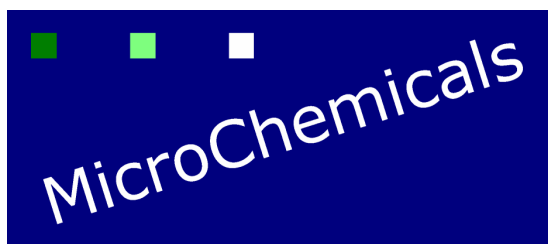


Storage, Ageing, Refilling, and Dilution of Photoresists



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Storage Conditions for Photoresists and Ancillaries

Storage Temperature Limits

For the resist families AZ® 1500, 4500, ECI 3000, and the resists AZ® 5214 E, PL 177, and 111 XFS, the specified storage temperature ranges between 0-25°C. For AZ® nLOF 2000, 6600, 9200, and the 701 MiR, the manufacturer recommends 0-15°C. An elevated temperature of up to 35°C can be tolerated for a few hours in the case of less critical processes, any temperature beyond 35°C even for a short time results in a resists being 'out of specifications'.

High storage temperatures cause accelerated resist ageing, with particle formation and photo active compound loss as a result. Therefore, in case of critical processes or the demand for maximum reproducibility until the resists expiry date, a storage temperature of 5-10°C reduces the degradation to a minimum. In this case, it is obligatory to adapt the resist bottles to room temperature some hours before opening them, otherwise condensed water may deteriorate the resist.

Aqueous solutions such as developers should not be cooled below their freezing point, while temperatures beyond the recommended 35°C for hours or days generally does not deteriorate the product performance.

Storage Illumination Conditions

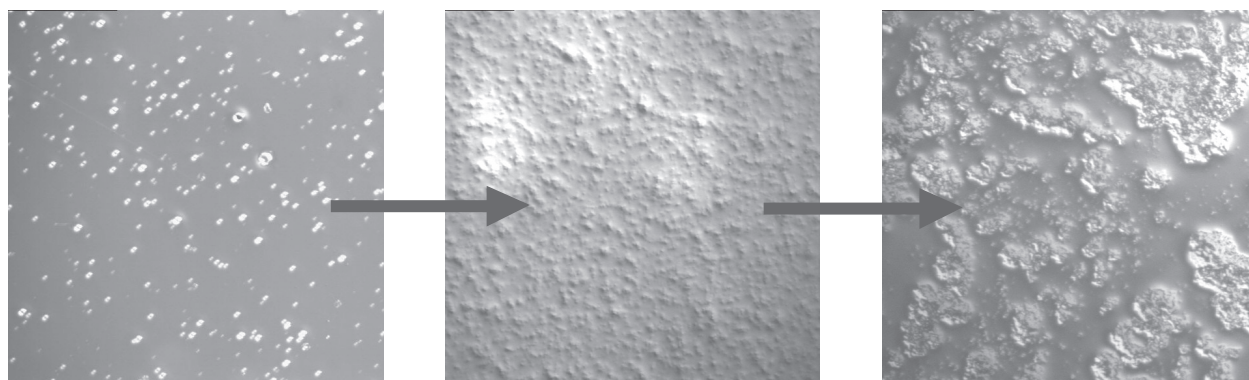
All AZ® and TI photoresists are shipped in light-resistant brown or black bottles in order to protect the resist from exposure during shipping and storage. Direct sun exposure should be avoided due to the build up of heat.

Daylight, light bulbs, and fluorescent lamps emit also blue and green light which matches the spectral sensitivity of many photoresists (g-line = 435 nm!), for details please consult the document [Optical Parameters of Photoresists](#). After coating, the resist film has to be protected against short-wavelength light. Otherwise, positive resists will show an elevated dark erosion during development, and negative resists will partially crosslink near the resist surface which makes development impossible.

Therefore, we strongly recommend the use of yellow foil to block any illumination with wavelengths < 500 nm.

Developers and other ancillaries are generally not sensitive to light.

Ageing of Photoresists



Appearance of more and more (from left to right) aged photoresist after coating: With increasing concentration and size, particles conglomerate to clusters (each picture 500 x 500 µm).

Photoresists, developers, remover, adhesion promoters, etchants, and solvents ...

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Apart from the storage at the recommended temperatures longer than the given expiry date, also high temperatures over a longer time span, a too strong dilution and/or unsuitable solvents as well as chemical impurities (water, isopropyl, softener from plastics) cause an (accelerated) ageing of photoresists, which impacts the resist's performance:

Particles

The formation of particles, their growth and conglomeration into larger clusters is induced by precipitation of the photo initiator (Fig. below: light micrograph, each picture approx. 500 x 500 µm). With the naked eye one can see a rough surface, until in the advanced stage of ageing, the coating becomes increasingly inhomogeneous (strong ripples, coverage failures behind larger particles). Since the photo initiator is lost by precipitation in the resist, the development rate decreases and the dark erosion increases. This is why a filtration of photoresists with these particles is no solution.

With increasing storage time, thermal decomposition of the PAC concentration also causes a lower development rate, and a higher dark erosion. At the same time, nitrogen formed during storage which partly solves in the resist and may cause popping/bubbles during/after coating.

In the case of image reversal resists, the loss in the photo active compound strongly impacts the undercut profile: If less exposed PAC is available for the image reversal process, especially the substrate-near resist part remains developable thus forming a more pronounced undercut. Narrow resist structures hereby may peel from the substrate pretending an inferior resist adhesion.

Darkening

Gradual darkening of the photoresist originates from the formation of azo dyes (esterification of the photo initiator with the resin), but does not have a strong impact on the processing and performance of the resist: Even traces of such converted photo initiator significantly change the color of the resist in the visible part of the spectrum, but only marginally affect the UV-absorption responsible for the exposure process.

Solvent Evaporation

Very frequent opening of small bottles allows a part of the solvent to evaporate. Even a 1 % solvent loss increases the viscosity and thus the layer thickness obtained by spin coating significantly. As a consequence, the necessary exposure dose and development time can be increased. However, due to the low vapour pressure of the solvents generally used, this 'ageing' effect only impacts the process after opening the resist bottle over several 100 times, each time accompanied by the entire exchange of the solvent atmosphere in the bottle. Even then, a slightly higher resist viscosity can easily be compensated for by adjusting the spin speed.

Refilling Photoresists

We offer 250, 500 and 1000 cc bottles for almost all AZ® and TI photoresists. If nevertheless the resist has to be refilled into smaller bottles, a two-stage cleaning procedure of the bottles with i) acetone (removes organic impurities) and ii) isopropyl alcohol (rinses contaminated acetone off) is recommended. The very slowly evaporating isopropyl may interact with the photoresist chemistry and must be evaporated completely before filling the bottles.

The bottles and materials the resists get in contact with should only be suitable plastics (e. g. uncolored teflon, HD-PE without softeners) or low-sodium glass. Between refilling and resist coating, a delay of - depending on the viscosity - up to some hours is necessary, in order to outgas air bubbles that may lead to defects in the resist film.

Dilution of Photoresists

We supply different dilution grades for most resists, and ready-diluted mixtures for special coating techniques such as spray- or dip coating. The document [Photoresists, Developers, and Removers](#) gives an overview on the available viscosities of various resist families.

If nevertheless the resist should be diluted, it is strongly recommended to use resist-compatible solvents such as the high-boiling PGMEA (= AZ® EBR Solvent), butyl acetate, or ethyl

lactate. If low-boiling solvents are required, acetone or MEK are suitable for resist dilution. Isopropyl alcohol may deteriorate the resist and is therefore NOT a suited solvent.

Not all resists are suited for thinning. Low-viscosity and DNQ-rich resists such as the AZ® 1505 or 6612 will show particle formation after a period of time when further diluted, while thick resists such as the AZ® 4562 or 9260 tolerate higher dilution ratios. When diluting the resist, care has to be taken to ensure rapid mixing in order to avoid a highly-diluted interface of photoresist and solvent which might initiate particle formation.

Between refilling and resist coating, a waiting period of - depending on the viscosity - up to a few hours is necessary in order to outgas air bubbles that may lead to defects in the resist film during coating.

Disclaimer of Warranty

All information, process guides, recipes etc. given in this brochure have been added to the best of our knowledge. However, we cannot issue any guarantee concerning the accuracy of the information.

We assume no liability for any hazard for staff and equipment which might stem from the information given in this brochure.

Generally speaking, it is in the responsibility of every staff member to inform herself/himself about the processes to be performed in the appropriate (technical) literature, in order to minimize any risk to man or machine.

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