

The present invention relates to a process for the preparation of novolak resins having a low content of metal ions.

The quality of photoresists can be improved by substantially reducing the content of contaminating metal ions in the photoresists. Impurities contained in photoresists mostly comprise metal ions, in particular of iron, sodium, barium, calcium, magnesium, copper and manganese. These impurities are attributable to the resin component which is present as a binder in the photosensitive compositions. These resins of the novolak type are preferably condensation products of phenols or cresols with formaldehyde and the contaminating metal ions get into the resins chiefly as a result of the preparation process. The free phenolic OH groups in the novolak resin promote the incorporation of metal ions by proton exchange and by complexing on the polar groups.

Owing to this complexing, only a minor purifying effect is achieved when the impurities of a polymer dissolved in an organic solvent are washed out with water. The expenditure for separating metal ions is increased by the low content of only a few ppm of metal ions in the resin solutions used for the preparation of resists. To characterize the quality of the purified products it is sufficient to specify the contents of iron and sodium which serve as the indicator metal cations for evaluating the purifying effect.

Separation by volatilization such as, for example, by evaporation of the metal ions or the resin, is impracticable. Similarly, thermal purification processes cannot be used for novolak resins in a molten state, since the resins have a high viscosity and are chemically instable when they are relatively strongly heated. Only after dissolving in an organic solvent can the resins be subjected to a purifying operation. Precipitation processes are excluded, because the solubility product of sparingly soluble metal salts cannot be attained with the extremely low concentrations of metal ions concerned. Adsorption processes, in turn, fail due to an insufficient selectivity of the adsorbents with respect to traces of metal ions in the organic medium.

EP-A 0,251-187 describes a process for the purification of novolaks, which comprises dissolving the novolaks in organic solvents and subsequently extracting the metal ions from the solution by means of an aqueous acid. The aqueous acid used for this purpose is diluted hydrochloric acid, sulphuric acid or acetic acid and has a maximum pH of 3. Traces of these strong acids which remain in the novolak may, however, cause corrosion problems during the later use. Therefore, the publication recommends to remove the traces of acids from the novolak solution by additional washing with water.

It was the object of the present invention to provide a process for the preparation of novolak resins having a low content of metal ions, by means of which process the initial concentration of a few ppm of metal ions is, if possible, further reduced and resins can thus be made available, which meet the requirements for use in microelectronics.

The object of the invention is achieved by a process for the preparation of novolak resins having a reduced content of metal ions, in which a commercial novolak resin is dissolved in an organic solvent or solvent mixture in a concentration of about 25 to 50 % by weight, preferably 30 % by weight,

and the metal ion content of the resin solution is reduced by bringing the solution once or repeatedly into contact with an aqueous solution of an organic acid, wherein the organic acid is a low ^{(-molecular-weight,} multifunctional carboxylic acid comprising carboxyl, hydroxyl, oxo, amino or ester groups, vinylphosphonic acid, nitrilo triacetic acid, ethylene dinitrilo tetraacetic acid; 1,2 cyclohexylene dinitrilo tetraacetic acid, diethylene triamine pentaacetic acid or 3,6 dioxo-octamethylene dinitrilo tetraacetic acid.

By preference, the acidic, preferably complex-forming compound is dissolved in water in a concentration of about 0.01 to 20 percent by weight. Contact can be made by bringing together liquid and solid phases. Appropriately contact is effected in the form of a liquid-liquid extraction.

Contact is preferably obtained in a single-stage or multi-stage cross-flow or countercurrent treatment, cross-flow being advantageous due to its intensity.

The phase volume ratio of organic solvent phase (O) to aqueous extracting agent (W) is about (1 to 5):1, preferably (2.5 to 3):1.

With the aid of the process of the present invention, the metal ion content can be reduced by two to three decimal places and, as a result, materials can be prepared which meet utmost requirements in microelectronics.

It has been found that most metal ions can be separated to an extremely high degree from solutions of the novolak resins in organic water-insoluble solvents, if these organic solutions are extracted with aqueous solutions which contain the above-mentioned acids. Preferred are the organic acids which must be soluble in water and which can sometimes be used in extremely small amounts, for example: low-molecular, polyfunctional carboxylic acids which contain, in further

polar groups, active hydrogen or electron donors, such as carboxyl, hydroxyl, oxo, amino or ester groups and thus have enhanced complexing properties. Such acids include, in particular, dicarboxylic acids, for example, oxalic acid, malonic acid, succinic acid or, as an unsaturated acid, maleic acid.

A similar complexing action is also exhibited by ketocarboxylic acids or hydroxycarboxylic acids such as, for example, glycolic acid and lactic acid or, of the aromatic compounds, salicylic acid. In addition, the oxidation products of polyhydric alcohols are particularly effective, for example, tartaric acid which shows a good complexing action, citric acid, mesoxalic acid or 1-ascorbic acid. Another particularly suitable class of compounds includes the acidic chelating agents used in complexometry, for example, nitrilotriacetic acid, ethylenedinitrilotetraacetic acid, 1,2-cyclohexylenedinitrilotetraacetic acid, diethylenetriaminepentaacetic and 3,6-dioxaoctamethylenedinitrilotetraacetic acid, which are commercially available as (R) Titriplex types (Manufacturer Merck, Fed. Republic of Germany). Suitable extracting agents for metal ions further comprise acidic esters of phosphoric acid, phosphonic acid and phosphinic acid.

In recent years, a number of complexing or chelating agents having selective properties with respect to particular metal ions have been developed for use in hydrometallurgical extraction and purification processes. The active (acidic) hydrogen of these agents can be replaced by metal ions. Furthermore, there are secondary valence bonds with other radicals carrying electron donors, which have N, P and O atoms in their molecules. These include, inter alia, hydroximes, oxime derivatives, β -diketones and the dioximes of α -diketones. The long-chain extrac-

ting agents which were developed for separating metal ions from aqueous solutions are insoluble in water, to meet the requirements of their specific application. The shorter-chain extracting agents, on the other hand, which are inappropriate for hydrometallurgical use show a certain water solubility and can consequently be used for the purification of resins according to the process of the present invention, for example, dimethylglyoxime and acetylacetone.

Apart from the acidic extracting agents which are dissolved in water, solid cation exchanger resins with acidic functional groups (e.g. $\text{-SO}_3\text{H}$, -COOH) also produce a certain, although less pronounced purifying effect. If such a solid ion exchanger resin is used, particular care must be taken to prevent the resin from being partly swollen or dissolved by the organic solvent of the novolak resin.

To prepare liquid phases of the novolak resins, which are required for the purification process, any solvents can be used, in which these resins are soluble. Polar solvents are preferred, for example, relatively high-molecular ketones, such as methylisobutylketone, glycol derivatives containing ester or ether groups, carboxylic acid esters, relatively high-molecular alcohols and mixtures of various solvents. The resin content in the solution is in the range from 25 to 50 percent by weight and is preferably about 30 percent by weight.

It is sufficient for the aqueous solutions of the extracting agents to contain less than 20 percent by weight, preferably between 0.05 to 3 percent by weight, of the extracting agents. Some extracting agents which have a limited solubility in water, are contained in the aqueous solution in a quantity ranging from 100 to 1,000 ppm.

Extraction can be carried out in one stage by mixing once or by mixing repeatedly (multi-stage), each time with a fresh

solution of the extracting agent (cross-flow extraction) or by multi-stage countercurrent extraction. Although room temperature is preferred it is also possible to run the extraction process at other temperatures, provided the resin is not impaired.

After extraction and phase separation, the fractions of water which are dissolved in the organic phase can be removed without difficulty by vacuum distillation.

The novolak-resin solutions so treated can be directly used for the preparation of photoresist compositions.

The following examples are given to explain the process of the invention in further detail, with regard to the modified sodium and iron contents of the resin solution.

Examples

1. The starting solution used is a resin solution comprising 30 percent by weight of novolak resin (termed "resin" in the following examples) in an organic solvent mixture composed of ethylglycol acetate, n-butyl acetate and xylene (termed "EBX solvent" in the following examples). This organic solution is contaminated with 2.8 ppm of sodium ions and 1.3 ppm of iron ions. To separate the metal ions, the organic resin solution (O) is subjected, at room temperature, to a single-stage extractive mixing with an aqueous solution (W) containing the extracting agent in distilled water, at a phase volume ratio O:W of 3:1. The results of the extractive treatments using various inorganic acids as the extracting agents are compiled in the following Table 1. For comparison, the table also indicates an extraction under identical conditions, but using pure distilled water.

To determine the element sodium in the resin solutions a conventional flame atomic absorption is carried out. For this purpose, the samples are diluted with propylene-glycol monome-

thylether acetate and measured by direct measurement against standards of known concentration.

For the determination of iron the samples are diluted with the same solvent and subjected to graphite furnace atomic absorption and Zeeman background compensation. Also in this case standards of known concentration are measured at the same time for comparison.

Table 1

Extracting Agent in Water			Organic Solvent Phase		
Comparative Examples	Wt. %	Na content ppm	degree of extraction %	Fe con- tent ppm	degree of extraction %
Sulfuric acid	1.0	0.10	96.4	0.02	98.5
Hydrochloric acid	1.0	0.09	96.8	0.02	98.5
-		2.3	17.9	1.0	23.0

2. The starting solution used is the same resin solution as in Example 1 showing the same degree of contamination. Extractive purification is carried out under the same conditions as specified in Example 1, but using organic extracting agents in the aqueous phase. The results are compiled in Table 2.

Table 2

Extracting Agent in Water	Organic Solvent Phase				
	Wt. %	Na content ppm	degree of extraction %	Fe con- tent ppm	degree of extraction %
Acetic acid)*	1.0	0.13	95.4	0.09	93.1
Glycolic acid	1.0	0.05	98.2	0.03	97.7
Lactic acid	1.0	0.11	96.1	0.03	97.7
Oxalic acid	1.0	0.05	98.2	0.004	99.7
Malonic acid	1.0	0.09	96.8	0.02	98.5
Succinic acid	1.0	0.10	96.4	0.05	96.2
1-(+)Tartaric acid	1.0	0.20	92.9	0.02	98.5
Citric acid	1.0	0.17	93.9	0.02	98.5
1-Ascorbic acid	1.0	0.23	91.8	0.02	98.5
Salicylic acid	1.0	0.34	87.9	0.08	93.8
Vinylphosphonic acid	1.0	0.11	96.1	0.005	99.6

)*: Comparative Example

3. The resin solution (O) of Examples 1 and 2 is used as the starting solution. The extracting agent is now an aqueous solution (W) containing organic chelating agents. Extraction is carried out in two stages according to the cross-flow process, in each case at a phase volume ratio O:W of 2.4:1 and at room temperature. The results are compiled in the following Table 3.

Table 3

Extracting Agent in Water	Organic Solvent Phase				
	Wt. %	Na content ppm	degree of extraction %	Fe content ppm	degree of extraction %
Nitrilotriacetic acid	0.09	0.10	96.4	0.02	98.5
Ethylenedinitrilotetraacetic acid	0.12	0.16	94.3	0.12	90.8
1,2-Cyclohexylenedinitrilotetraacetic acid	0.023	0.13	95.4	0.04	96.9
3,6-Dioxaoctamethylenedinitrilotetraacetic acid	0.033	0.14	95.0	0.07	94.6

4. The starting solution used is a 30 % concentration novolak resin solution in propyleneglycol monomethylether acetate, containing 2.6 ppm of iron ions and 4.2 ppm of sodium ions. Extraction is carried out with aqueous solutions containing oxalic acid or acetylacetone or dimethylglyoxime. The results are specified in the following Table 4.

Table 4

Extracting Agent in Water	Organic Solvent Phase				
	Wt. %	Na content ppm	degree of extraction %	Fe content ppm	degree of extraction %
Oxalic acid	1	0.12	97.1	0.012	99.5
Acetylacetone	1	0.16	96.2	2.1	19.2
Dimethylglyoxime	0.04	0.5	88.1	0.3	88.5

5. The starting solution (O) is a solution of 30 % of novolak in methylisobutylketone containing 5.1 ppm of sodium ions and 3.7 ppm of iron ions. The extracting agents comprise aqueous solutions (W) containing 1 % by weight or 15 % by weight of oxalic acid. Extraction is carried out in one stage at room temperature and at a phase volume ratio O:W of 3:1. The results are given in Table 5.

Table 5

Extracting Agent in Water	Organic Solvent Phase				
	Wt. %	Na content ppm	degree of extraction %	Fe con- tent ppm	degree of extraction %
Oxalic acid	1	0.08	98.4	0.02	99.5
Oxalic acid	15	0.05	99.0	0.01	99.7

6. The purifying action of solid ion exchangers is determined by means of the following 30 % by weight concentration novolak resin solutions:

Solution A with EBX solvent contains 2.8 ppm of sodium ions and 1.3 ppm of iron ions.

Solution B with propyleneglycol monomethylether acetate contains 4.1 ppm of sodium ions and 3.1 ppm of iron ions.

The ion exchanger is stirred into the resin solution at room temperature and the equilibrium is established with stirring. The results are compiled in the following Table 6.

Table 6 (Comparative Examples)

Starting Material				Organic Raffinate		
resin solu- tion ml	ion exchanger	g	Na content ppm	reduction %	Fe con- tent ppm	reduction %
120 A	Amberlyst	3	0.5	82.1	1.3	0
120 A	Nafion	2	0.8	71.4	1.3	0
120 A	Lewatit	3	0.6	78.6	0.9	30.8
120 A	Lewatit	3	0.8	71.4	0.8	38.5
120 A	Lewatit	3	0.7	75.0	0.8	38.5
120 B	Amberlyst	3	0.7	83.0	3.0	3.2
120 B	Lewatit	3	0.9	78.0	1.7	45.2

(R) Amberlyst, manufacturer Röhm + Haas, U.S.A.

(R) Nafion, manufacturer DuPont, U.S.A.

(R) Lewatit, manufacturer Bayer AG, Fed. Republic of Germany



PATENT CLAIMS

1. A process for the preparation of novolak resins having a reduced content of metal ions, in which a commercial novolak resin is dissolved in an organic solvent or solvent mixture in a concentration of about 25 to 50 % by weight, and the metal ion content of the resin solution is reduced by bringing the solution once or repeatedly into contact with an aqueous solution of an organic acid, wherein the organic acid is a low^(-molecular-weight) multifunctional carboxylic acid comprising carboxyl, hydroxyl, oxo, amino or ester groups, vinylphosphonic acid, nitrilo triacetic acid, ethylene dinitrilo tetraacetic acid, 1,2 cyclohexylene dinitrilo tetraacetic acid, diethylene triamine pentaacetic acid or 3,6 dioxo-octamethylene dinitrilo tetraacetic acid.
2. Process as claimed in claim 1, wherein the organic acid is dissolved in water in a concentration of about 0,01 to 20 % by weight.
3. Process as claimed in claim 1, wherein the contact is made by carrying out a liquid-liquid extraction.
4. Process as claimed in claim 3, wherein the contact is carried out in a single-stage or multi-stage cross-flow or counter-current treatment.
5. Process as claimed in claim 1, wherein a novolak resin solution of about 30 % by weight is used.
6. Process as claimed in claim 2, wherein a solution of the organic acid of about 0,05 to 3 % by weight is used.
7. Process as claimed in claim 1, wherein the organic acid is oxalic acid, malonic acid, glycolic acid, lactic acid, tartaric acid or citric acid.