

The present invention relates to a package for dry-resist material which is wound up into rolls or stacked in the form of sheets, corresponding to the generic part of claim 1 (disclosed in EP-A - 52 560).

So-called "dry resists" comprise photoresists which can be processed with aqueous-alkaline solutions or organic solvents and are formed of three-layer systems, in which the photopolymer layer is sandwiched between a support film and a protective film. The support film used frequently comprises a polyester film, for example, of polyethylene terephthalate, and the protective film a polyolefin film, for example, of polyethylene.

For sale, transportation and storage, the photoresists are, in general, wound up into rolls, wrapped in opaque packaging films and placed in cardboard boxes. The material used for the packaging films often comprises polyethylene which has been dyed with carbon black. To the end faces of the winding cores of the rolls, square or rectangular discs are attached, which are to protect the rolls from mechanical damage during transport and handling.

The known package serves, in the first place, to protect the photoresists from an undesirable influence of light, in particular, ultraviolet radiation, from atmospheric effects, mechanical damage during transport, and soiling.

In practice, it appears that, after transport over relatively long distances and/or prolonged storage periods, photoresists packaged in this way tend to form fused places at the front edges, which are particularly pronounced at the front edges close to the winding core of the roll. In these

cases, small amounts of the photoresist emerge from the front edges of the roll and cause the individual layers of the roll to stick together. Fused places of this kind drastically hamper processing of the dry resist, since upon unwinding the photoresist from the roll, small resist particles are torn away, which may soil the plates, for example, printing plates or printed circuit boards, to which the photoresist is laminated. Such fused places at the front edges of photoresist rolls do not only occur as a result of long storage periods. It has rather been found that the storage conditions as such also have a considerable influence on the processing characteristics of a photoresist. It can happen, for example, that a photoresist roll which has been stored for one year, can still be processed without difficulty, while another photoresist roll, from the same batch, which has been stored in another place under different storage conditions has become useless for processing after only three months.

This different behaviour of photoresist material coming from the same batch clearly shows that the storage conditions and the mode of transport have a considerable influence on the processability of the photoresist material. Closer investigations show that the fused places at the front edges of the photoresist rolls can be attributed to the flow of the photopolymer layer of the photoresist material.

It is therefore the object of the present invention to prevent the flow of a stored dry-resist material, irrespective of the time elapsing between manufacturing and processing of the dry-resist material and of the duration and conditions of storage.

According to the invention this object is achieved in such a way that the material of the package has a permeability to water vapor of less than 0.01 gram of water vapor per square meter and day, at a relative humidity of the air of 97 % and an ambient temperature of 23 °C.

The further development of the present invention is indicated by the characterizing features of claims 2 to 9 (sic.).

The package according to the present invention can, of course, also be used for a dry-resist material which is stacked in the form of sheets.

The invention offers the advantage that there are practically no resist outflows at the edges of photoresist material enclosed in the package which is absolutely impermeable to humidity, even if the photoresist material is stored for a very long time. In this connection, "absolutely impermeable to humidity" refers to a package, the permeability to atmospheric water vapor of which is so low that it can no longer be detected by the most sensitive measuring instruments available at the present time. At present, the threshold of detection is about $0.001 \text{ g/m}^2\text{d}$.

This result is highly surprising since the polyethylene films customarily used for packaging are generally considered impermeable to water vapor.

Below, the invention is explained in detail with reference to the accompanying drawings. In the drawings:

- Figures 1 and 2 show the speed of water absorption of a photoresist,
- Figure 3 shows the viscosity of two different photoresists, as a function of their water contents,
- Figure 4 is a diagrammatic, perspective sectional view of the front edges of a photoresist roll which has been stored in a package according to the present invention for a prolonged period of time,
- Figure 5 is a diagrammatic, perspective sectional view of the front edges of a photoresist roll which has been stored in a conventional package, and
- Figure 6 shows a cross-sectional view of a film tubing material for use in the package.

Based on Figures 1 to 4, the results of investigations carried out on photoresist materials are described, the evaluation of which led to the package according to the present invention.

Systematic investigations into the absorption of water and the viscosity of negative-acting photoresists have shown that the viscosity of the photoresists which are supplied in the dry state after manufacture, decreases considerably during storage due to the absorption of humidity from the atmosphere by diffusion. The photoresist which becomes highly fluid as a result of the decrease of viscosity can then emerge from the front edges of the photoresist roll, under the influence of the winding tension. There are two

additional effects which increase the outflow of photoresist at the front edges due to the absorption of humidity by the photoresist. The photoresist swells when it absorbs water and the swelling pressure squeezes the highly fluid photoresist out at the edges of the photopolymer layer. If the winding cores are made of water-absorbing materials, for example, of cardboard, they start to swell from the atmospheric humidity such that their pressing effect rises and contributes to the above-enumerated effects.

The speed at which a photoresist absorbs water from the atmosphere naturally depends on outside conditions. Figure 1 shows the absorption of water by a photoresist sample comprising three layers, in which the photoresist was exposed to atmospheric humidity, without support and covering films. The photoresist sample is first briskly dried over phosphorus pentoxide and then exposed to an atmosphere of 53 % relative humidity. At room temperature, saturation of the sample is reached after 1.5 hours.

Figure 2 shows the absorption of water by a photoresist sample which is covered with films on both sides and comprises three layers, exactly as the aforementioned photoresist sample. This sample is also first briskly dried over phosphorus pentoxide and then exposed to an atmosphere of 53 % relative humidity. After 20 hours, equilibrium had not yet been reached.

With respect to the process of water absorption by a photoresist roll stored in the air, these investigations show that humidity will penetrate more rapidly from the front

edges of the roll than through the layers of the photoresist material which are protected by films.

In Figure 3, the viscosities of two different photoresist materials are plotted as a function of the water contents of the photoresist materials. The water content of the individual photoresist is, in a rough approximation, proportional to the atmospheric humidity. The viscosity curves indicate that photoresists which are substantially dry after manufacture and have a high initial viscosity absorb water when they are stored in the air, which generally always possesses a certain degree of atmospheric humidity, and thus become highly fluid, in other words, their viscosity decreases.

The respective ambient temperature has an influence on the viscosity of the photoresists, insofar as viscosity decreases with rising temperatures.

The absorption of water causes swelling of the photoresists, which may result in an increase of thickness and volume of up to 4.6 % to 13.8 % respectively, when the relative humidity of the air is raised from 0 % to 97 %, at an ambient temperature of 23 °C.

From the above statements follows that the absorption of water by the photoresist material caused by the relative humidity of the ambient air favors the outflow of photoresist material from the front edges of rolls. As a consequence, an ideal package must be absolutely water-tight such that the low humidity of the material which is adjusted in the manufacture of photoresist material is retained up to the

moment of use and even a temperature rise in storage does not cause the photoresist material to become too highly fluid. The package according to the present invention, which reliably protects the quality of the photoresist material over long periods of time, can be differently constructed.

As shown in Figure 4 in a diagrammatic and perspective sectional view, a photoresist roll 2 is enclosed in a package 1 comprising a film tubing of a material which is impermeable to water vapor. At the two ends the film tubing is closed by welding or glueing. The ends of the winding core of the photoresist roll 2 are closed by covering discs which are not shown. The upper front edges of the wound up photoresist roll 2 are free from squeezed out photoresist material. In the packaging process it is irrelevant whether the photoresist roll 2 is directly welded into the package 1 comprising the film tubing or whether the photoresist roll 2 is first provided with the covering discs and then packaged. The only prerequisite is that the package 1 does not contain materials which give off water vapor, for example, winding cores made of cardboard, since these would naturally limit the effect of the water-vapor tight package 1.

The effect of the impermeable package can be further improved by removing the air which is present in the interior of the film tubing or by replacing it with dry air or a dry gas, immediately before the package 1 is closed by welding or glueing.

When packaging the photoresist roll 2 in a film tubing, care has to be taken to avoid damaging the film tubing. Air, which always has a certain atmospheric humidity, can enter

into the package 1 through small holes or tears, especially in the case of temperature variations, so that the effect of the package is partially neutralized. The water vapor introduced by air penetrating through a damaged package 1 can be controlled to a certain extent by means of a receptacle 6 containing a desiccant 10. The receptacle 6 can be disposed in the package 1 in different ways. It is either packaged together with the photoresist roll 2, or slipped into a sling or pocket provided on the inside of the package 1, or introduced into the interior of the winding core of the photoresist roll. The desiccant which is present in the receptacle 6 provides protection only in the case of a slightly damaged package 1 and can by no means be a substitute for the package 1 as such. Suitable desiccants comprise, for example, commercial silica gel types.

As another package for one or several photoresist rolls 2 the present invention provides a drum made of tinplate which accommodates an individual roll or a number of photoresist rolls and is closed by soldering, such that no atmospheric humidity whatsoever can penetrate into the interior of the package.

Figure 5 represents in a diagrammatic, perspective sectional view, a photoresist roll 2 which was stored for eleven days at 97 % relative humidity of the air in a polyethylene film tubing 11 dyed black. The photoresist roll 2 stored over a saturated potassium sulfate solution to maintain a relative humidity of the air of 97 % shows, after this kind of storage, the diagrammatically indicated photoresist outflows 5 at the front edges, resulting from moist air entering into the polyethylene film tubing 11

serving as the package, which generally has a permeability to water vapor which is considerably higher than $1 \text{ g/m}^2 \text{ d}$, at a difference of relative humidity of 85 % and an ambient temperature of 23°C .

Figure 6 is a sectional view of a film material used for the package 1. The material is a polyester-aluminum composite consisting of a biaxially stretched polyester film 7, as the support film, e.g. a polyethylene terephthalate film (^(R)HOSTAPHAN) manufactured by KALLE Niederlassung der Hoechst AG, which is laminated with an aluminum foil 8 or vacuum-metallized with aluminum and laminated with a polyethylene film 9. The polyethylene film 9 can also be applied by extrusion-coating. The polyester film 7 has a thickness of about $12 \text{ }\mu\text{m}$, the aluminum foil 8 is from 7 to $12 \text{ }\mu\text{m}$ and the polyethylene film 9 from 70 to $100 \text{ }\mu\text{m}$ thick. The first-mentioned material layer, i.e. the polyester film 7 of the composite structure, invariably forms the outside of the package 1; the last-mentioned layer faces the packaged material. The sealing temperature for the film composite ranges between 130 and 180°C . The permeability to water vapor is below $0.001 \text{ g/m}^2 \text{ d}$ and thus provides an adequate tightness for the storage of photoresist rolls, even under extremely unfavorable conditions.

To test the effectivity of the package in preventing photoresist outflows, the comparative investigations described in the following examples were carried out.

Example 1

A photoresist roll 100 m in length and 400 mm in width of the photoresist material (^(R)Ozatec T 138, manufactured by KALLE

Niederlassung der Hoechst AG, was placed immediately after manufacture into a cylindrical tinplate container which was closed with a lid and then sealed by soldering. A second photoresist roll of the same photoresist material was wrapped in a polyethylene film which had been dyed black. The ends of the film were loosely tucked into the hollow winding core of the photoresist roll. The two differently packaged photoresist rolls were stored for four weeks at an ambient temperature of 23 °C, lying on a grate in a plastic container. During this period, water was present in the bottom of the plastic container, at a height of level of 2 cm, so that the atmospheric humidity in the interior of the plastic container was invariably very high. After four weeks storage, the two photoresist rolls were removed from the plastic container, taken out of their packages and visually examined. The photoresist roll packaged in the tinplate container did not show any change at the front edges which were absolutely flawless and free from photoresist outflows.

The photoresist roll packaged in the polyethylene film, on the other hand, showed a severe outflow of photoresist material at the front edges and fused places formed by these outflows which drastically impair the processability of the photoresist material, as is known from experience.

Example 2

The procedure of Example 1 was repeated, but instead of the tinplate drum a film tubing comprising the above-described polyester-aluminum composite manufactured by KALLE Niederlassung der Hoechst AG was used and the free tubing ends were closed by welding immediately after packaging the photoresist roll. After four weeks storage, the photoresist

roll packaged in this manner did not show any changes at its front edges, which were absolutely flawless. Consequently, this result is, without any limitation, comparable to the result obtained in the case of the photoresist roll packaged in a tinplate drum sealed by soldering, according to Example 1.

The photoresist roll which had been loosely packaged in the polyethylene film, on the other hand, showed a severe outflow of photoresist at the front edges and corresponding fused places formed by the photoresist outflows, just as in Example 1.

Example 3

The testing arrangement was identical to that of Example 1. A photoresist roll of the same type as in Example 1 was packaged in a film tubing of a polyester-aluminum composite and the latter was closed by welding. The film tubing was intentionally damaged by repeatedly bending; in the process, only the aluminum film was ruptured, while the support film and the polyethylene film laminated on top remained intact, as far as this could be judged by visual examination. A second photoresist roll of the same type was welded into another film tubing which was treated in the above-described manner. Together with this second photoresist roll, a bag containing 100 g of a granular silica gel was packaged. The two packaged photoresist rolls were stored for four weeks over water, as in Example 1. Examination of the photoresist rolls after this period showed a slight outflow at one front edge of the photoresist roll which had been packaged without desiccant, whereas the photoresist roll which had been

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packaged together with the desiccant was in an absolutely perfect condition.

PATENT CLAIMS

1. Packaged photoresist material wound up into rolls or stacked in the form of sheets, with a virtually water vapor-impermeable, sealed package, characterized in that the packaging material has a permeability to water vapor of less than 0.01 gram of water vapor per square meter and day, at a relative air humidity of 97 % and an ambient temperature of 23 °C.

2. The packaged photoresist material as claimed in claim 1, wherein the permeability to water vapor is less than 0.001 gram of water vapor per square meter and day.

3. The packaged photoresist material as claimed in claim 1, wherein the package (1) comprises a film tubing which is closed at the two ends thereof and comprises a composite material formed of a polyester film (7) which is vacuum-metallized with aluminum or laminated with an aluminum foil (8), and a polyethylene film (9) applied by laminating or extrusion-coating.

4. The packaged photoresist material as claimed in claim 3, wherein the interior of the film tubing is filled with dry air or a dry gas before the ends of the film tubing are hermetically sealed by glueing or welding.

5. The packaged photoresist material as claimed in claim 3, wherein the air in the interior of the film tubing is exhausted before the ends of the film tubing are hermetically sealed by glueing or welding.



6. The packaged photoresist material as claimed in claim 1 or claim 2, wherein the package comprises a tinplate container which has the shape of a cylinder or a rectangular parallelepiped, the ends of which are closed by soldering.

7. The packaged photoresist material as claimed in claim 3, wherein a desiccant (10) packaged in a receptacle (6) is present in the interior of the package (1).

