive adhesive formulation, it has proved advantageous to combine the poly-(butyl acrylate) A with one or more resins B and with one or more resins C.
- In the preferred composition, the proportions of polymer A are 35 - 90%, the proportions of polymer B are 0 - 40% and the proportions of polymer C are 0 - 25%. The desired properties can be adjusted within these limits. The resin B added regulates, for example, the plasticity of the adhesive composition, and the resin C determines the force of

adhesion.

It is also possible, if required, to add fillers, such as, for example, colloidal SiO₂ or aluminium stearate to the formulation and further to optimize the properties of the pressure-sensitive adhesive.

5 The force required for peeling off at 340 mm/minute a 10 mm wide strip stuck on a polyethylene terephthalate film is taken as the force of adhesion. The force of adhesion required for using the material according to the invention is within the limits from about 200 gf - 1,600 gf.

10 An excessive force of adhesion is undesirable since otherwise a sample, once stuck on, is then difficult to detach from the temporary base, and frequently only with the material tearing apart.

The pressure-sensitive adhesive formulations according to the invention give good tackiness of, as a rule, more than

15

10 gf. cm.
mm

15

20 This has the effect that, in particular, edges and corners adhere well to the substrate and do not lift off in the course of time, thus providing points of attack for mechanical forces.

To prepare the coating solution, the base materials that are normally supplied in solution, are weighed, then mixed and, if required, diluted with further solvents in which the components obtainable as solids have been dissolved.

25 The diluents used are above all low-boiling liquids, such as a 60/95 gasoline fraction or an 80/110 gasoline fraction, acetone or ethyl acetate, but alcohols, e.g., isopropanol, may also be used.

30 The pressure-sensitive adhesives are applied to the back of sensitized biaxially stretched polyester films, for example polyethylene terephthalate films, or cellulose acetate films. After drying, the pressure-sensitive adhesive layer is covered with adhesive paper or an appropriately prepared film in order to protect it adequately against dust, dirt and mechanical damage. For despatch, the product is then packaged preferably in the form of sheets in order to facilitate handling by the user.

35 The use of a self-adhesive diazotype material constructed according to the invention is advantageous whenever photoprintable elements, such as, for example, symbols, patterns, drawings of constructional components, art designs, stencils, or masks are to be duplicated, and to duplicate by making a drawing, which turns out to be substantially more expensive, is to be avoided.

40 For the further use of the elements once prepared, it is envisaged that they will be employed *inter alia* in network planning, in the preparation of blanks for printing processes or for chemical milling and in the design of an advertising layout, that is to say whenever a disposition, limited to a surface area, of individual elements is required.

45 These uses necessarily demand that corrections can be made in a simple manner. The ease of detaching the individual elements used and of sticking them back onto the mounting film used as a base is here determined by the magnitude of the force of adhesion and the degree of tackiness of the pressure-sensitive adhesive used.

50 The product according to the invention meets the object of the invention and combines optimum properties with respect to the technology of adhesion with excellent optical properties. The disadvantages known from the commercially available products do not arise, as shown by a comparative experiment in Table 2, below.

The examples which follow illustrate the invention.

All the viscosities mentioned in the Examples were determined using a STV Epprecht Viscometer.

55 Example 1

The following procedure was used for preparing a self-adhesive diazotype material:

A coating solution is prepared from

30 parts by weight of a 25% strength solution of a poly-(butyl acrylate) I in 3:1 gasoline/acetone, having a viscosity of 80 - 140 P at 25°C,

60 7.5 parts by weight of a 50% strength solution of a copolymer of butyl acrylate and vinyl isobutyl ether in ethyl acetate, having a viscosity of 33 cP at 20°C in a 25% strength solution in ethyl acetate,

2.5 parts by weight of a completely hydrogenated glycerol resin ester having an acid number of 3 - 10 and a softening range of 80 - 88°C, and

65 25 parts by weight of acetone.

65

The viscosity of this solution is 200 cP at 20°C.

- This solution is applied to the back of a 50 μ thick, biaxially stretched polyethylene terephthalate film, the front of which is coated with a light-sensitive diazo preparation, and the film is then dried at 120°C to remove the solvent. The dry weight of the pressure-sensitive adhesive layer is 20 g/m². The pressure-sensitive adhesive layer is covered with a polyethylene film to protect it against damage or contamination.

Example 2

- A coating solution is prepared from 30 parts by weight of a 25% strength solution of a poly-(butyl acrylate) I in gasoline/acetone as used in Example 1, 10 parts by weight of a 50% strength solution of a poly-(butyl acrylate) II in ethyl acetate, having a viscosity of 250 cP at 25°C in a 25% strength solution in ethyl acetate, 2 parts by weight of the hydrogenated glycerol resin ester used in Example 1 and 10 parts by weight of gasoline (boiling point 80° - 110°C).

- The viscosity of the solution at 20°C is 1,500 cP.

The solution prepared is then cast onto the back of a 50 μ thick cellulose 2 1/2 - acetate film, the front of which has been sensitized by diffusion with a light-sensitive diazo formulation, using the recipe given below, and the film is dried to remove the solvent.

- 40 parts by volume of water

- 60 parts by volume of isopropanol

- 1 part by volume of glacial acetic acid

- 6 parts by weight of sulfosalicylic acid

- 4 parts by weight of 4,4-diresorcylic sulfide

- 8 parts by weight of 4-diethylaminobenzenediazonium tetrafluoroborate.

- The relationship between parts by weight and parts by volume is the same as that between the kilogram and the litre.

The pressure-sensitive adhesive layer applied has a layer weight of 20 g/m².

- The pressure-sensitive adhesive is protected from damage by covering it with a release paper (kraft paper, the surface of which has been coated with extruded polyethylene and then treated with silicone).

Example 3

The storage stability and the resistance to yellowing of a pressure-sensitive adhesive formulation was tested as follows:

- a coating solution is prepared from 30 parts by weight of a 25% strength solution of a poly-(butyl acrylate) III in acetone/gasoline 1:3, having a viscosity of 30 - 70 P at 25°C, 4.5 parts by weight of a 50% strength solution of a copolymer of butyl acrylate and vinyl isobutyl ether in ethyl acetate, as in Example 1, and

- 15 parts by weight of ethyl acetate and applied, using a coating machine, to a 50 μ thick, biaxially stretched polyester film, the whole is dried at 130°C and then covered with a repellent paper.

The dry weight of the layer of adhesive is 20 g/m².

- On storing the tacky layers for 14 days at 60°C and also on continuous irradiation thereof for 7 days using actinic fluorescent tubes (at a distance of 10 cm), their adhesive power remains unchanged and, furthermore, no yellowing can be observed.

Example 4

A coating solution consists of the following components:

- 30 parts by weight of a 25% strength solution of the poly-(butyl acrylate) I in gasoline/acetone,

- 4 parts by weight of a 25% strength solution of a poly-(butyl acrylate) IV in ethyl acetate, having a viscosity of about 12 cP at 20°C,

- 2.5 parts by weight of dihydroabietyl phthalate and 25 parts by weight of gasoline (boiling point 80 to 110°C).

- The viscosity of the solution is 550 cP at 20°C.

For the purpose of testing its suitability, the solution is cast onto the back of a 50 μ thick, biaxially stretched polyester film sensitized on one side, the whole is dried and then covered with release paper, the surface of which has been siliconized.

- For the suitability test itself, the methods described below were employed; the numerical values determined with their aid make a quantitative comparison of the tested layers possible:

The measurement of the tackiness was carried out using a Tack-Tester which was constructed in accordance with the description by J. Dow "Manufacture of Adhesive Tapes", Trans. Proc. Inst. Rubber Ind., August 1954, page 112.

- The accompanying drawing is a diagrammatic representation of the measuring

arrangement used for measuring the tackiness. A roller bearing R is fixed by means of an electro-magnet A on a plane inclined at 30° to the horizontal and, after switching off the current, the roller R starts to roll over an accelerating length C and strikes zone B on which is placed a length of the adhesive material being tested with a kinetic energy of

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$$\frac{mv^2}{2} = g \times h,$$

10

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with m = mass, v = velocity and h = height of fall, and is braked there. The bearing which, at 20°C, is still just stopped and fixed by the adhesive tape, is determined; the width of the roller also enters into the calculation of the effective energy.

The set, used for the test, of 21 different rollers which differ in their diameters and hence in their effective energy

$$5 \quad \frac{\text{weight} \times \text{height of fall}}{\text{effective width}} \quad 5$$

10 is tabulated below: 10

TABLE 1

15	No. of the bearing	Weight gf	Width mm	Effective width $\frac{\text{gf} \cdot \text{cm}}{\text{mm}}$	15
	1	1.5	4.0	1.8	
20	2	1.6	3.5	2.2	20
	3	2.9	4.2	3.4	
25	4	4.8	4.2	4.8	25
	5	4.9	4.2	5.1	
30	6	6.8	5.3	5.9	30
	7	7.4	4.7	7.6	
	8	11.6	5.7	8.5	
35	9	12.4	5.7	9.3	35
	10	13.7	5.7	9.9	
40	11	19.2	6.6	12.0	40
	12	22.1	6.7	13.5	
	13	24.3	6.5	15.1	
45	14	24.5	6.5	15.3	45
	15	35.4	7.8	18.0	
50	16	29.7	6.5	18.3	50
	17	44.3	9.3	19.3	
	18	53.9	9.3	22.5	
55	19	65.0	9.3	27.0	55
	20	103.4	11.1	34.9	
60	21	124.9	12.3	36.9	60

The effective energy destroyed by braking and fixing is a measure of the tackiness of the tested layers and is equated to the tackiness, that is to say the higher the effective energy, the higher in proportion is the tackiness.

65 Table 2 which follows contains the values for the samples, tested by the procedure described above, from Examples 1 - 4 and for the commercially available product 65

(Spang-Neulipa self-adhesive film) tested for comparison.

Column 1 gives the values for tackiness obtained at 20°C.

To determine the cohesion or the adhesive power, the test pieces of 100 cm² size, freed from their covering materials, are mounted, without bubbles, on 75 μ thick, biaxially stretched polyester film at room temperature and the composite thus obtained is, on the one hand, stored at 20°C and, for comparison, under more severe conditions at 60°C, in either case for 24 hours. Subsequently the adhesive photoprinting film is peeled off and the residue of adhesive on the polyester base is determined gravimetrically.

Columns 2 and 3 record the resulting quantities of residual adhesive in mg/100 cm², obtained on storage of the composite with polyester film. A low residue of adhesive is equivalent to high cohesion of the pressure-sensitive adhesive layer.

The results show clearly that the pressure-sensitive adhesive according to the invention is superior to those which are commercially available and are used for diazotype materials; this can be seen from the higher values for tackiness and cohesion.

TABLE 2

Sample	Tack gf · cm mm at 20°C	Residue after detaching the adhesive film, in mg/100 cm ²	
		Storage for 24 hours at 20°C	Storage for 24 hours at 60°C
Example 1	15.3	1	0.5
Example 2	18.3	0.5	1
Example 3	15.1	1	1
Example 4	18.3	0.5	6
Comparative sample	0.1	1	16

WHAT WE CLAIM IS:

1. A diazotype material comprising a film, at least substantially transparent to ultraviolet radiation having a diazo compound in the region of one surface thereof and a pressure-sensitive adhesive on the opposite surface, the adhesive comprising

(A) from 35% to 90% by weight of a poly-(butyl acrylate), a 25% by weight solution of which either in gasoline/acetone (weight ratio of 3:1) or in ethyl acetate has a viscosity of at least 10 P at 25°C;

(B) from 0 to 60% by weight of a synthetic resin a 25% by weight solution of which either in gasoline/acetone (weight ratio of 3:1) or in ethyl acetate has a viscosity of less than 10 P at 25°C; and

(C) from 0 to 50% by weight of a natural resin or a derivative of a natural resin.

2. A material as claimed in claim 1, wherein the proportion of component (A) is 40 to 80% by weight.

3. A material as claimed in claim 1 or claim 2, wherein the proportion of component (B) is 0 to 40% by weight.

4. A material as claimed in any one of claims 1 to 3, wherein the proportion of component (C) is from 0 to 25% by weight.

5. A material as claimed in claim 1, wherein the proportion of component (A) is from 40 to 80%, of component (B) is 0 to 40% and of component (C) is from 0 to 25%, the percentages being by weight.

6. A material as claimed in any one of claims 1 to 5, wherein component (B) is a low viscosity poly-(butyl acrylate) or a copolymer of butyl acrylate with vinyl ether or vinyl acetate.

7. A material as claimed in any one of claims 1 to 6, wherein component (C) is a modified hydrogenated rosin.

8. A material as claimed in any one of claims 1 to 7, wherein the surface of the adhesive layer remote from the film is covered by a protective layer.

9. A material as claimed in any one of claims 1 to 8, wherein the diazo compound is present in a layer on the said one surface of the film.

10. A material as claimed in claim 1, substantially as described in any one of the Examples herein.

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