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(54) METHOD FOR PREPARING PAPER HAVING TRANSPARENT PORTIONS, AND PAPER HAVING TRANSPARENT PORTIONS PREPARED USING SAID METHOD

(57) The invention relates to the pulp and paper industry, and specifically to the manufacture of paper for producing banknotes, checks, passports, identity cards, and other documents requiring counterfeit protection. The method includes locally impregnating portions of paper, said portions having certain shapes, using a solution of compounds with epoxy groups in the presence of a curing agent. According to the invention, the compounds with epoxy groups may be glycidyl ethers of monohydric and polyhydric alcohols having a dynamic viscosity at a temperature of 25°C of no more than 150 mPa·s. The technical result consists in producing transparent portions on paper without forming, on the surface of the paper, hard films which would hinder a subsequent printing process.

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Description

Technical field

[0001] The invention relates to the pulp and paper industry, and particularly to the manufacture of paper for producing banknotes, checks, certificates, bills, passports, identity cards, fuel vouchers, entertainment tickets, and other documents requiring protection against counterfeit.

Prior art

[0002] A method is known (JP2-127599, 16.05.1990) to obtain the imitation of watermarks on paper, in which a liquid composition obtained by mixing paraffin, oil and a saturated fatty acid with a resin solution in an organic solvent is applied onto the paper using a printing method.

[0003] Furthermore, a method is known (GB1139487, 08.01.1969) to obtain the imitation of watermarks, according to which method a composition comprising hexamethoxymethylmelamine, a curing agent and a colorless polar solvent is applied to the paper.

[0004] A closest prior art to the claimed technical solution is a method (US3140959, 14.07.1964) to obtain paper with a simulated watermark, in which the paper portions corresponding to a watermark design are impregnated with a solution of a thermosetting resin in an organic solvent in the presence of a curing agent. It was particularly suggested to use epoxy resins as the thermosetting resin. In this case, after evaporating the solvent and curing the thermosetting resin, transparent portions simulating the watermark are formed on the paper.

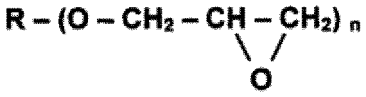
[0005] A disadvantage of this technical solution is that the epoxy resins are characterized by a high dynamic viscosity at a temperature of 25°C and, therefore, prepared solutions based on the epoxy resins in organic solvents at a concentration of more than 50% penetrate poorly into the paper structure and, after curing, form a solid film on the surface of the paper, which film creates difficulties in the subsequent printing of these paper portions. On the other hand, use of solutions having a concentration of less than 50% does not allow to introduce into the paper a sufficient amount of the resin to provide a desired transparency.

Disclosure of the invention

[0006] A problem to be solved by the invention is the preparation of transparent portions on paper without the formation, on a paper surface, of solid films hindering a subsequent printing process.

[0007] This technical result is particularly noticeable on papers having a high degree of opacity, which are used for example for the production of banknotes, because the solution compositions known from the prior art do not enable to obtain portions having a sufficiently high transparency on such papers by impregnation.

[0008] The technical result is achieved by that in a method for manufacturing paper having transparent portions of certain shape, in which the paper portions are impregnated locally with a solution of compounds having epoxy groups in the presence of a curing agent, according to the invention, glycidyl ethers of monohydric and polyhydric alcohols expressed by the following general formula are used as the compounds having epoxy groups:



where n = 1-3, and R is a residue of the monohydric or polyhydric alcohol,
and characterized by a dynamic viscosity of not more than 150 mPa·s at a temperature of 25°C.

[0009] Advantageously the glycidyl ethers of monohydric and polyhydric alcohols are dissolved in an organic solvent in a mass ratio of from 30% to 90%.

[0010] Advantageously the solutions of the glycidyl ethers of monohydric and polyhydric alcohols in an organic solvent are applied by a printing method onto paper portions of a thickness no more than 80 μm, which have been produced in the paper during sheet formation on a paper making machine.

[0011] In particular, the transparent portions have a shape of geometrical figures, symbols, letters or numbers that are visible in transmitted light.

[0012] Specifically, printing images are applied onto the paper having the transparent portions. In another embodiment, printing images are preliminary applied onto the paper, and then the impregnation of the paper is performed to obtain the transparent portions.

[0013] Paper having transparent portions, said paper being manufactured by the claimed method is proposed.

[0014] Monoglycidyl ether of n-butanol, butyl cellosolve monoglycidyl ether, 2-ethylhexanol monoglycidyl ether, diethylene glycol diglycidyl ether, polyoxypropylene glycol diglycidyl ether, polyoxypropylentriole triglycidyl ether, 1,4-butanediol diglycidyl ether, neopentyl glycol diglycidyl ether, trimethylolpropane triglycidyl ether, and others are used in the method of the invention as the glycidyl ethers of monohydric and polyhydric alcohols. Moreover, to achieve the required effect, said compounds may be used either separately, or as a mixture of two or more compounds.

[0015] These compounds are colorless or pale yellow low-viscous liquids that contain epoxy groups in a mass fraction from 7.5% to 30%, and are well compatible with all known epoxy resin curing agents (hardeners). For example, aliphatic or aromatic polyamines, acid anhydrides, Lewis acids, etc. can be used for their curing. Isopropyl alcohol, ethyl acetate, propyl acetate, methyl ethyl ketone, methyl isobutyl ketone, dimethylformamide, and also their mixtures, etc. are used as the solvents for

these compounds.

[0016] In accordance with the invention, a dynamic viscosity of the glycidyl ethers of monohydric and polyhydric alcohols at a temperature of 25°C has to be not more than 150 mPa·s, or, more preferably, not more than 50 mPa·s. If their dynamic viscosity at a temperature of 25°C exceeds 150 mPa·s, when the product is dissolved in an organic solvent in a mass ratio of more than 50%, problems associated with deterioration of penetration of the resulting solution into the paper structure are observed.

[0017] Other compounds containing epoxy groups may be added to the solutions of the glycidyl ethers of monohydric and polyhydric alcohols. For example, homooligomeric epichlorohydrin diglycidyl ether, alkyl phenol monoglycidyl ether, tert-butylphenol monoglycidyl ether can be used as these compounds. In addition, in order to protect against counterfeiting, compounds which are soluble in organic solvents, which have luminescence properties when irradiated with UV radiation at an excitation wavelength of 365 nm or 254 nm, and which also have absorption properties in IR region of spectrum, may be added to the solutions of the glycidyl ethers of monohydric and polyhydric alcohols.

[0018] The solutions of glycidyl ethers of monohydric and polyhydric alcohols in organic solvents (hereinafter the solutions) are applied onto predetermined portions of paper by printing methods. To do this, a deep printing, screen printing or flexographic printing method can be used. For example, when a flexographic printing method is used, these solutions can be applied onto paper using anilox rolls having a screen ruling of 60-120 lines/cm^2 and an ink receptivity of 10-24 cm^3/m^2. In this case, the solution viscosity measured on a funnel with an opening diameter of 4 mm, should be in the range of 10-35 seconds, or even more preferably, in the range of 10-15 seconds.

[0019] If necessary to improve the transparency, the solutions can be applied onto predetermined portions simultaneously on both sides of the paper.

[0020] Formation of transparent portions after applying the solutions onto the paper by printing methods is performed conventionally in two stages. At a first, shortest stage, evaporation of the solvent and also absorption of the solution into the paper occur. To speed up the process at this stage, it is advisable to heat the paper to a temperature of 85-140°C. In a second stage which is the most durable in time and is fully completed already on the reel or stack, the solution soaked into the paper undergoes a final curing. This stage normally lasts for 3-4 days after applying the solution onto the paper.

[0021] The paper is manufactured on a cylinder paper making machine or a fourdrinier former. It may contain wood, cotton pulp, and also synthetic fibers (capron, polyester) in its composition. Furthermore, the paper composition may contain fillers (titanium dioxide), additives to enhance the strength of paper in a dry and wet state (sodium salt of carboxymethyl cellulose, polyamide(amine) epichlorohydrin resin), materials for paper sizing in mass (alkyl ketene dimers), dyes (direct dyes, acid dyes). During the manufacturing process, the paper is sized from the surface with an aqueous solution of polyvinyl alcohol, and also, which is less preferable, with aqueous dispersions of polyurethane, acrylate, or styrene-acrylate copolymer. If necessary, the paper may contain watermarks, fibers, filaments, and other security features.

[0022] The solutions are preferably applied onto the paper portions of a thickness not more than 80 μm. This enables to obtain transparent portions with a high transparency on the paper after infiltration of the solution and curing. Typically, the paper used for the production of banknotes has a thickness of 100-130 μm at a grammage of 90 g/m^2. In such paper, portions of a predetermined shape and size, which have a smaller thickness as compared to the thickness of the paper, can be formed in the paper web during sheet formation. For instance, to fabricate these portions in the sheet formation process using a paper making machine, one can use a dandy roll or design cylinder having watertight elements (watermarks) which have the size and shape of these portions. In this case, the thickness of the paper can be varied by rasterization and by changing the thickness of these watertight elements. Furthermore, the portions of a smaller thickness can be formed on the paper by using a method described in US6402888, 11.06.2002.

[0023] The transparent portions obtained by applying the solutions onto paper by printing methods (hereinafter the transparent portions) should have a shape and size envisaged by the design of a product. For example, they may be located on a sheet of paper symmetrically to overlapping fragments of a watermark (RU2475578, 20.02.2013). In this case, they are shaped and sized according to the overlapping fragments of the watermark. In the simplest case, the transparent portions may have a square, circle, ellipse shape, etc.

[0024] After complete curing of the solution, the transparent portions may be printed by conventional printing methods used for the production of valuable documents and, in particular, banknotes. For example, the printing at the transparent portions can be carried out by a offset printing, metallographic printing, relief printing or screen printing method. Furthermore, it is possible that the printing of predetermined portions of paper is performed firstly by the above-mentioned printing methods, and then the solution is applied onto these predetermined portions in order to obtain the transparent portions.

[0025] A transparency level of the transparent portions was evaluated by measuring an optical density of the paper by means of an X-Rite transmission densitometer. Meanwhile, a decrease in optical density meant an increase in the transparency of the paper.

[0026] Next, the claimed method will be explained in details by examples. The content of the components of the solutions in all examples is expressed in parts by mass.

The best examples of embodiment of the invention

Example 1.

[0027] A banknote paper having a grammage 90 g/m^2 was produced on a cylinder paper making machine according to a known technology, using a design cylinder having watertight elements fixed on a mesh in certain positions. The paper was sized in an impregnating bath with a 4% aqueous solution of PVA. At this time, symmetrically to an arrangement of the watertight elements on the mesh, portions whose thickness was less than the thickness of the paper (110 μm) and varied in the range of 60-96 μm were formed on the paper.

Example 2.

[0028] A solution of the following composition was applied onto the paper prepared in accordance with Example 1 by a flexographic printing method:

Polyoxypropylentriole triglycidyl ether (dynamic viscosity at 25°C is 115 mPa·s)	35 parts
Ethyl acetate	25 parts
Curing agent PEPA	4 parts

[0029] The solution was applied onto both the paper portions of the thickness 110 μm and the thinner portions formed on the paper symmetrically to the arrangement of the watertight elements. After drying and full curing of the solution (after 72 hours), transparent portions visible in transmission mode were formed in those locations where the solution had been applied onto the paper.

Example 3.

[0030] The same as in Example 2, except that diethylene glycol diglycidyl ether (dynamic viscosity at 25°C is 38 mPa·s) was used in the solution composition instead of the polyoxypropylentriole triglycidyl ether.

Example 4.

[0031] The same as in Example 2, except that butyl cellosolve monoglycidyl ether (dynamic viscosity at 25°C is 6 mPa·s) was used in the solution composition instead of the polyoxypropylentriole triglycidyl ether.

Example 5.

[0032] The same as in Example 2, except that n-butanol monoglycidyl ether (dynamic viscosity at 25°C is 1.5 mPa·s) was used in the solution composition instead of the polyoxypropylentriole triglycidyl ether.

Example 6.

[0033] The same as in Example 2, except that a solution of the following composition was used for printing:

Polyoxypropylentriole triglycidyl ether (dynamic viscosity at 25°C is 115 mPa·s)	25 parts
Isopropyl alcohol	36 parts
Curing agent PEPA	3 parts

Example 7.

[0034] The same as in Example 2, except that a solution of the following composition was used for printing:

Polyoxypropylentriole triglycidyl ether (dynamic viscosity at 25°C is 115 mPa·s)	25 parts
Isopropyl alcohol	31 parts
Curing agent XT-116, component B ("CHIMEX Limited", CJSC)	8 parts

Example 8 (comparative).

[0035] The same as in Example 2, except that a low-viscosity resin ELAD EDB (dynamic viscosity at 25°C is 950 mPa·s) was used in the solution composition instead of the polyoxypropylentriole triglycidyl ether.

[0036] Analysis of the results obtained has shown that the application of the solutions prepared according to the claimed method (Examples 2-7) onto the paper allowed a higher transparency to be obtained (an optical density value in transmission mode turned out less by 5-35%) as compared to the closest prior art (Example 8). Furthermore, these solutions were absorbed efficiently into the paper structure without forming, on a surface of the paper, films hindering the subsequent printing process. And the best result in terms of improving the transparency was obtained when applying these solutions onto the paper portions with a thickness of not more than 80 μm.

[0037] Thus, the claimed method allows those portions to be obtained on the paper which have, as compared to the known prior art, a higher transparency without forming, on the surface of the paper, the films hindering the subsequent printing process. The result is achieved by applying onto the paper the solutions of glycidyl ethers of monohydric and polyhydric alcohols which are well absorbed in the paper structure, even when a concentration of the glycidyl ethers of monohydric and polyhydric alcohols in the solution is more than 50%. Moreover, the greatest effect of using the method of the invention is achieved for papers having a high degree of opacity, which are used for example for the production of banknotes or other valuable documents.

Industrial applicability

[0038] The invention is industrially applicable in the pulp and paper industry, in particular, for the manufacture of paper for producing banknotes, checks, certificates, bills, passports, identity cards, fuel vouchers, entertainment tickets, and other documents requiring protection against counterfeit.

Claims

1. A method for manufacturing paper having transparent portions of certain shape, in which the paper portions are impregnated locally with a solution of compounds having epoxy groups in the presence of a curing agent, **characterized in that** glycidyl ethers of monohydric and polyhydric alcohols having a dynamic viscosity of not more than 150 mPa·s at a temperature of 25°C are used as the compounds having epoxy groups.

2. A method according to claim 1, **characterized in that** the glycidyl ethers of monohydric and polyhydric alcohols are dissolved in an organic solvent in a mass ratio of from 30% to 90%.

3. A method according to claim 1 or claim 2, **characterized in that** the solutions of the glycidyl ethers of monohydric and polyhydric alcohols are applied by a printing method onto the paper portions of a thickness not more than 80 μm, which have been produced in the paper during sheet formation on a paper making machine.

4. A method according to any one of claims 1 to 3, **characterized in that** the transparent portions have a shape of geometrical figures, symbols, letters or numbers that are visible in transmitted light.

5. A method according to any one of claims 1 to 4, **characterized in that** printing images are applied onto the paper having the transparent portions.

6. A method according to any one of claims 1 to 4, **characterized in that** printing images are preliminary applied onto the paper, and then the impregnation of the paper is performed to obtain the transparent portions.

7. Paper having transparent portions, being manufactured by the method as defined in any of claims 1 to 6.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2127599 A **[0002]**
- GB 1139487 A **[0003]**
- US 3140959 A **[0004]**
- US 6402888 B **[0022]**
- RU 2475578 **[0023]**