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Diazo Film Technologies

The discovery of the diazo process occurred towards the end of the 19th century when diazonium salts were first synthesised. However, only in the 1920s the diazo process emerged as a commercial possibility when in Europe diazo-type reproduction was introduced as a competitor to the ferroprussiate (blueprint) process in the field of technical reproduction. The early materials and processing machines were crude, but the essential simplicity of the process, its versatility and its ability to use cut sheets as well as rolls gave the process wide acceptance. Most important, however, was the speed with which the prints could be produced.

The industry was given further impetus by the growth of communications during World War II and then again at the end of the war when previously classified information became available. Many manufacturers entered the field through licensing arrangements or after expiration of the basic patents and today it is one of the most important fields in the reproduction industry.

The diazo process is widely used as a duplicating medium. It was originally associated with the reproduction of engineering drawings. However, it's versatility, low cost and aesthetic capabilities have opened many other application areas, including microfilm and the manufacture of printed circuit boards. Diazo-type formulas are now coated onto a variety of papers, cloths and films.

The diazo process is used extensively in the microfilm industry for producing duplicates with many different coating formulas from which to choose: high or medium contrast, blue or black colouring and high or medium speed. Diazo films are available in various configurations and base thickness can be 2.5, 4.0, 5.0 or 7.0 mil (0.06, 0.10, 0.12 or 0.18 mm).

Diazo Process - Basic Mechanism

The diazo process is based on the ability of diazonium salts to combine with dye couplers to form a strongly coloured dye. When exposed to ultraviolet radiation the diazonium salts are destroyed along with their dye-forming capability. Exposure to ultraviolet radiation causes a photolytic process in which the diazonium salts decompose, leaving an inert product and liberating nitrogen gas.

The coupling process occurs whenever the diazonium salts and dye couplers are brought together. However, it is necessary to inhibit coupling (and dye formation) until after the exposure. The requirement can be achieved by adding a stabilising agent or stabiliser.

Image Formation

Figure 1 illustrates a simplified diagram of the diazo imaging process. In practice, the two films - the silver master and the unexposed diazo film - must be held in intimate contact (emulsion to emulsion). The master controls the light that reaches the diazo film. The light is transmitted through clear areas of the master and is blocked by the dense areas. When the transmitted light strikes the diazo coating, the diazo salts are broken down to a clear product, no longer capable of coupling to form a dye (photolysis), and nitrogen gas is emitted from the coating. It is important to note that the plastic layer that holds the chemical products is constructed to permit the nitrogen to escape. In the areas unaffected by ultraviolet light the coating still contains the salts, the coupler and the stabilisers.

If the exposed diazo film is treated with alkaline substance such as ammonia, the alkali neutralises the stabiliser. The coupling process will then occur, providing the dye, which will be formed in those areas unaffected by ultraviolet light, i.e., the areas corresponding to the dense areas of the master. The duplicate retains the same *polarity* as the master; that is, dark or black areas on the master will remain dark or black on the diazo duplicate, while clear areas on the master will remain clear on the diazo duplicate. Therefore the diazo process is a sign-maintaining system.

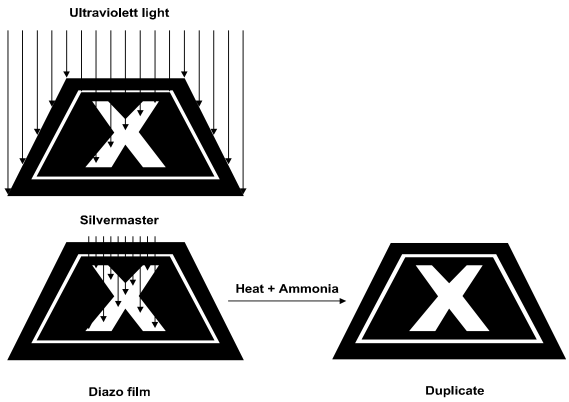


Figure 1: The diazo process

Diazo Development

When diazo material is exposed to ultraviolet radiation, sufficient energy (100 to 220 mJ/cm^2 in the range of 380 to 410 nm) must be provided to destroy all the diazonium salts in exposed areas. The exposure energy is responsible for forming the image by destroying the dye-forming capability of the diazo coating in the exposed areas.

Diazo film is developed by neutralising the stabiliser to cause dye formation in the unexposed areas. This process differs greatly from that used for conventionally processed silver film, in which a dense image is formed in the exposed areas.

The dye that produces the dense areas results from the chemical coupling of the diazonium salts and the dye couplers. Full development occurs when the stabiliser has been neutralised and all the salts and couplers have been combined. Over-development cannot occur (while under-development can!). Once the stabiliser has been neutralised, the alkaline developer (ammonia vapour) has no further effect on the film, and prolonged development cannot degrade the image. Amplification (see chapter "Microfilm") cannot occur during development; therefore, the latent and the final images are identical. The energy required to form a diazo image is over a million times greater than that needed in the silver-halide process, because, unlike the silver process, the image is completely formed before the developing stage and no additional energy is provided by the developer (that's why the amplification factor is 1).

In microfilm systems ammonia is generally used as the alkaline agent to neutralise the stabiliser. Since coupling speed is of great importance in the practical use diazo film heat is used in most diazo development systems because it accelerates the reaction and enhances the coupling speed.

Colour Shift

The effect of the heat varies for different dyes and couplers and may affect the final colour of the film. For this reason, temperature variations may cause a shift in the final colour of the film. This shift is most noticeable in those films employing multiple dye colours to produce the final colour (e.g., the neutral black). The coupling speed of each dye depends on the temperature in the developer chamber. As the temperature is increased or decreased, one dye may couple faster than the other, resulting in a colour shift. Therefore, temperature adjustment may be critical to achieve the desired final colour, and any deviation from this temperature may result in a deviation of the final diazo colouring. Generally, higher temperatures promote the blue dyes, and lower temperatures promote the brown or sepia dyes. The colour also may shift depending on the ammonia system used in the developing process.

Development Processes

Two different methods for processing diazo films are used in the microfilm industry: The *vapour diazo process*, which is most commonly used, and the *thermal development*.

The *vapour diazo process* has the following characteristics:

- The film coating contains the diazonium salts, dye couplers and acid stabilisers
- The ammonia vapour causes image development with heat used as an accelerator.

The ammonia used in the developer section of the diazo duplicator is either *anhydrous ammonia* or *aqueous ammonia*. **Anhydrous ammonia** is in gaseous form and contains no water. Systems using anhydrous ammonia feed it into the developer chamber under pressure which further accelerates coupling by forcing ammonia into the coating. Anhydrous ammonia systems require a very short development time and thus are most suitable for rapid processing.

Aqueous ammonia is ammonia in a water solution in which the water is used as a medium or carrier and assists the ammonia in penetrating the emulsion. Aqueous ammonia is less active than anhydrous ammonia. The aqueous ammonia solution (23 to 26° Baumé) is heated (approx. 150 °F, 65 °C) and generally reaches the film as vapour.

The type of used ammonia system affects the rate of coupling of the diazonium salts and couplers. In addition, film colour may shift when processed in one or the other of these systems, even though the developer temperature is held constant. The primary advantage of anhydrous ammonia systems is that their chemical action is very fast and therefore development can be completed in a very short time.

The disadvantages include the need to use pressure systems in the development chamber with the associated problems of pressure tubing and valves and the safety and legal precautions related to the use of ammonia cylinders. On the other hand aqueous ammonia systems require more time to achieve complete development. Their main advantage is the convenience of use in an office environment.

Thermal Development

Thermal developed diazo films differ from conventional diazo products because heat is used as the developing agent rather than ammonia. In the one product commercially available heat causes migration of the salts and couplers to form dye image.

Diazo Image Colour

As mentioned earlier, diazonium salts react with the couplers in the coating to form a coloured dye, which has a particular colour because it transmits light of that colour (wavelength) and absorbs (blocks) the other colours (wavelengths, figure 2). In a more general sense, the spectrum can be broken up into the colours shown in figure 3.

The primary colours are red, blue and green. In an *additive* system, red added to green plus blue equals white. However, some systems like diazo are *subtractive*; that is, certain colours are removed. The colours absorbed or transmitted by diazo film can be determined from the spectral density curve available from most manufacturers. Such a curve shows film density using illumination across the visible/ultraviolet spectrum. In figure 4, the film blocks (absorbs) yellow/red components with maximum (peak) absorption at 575 nanometers (nm). There is little absorption in the blue part of the spectrum and the eye sees the blue colouring.

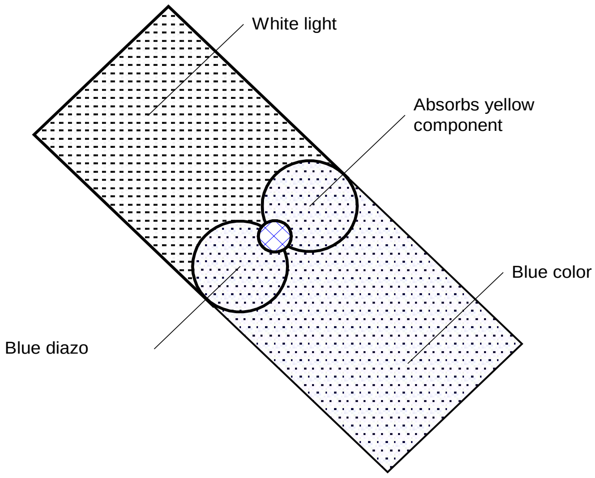


Figure 2: The coloured dye (in this case blue) formed by the diazonium salts and couplers transmits the blue light, but blocks or absorbs other colours, forming blue diazo film

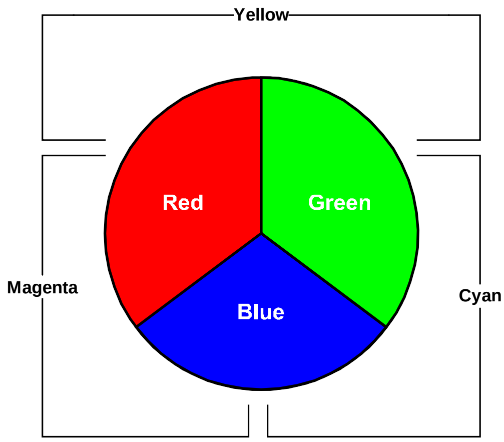


Figure 3: The colour spectrum

In order to produce a diazo film that appears neutral black it is necessary to absorb the colours evenly across the spectrum.

Dye colour	Absorbs (blocks)
Black	White (yellow + cyan + magenta)
Blue	Yellow (red + green)
Red	Cyan (green + blue)
Green	Magenta (blue + red)

It is impossible to achieve this effect with a single dye, and multiple dyes (sepia and blue) are usually used. Sepia is a dye colouring which is very effective in absorbing ultraviolet and blue. The spectral density curve of a black diazo film appears as shown in figure 4 and can also be represented symbolically as shown in figure 5.

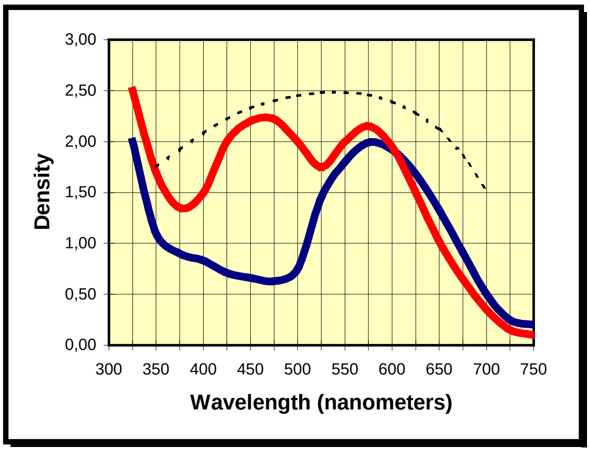


Figure 4: Comparison of the spectral density curves for blue and black diazo film. The dotted line shows the theoretical neutral black diazo film.

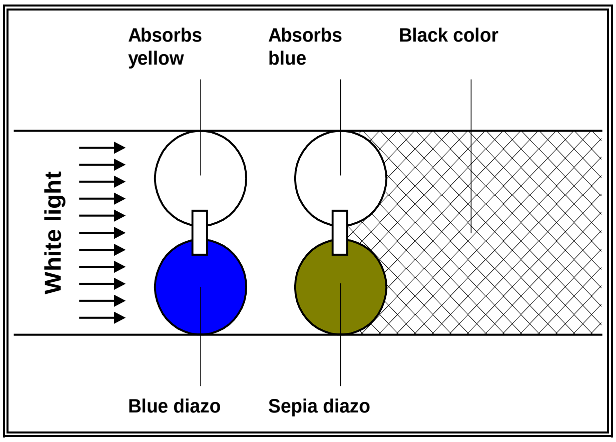


Figure 5: Black diazo film is created by using a combination of dyes such as blue and sepia

Film Structure

When the diazo process was first used in the microfilm industry the emulsion was adhered to an acetate base. Today, however, most diazo films use polyester base because of the advantages they offer for the everyday use of a duplication film.

The cross section of diazo film on a polyester base, shown in figure 6, depicts its structure (the relative thicknesses are not drawn to scale).

Film Structure

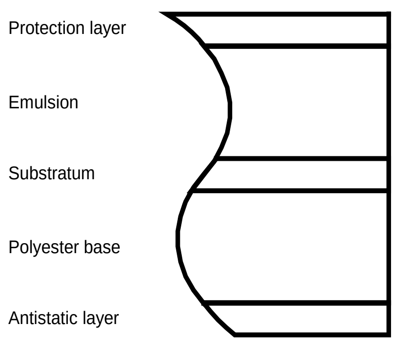


Figure 6: Cross section of a diazo film

The photosensitive coating or *emulsion* is a plastic layer that contains the following chemical compounds:

- Diazonium salts which are decomposed by action of ultraviolet light and constitute the photosensitive element
- Dye couplers, which couple with the salts to form a coloured dye and subsequently absorb e.g. ultraviolet light
- The stabiliser, which prevents coupling until the desired conditions are established, i.e. after exposure

The *substratum* layer assists in binding the emulsion to the polyester film base. Silver photo tools use gelatin in the image layer where diazo films typically use cellulose acetate as coating binder. Photo tools of either type may rely of back coates to control curl and back coats for antistatic protection. Finally, some diazo photo tools (like METODIAZ D-18-SLPI) will have a top coat on the image layer to provide abrasion and/or chemical resistance to liquid photo resists (LPI).

Sensitometric Properties

As diazo films cannot be overdeveloped and do not involve an amplification process the sensitometric characteristics of a particular strip of film depend almost entirely on the actual formulation of the diazo (coating). Again, this process differs greatly from silver emulsions in which the shape of the characteristic curve can be modified by processing conditions. Thus, diazo film is a very simple and reliable duplicating medium.

Spectral sensitivity

Because the diazo process does not include energy amplification, powerful light sources, rich in violet and ultraviolet, must be used for exposing the diazo coating (decomposing the diazonium salts). High-pressure mercury lamps are best suited for this purpose, and the light emission is well matched to the spectral sensitivity of the diazo coating (peak at about 408 nm) which means that diazo films have little colour sensitivity according to visible light spectrum and can therefore be used in ordinary room light. Window glass greatly absorbs ultraviolet rays from the sunlight, however, a clear or gold UV-filterfoil (such as ASMETEC ASF-C-20) mounted to the outside-windows provides additional safety.

However, ultraviolet compounds of a room's light source, such as fluorescent lamps, will adversely affect the film by decomposing the diazonium salts. The extent to which the decomposition occurs depends on strength of the ultraviolet compound and the amount of time that the film is left exposed. Again, filter foils or filter sleeves (such as ASMETEC ASR-C-20 or ASR-G-10) absorb the UV-radiation of the neon lamps and ensure UV-free light in working areas.

Speed

Sensitometrically, the diazo film speed is measured by the exposure ($I \times t$) required to fully burn through the diazo coating. The final image is defined at the time of exposure; with this in mind, you should note that a master with high D_{min} significantly reduces the copying speed of diazo film by blocking the light energy in the low density areas and making it more difficult to decompose the diazonium salts. Other points of interest regarding diazo film speed are:

- Black film is generally slower than blue film.
- The higher the D_{max} the slower the film.

Contrast

Diazo films are classified as medium to high contrast. The characteristic curves seldom have a straight-line portion, and *bar gamma* is more frequently used to technically describe the characteristics of the film. A high-contrast film has *bar gamma* of 1.5 or above while a medium-contrast film has *bar gamma* of less than 1.5.

Characteristic Curve

Typical characteristic curves of diazo film are illustrated in figure 7. Generally, two curves are given: One for the second generation (one generation removed from the master film) and one for the third generation diazo film. In the case of the second generation curve the vertical axis shows the densities that can be produced on the diazo film from a silver step tablet. The shape of the curve is typical for a non-reversing system. High-density areas on the silver tablet produce high density areas on the diazo duplicate.

A density differential on the step tablet yield a corresponding differential on the diazo film. High-contrast films tend to expand the differential more than medium-contrast films. From a user standpoint this type of curve is very useful since it will allow you to predict, for a given diazo film, how much density amplification will occur for a particular silver density.

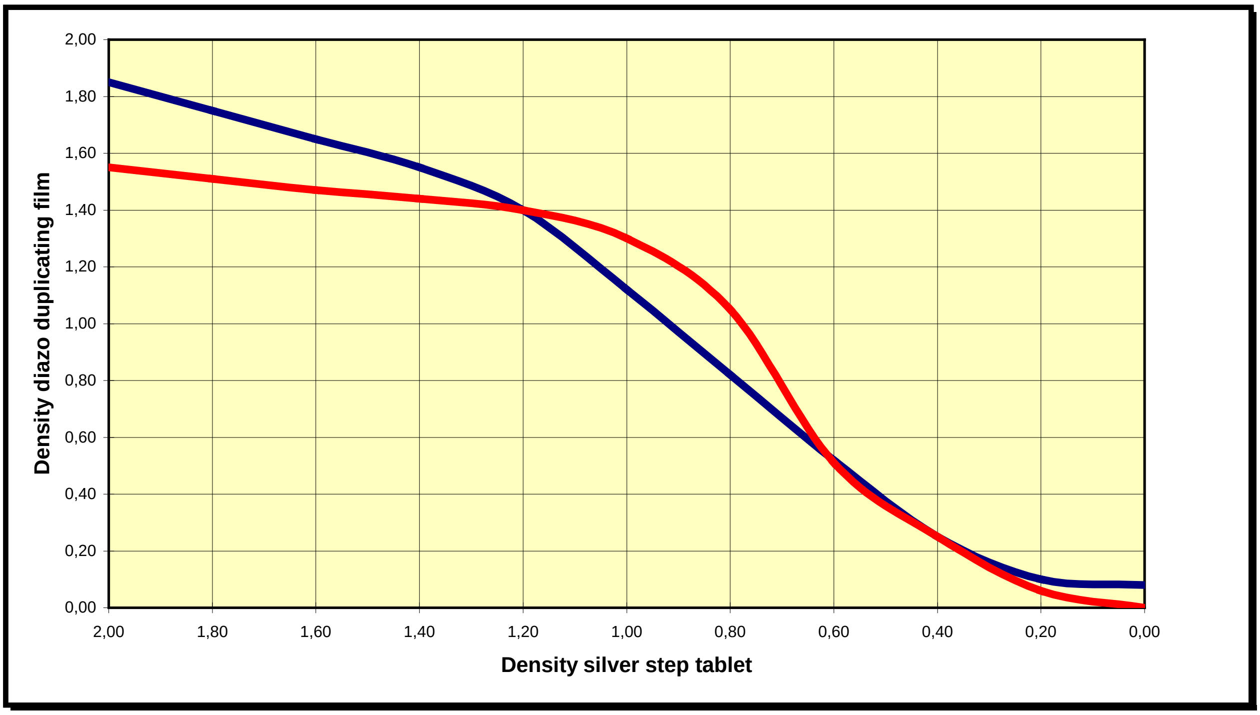


Figure 7: A typical characteristic curve for diazo film, showing high contrast

Resolution

The resolution of the copy photo tool is a function of many factors which includes:

- Copy film acutance
- Master film image quality
- Film-to-film contact uniformity
- Grain size
- Exposure source collimation

The image on a diazo film becomes visible as a result of the dye formed within the coating which results from the coupling of the diazonium salts and dye couplers. The coupling occurs at a molecular level. Resolution depends on the "*grain size*" (in this case a molecule) and therefore diazo films have very high resolution capabilities and have been determined to be in excess of 1000 line pairs per millimeter. In practice, this figure can have little meaning since microfilm systems operate in the region of 100 to 200 line pairs per millimeter.

The acutance of the copy film is a function of the grain size and the contrast of the image. Diazo photo tools typically have gamma's, in excess of 4.0 (very high contrast, snap shot films typically have gamma's less than 1.0). The image structure is molecular in nature and thus not a limiting factor. With proper exposure, good collimation and contact the copy should be as good as the original. The contact between the original photo tool and the diazo copy film plays an important role in duplication. Poor contact will allow the exposure energy to diffuse between the two image layers causing a loss in contrast and image sharpness.

Molecular Dye Process

The image is formed by a molecular dye process which works by selectively absorbing ultraviolet light and certain visual frequencies while transmitting all others to leave a dense image and a translucent background. Molecular dye images are composed of molecules of diazo salts with an average size between 10 and 15 Angstroms or 0.00015 microns. Fine grain silver-halide images are made up of grains of 3000 Angstroms or 0.3 microns diameter. The tiny diazo molecules of METODIAZ DP-Series diazo film produce extremely sharp images.

Diazo film is a very suitable duplicating system, but the high value of the theoretical resolution will not necessarily produce a copy of high quality. Instead the quality of the master film will determine in a large part the quality of the final copy. The duplicator itself may play a role in determining the quality because some duplicators, due to either poor contact or poor collimation of the light source, can adversely affect resolution.

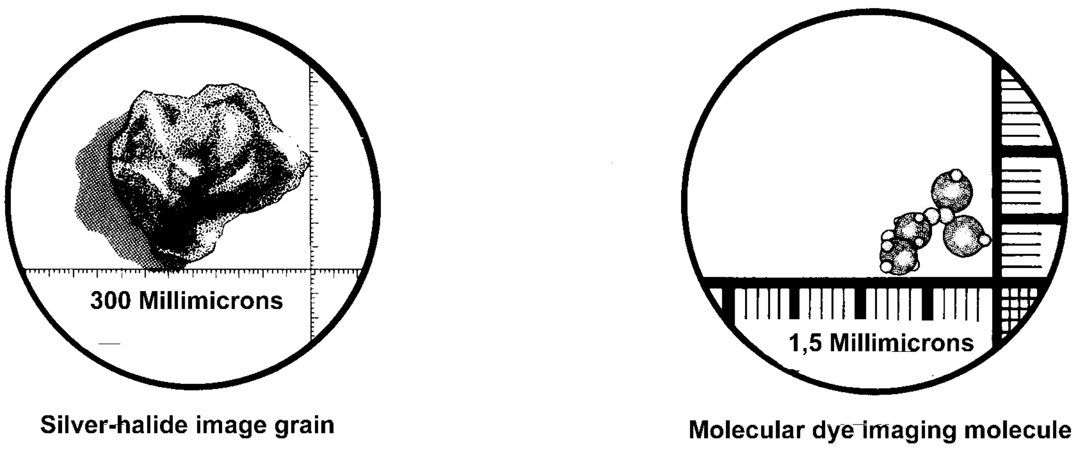


Figure 8: Comparison of silver halide image grain with molecular dye imaging molecules of METODIAZ Diazo films

Visually Transparent Images

While silver halide films block all light waves, including visual, UV and infrared, METODIAZ DP diazo films absorb UV and certain visual light frequencies. Even though the image is visually transparent, the image density allows them to be stripped alongside silver film without changing exposure. Molecular dye imaging films absorbs UV light and transmit all other frequencies to provide a visually transparent image on a translucent background (Figure 9).

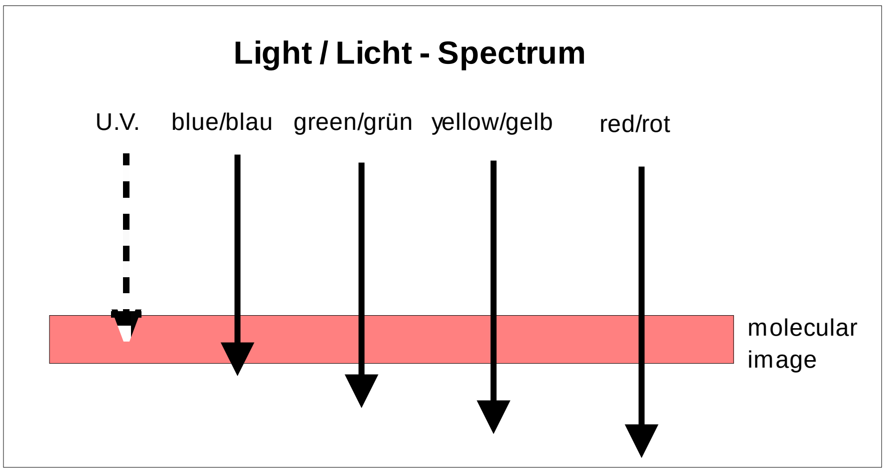


Figure 9: Light spectrum, U.V. is absorbed by the molecular image

Reproduction Characteristics

Reproduction characteristics are important to consider when diazo films will be used as a master to make paper copies on a printer or to make further diazo copies. Because diazo film modulates the specular characteristics of the light source by transmitting selected colours and blocking others it is necessary to consider the reproduction characteristics in the following terms:

- Spectral sensitivity of the reproduction system, i.e. the paper sensitivity or the unexposed diazo film sensitivity
- Specular density of the diazo film used as "master", i.e. its ability to block certain wave lengths

The image contrast that is the density differential (DD) between the characters and the background is very important in determining the suitability of a film for use as a master. However, with diazo film the background density will vary with the wavelength under consideration and therefore the contrast of the film at a given wavelength changes with the specular density characteristics. The diazo film maintains good contrast at those wavelengths in which the film effectively blocks the light.

In general, for satisfactory use in a reproduction system, the diazo master must have good contrast at those wavelengths to which the reproduction system is most sensitive. In the specific cases mentioned above this rule can be applied as follows:

- When reading the film on a viewer the sensitivity of the eye is the determining factor. The eye is most sensitive in the yellow/green areas and therefore a film with a blue dye will appear to have excellent contrast; that is either blue or back diazo film.
- Microfilm printers differ widely in their spectral sensitivities. You should consult the manufacturer and select a diazo film that offers good specular density at the wavelength to which the system is sensitive.
- In *autogeneration* (a duplicating process which uses the same type of film for both the master and the duplicates) in which diazo master must block the ultraviolet radiation - i.e. the diazo master must incorporate a sepia dye - a black film is very satisfactory.

Densitometry

Density measurement is a complex subject and a complete discussion is beyond the scope of this publication. There are two density issues which need to be discussed briefly:

- Density on dye systems
- Relationship between density and opacity (see also: *"Photographic Principles")*

Dye images (diazo photo tools are dye systems) do not necessarily block all types of light. For example diazo photo tools are designed to block violet and ultra violet light. The dye colour yellow/sepia was selected to block violet/ultraviolet energy. Different dyes would be selected if a "black appearing" image was needed.

Silver halide films block most energy thus a visual density reading will be very similar to a UV density reading. This is not the case with diazo photo tools. Specific filters need to be used for specific requirements. An UV-filter will be needed for measuring density in the UV and violet (350 to 410 nanometers) range. A visual filter will be needed for measuring in the visual range of 400 to 700 nanometers. This point can be demonstrated easily by reading the same diazo photo tool with a UV densitometer and next with a densitometer set up for visual readings. Most diazo photo tools have a visual D_{max} between 1.0 and 2.0 while the UV D_{max} measures between 4.0 and 5.0 (again varying with the calibration of densitometers). This explains why the low density "visual" image can work fine for blocking short wave length energy (violet to UV).

Technically speaking: Density is the logarithmic measure of opacity. Practically speaking: All you need to know is the relationship between opacity (image darkness) and the density numbers. You will note on the chart below that density numbers are not linear. A density of 2.0 is not twice as dark as 1.0. In fact, on this particular scale every 0.30 represents a doubling of density.

X-Rite density reading vs. % transmission (spectral response: 350 to 420 nm, peak at 380 nm)

X-Rite densitometer reading	% transmission of light through image	% of light blocked (absorbed) by image
0.30	50.000 %	50.000 %
0.60	25.000 %	75.000 %
0.90	12.500 %	87.500 %
1.00	10.000 %	90.000 %
2.00	01.000 %	99.000 %
3.00	00.100 %	99.900 %
4.00	00.010 %	99.990 %
5.00	00.001 %	99.999 %

Chart 1: UV density reading

Increasing the density of an image from a reading on the densitometer from 4.00 to 5.00 has only increased the blocking power by 0.009 %. Therefore, if a manufacturer of diazo photo tools argues his film has a higher density (e.g. 4.40) than a competitor's film (e.g. 4.30) this increase represents the following:

4.30 blocks 99.993 % of the light

4.40 blocks 99.994 % of the light

As these numbers indicate increasing density from 4.30 to 4.40 represents only a 0.001 % increase of the light blocking ability. This small difference will have no affect on the film performance. We have found that a density above 3.50 on the X-Rite densitometers is more than enough density to go to normal photoresist and a density of 4.00 is sufficient to expose solder masks.

Densitometer readings can vary from instrument to instrument. The popular X-Rite models 339 and 369 have separate ranges for silver and diazo. MacBeth TD 929 is another type of instrument.

Working Conditions and Shelf Life

One of the major advantages offered by diazo film is that it can be used and handled under ordinary room light since it is only very slightly sensitive to visible light. However, some precautions are necessary:

- Sunlight (daylight) <u>does</u> contain ultraviolet radiation; therefore the film should <u>always</u> be protected, especially from exposure to direct rays
- Fluorescent lights contain a small amount of ultraviolet radiation. Lengthy exposure (for more than few minutes) under these conditions should be restricted. Yellow fluorescent lights offer excellent protection and are highly recommended. Yellow filters (e.g. ASMETEC ASR-G-10, SFG-10) can effectively block all harmful radiation.
- Incandescent lamps are also relatively harmless and unlikely to affect the emulsion over a short period of time. In practice, the film should always be properly protected in order to avoid unnecessary risk.

The **shelf life** of diazo film is limited. After a specific time the stabiliser in the emulsion decomposes and pre-coupling of the dye may occur before exposure. The film is generally warranted for 6 months at 75° F (24 °C) which can be extended to 1 year at 60 °F (16 °C) and 18 months at 45 °F (7 °C). Unexposed diazo film cannot be harmed by X-ray or infrared radiation. Needless to say that the film must be stored away from any ammonia or ammonia fumes in order to prevent premature development of the coating. Though it seems to be convenient to have the diazo films near by it will cause trouble once you should store your film boxes in the same room where you do the diazo developing. Even if you do not smell it the air in the working area is enriched with ammonia.

It is important to know that ammonia in aqueous solution stored in PE-bottles (polyethylene) can diffuse through the polyethylene and enrich the air surrounding with additional ammonia. No film can be archival unless the storage conditions offer suitable protection. The most important recommendations for archival storage are the following:

- Temperature must be less than 70 °F (21 °C)
- Relative humidity must range from only 15 to 30 %
- Films with dye images must be stored in closed, opaque containers or else protected from light
- Provision must be made to prevent condensation in the storage area
- Adequate ventilation should be provided

Dimensional stability

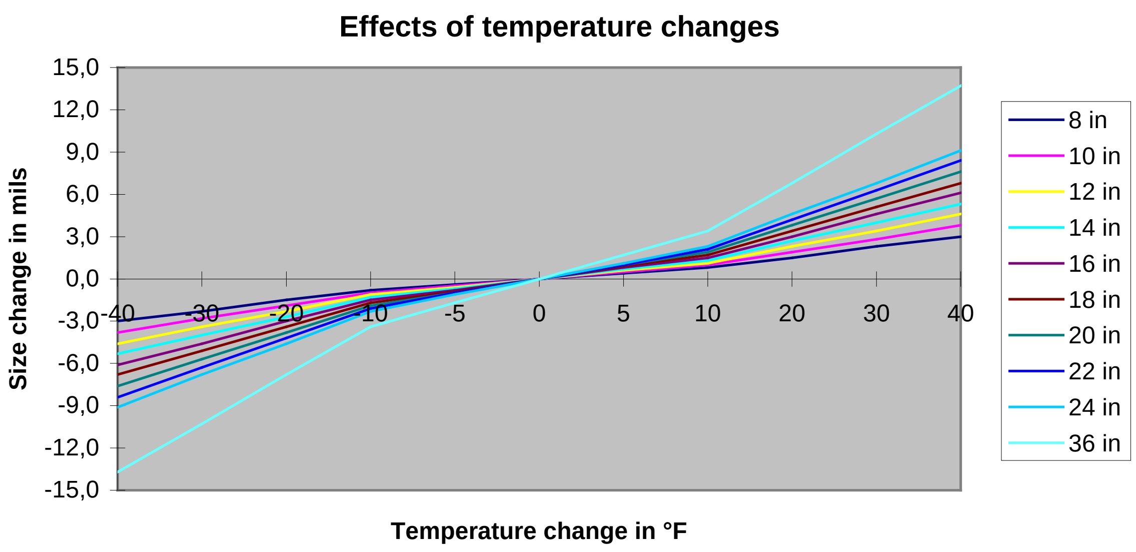
METODIAZ D-18 are coated on a 7 mil (0.18 mm) polyester base which provides excellent stability and durability. Further, the heat generated from infrared absorption in the molecular imaging process is extremely low. Therefore the film stays cooler during exposure which eliminates image creep and distortion.

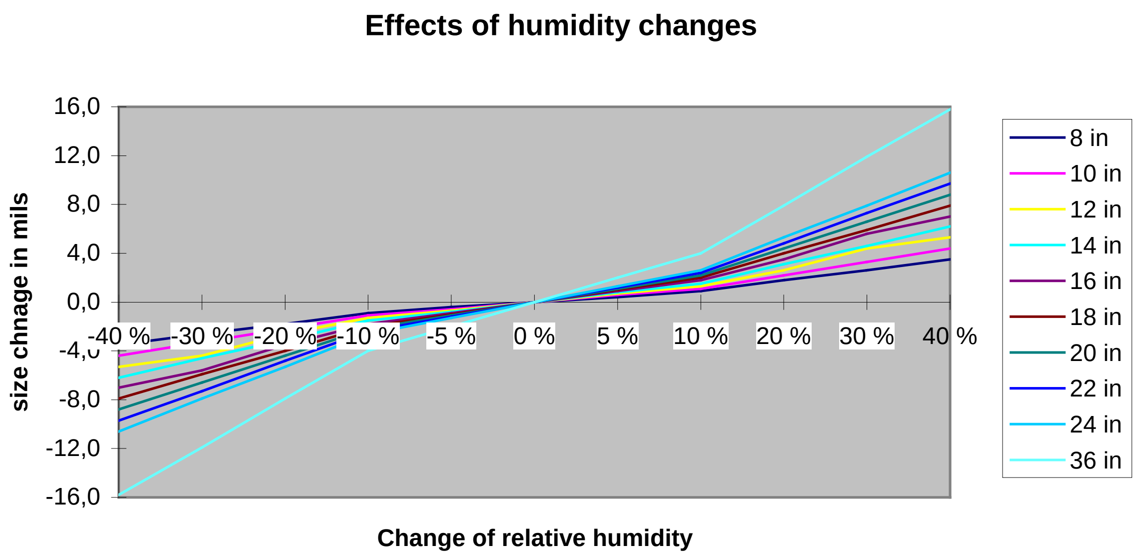
Polyester based photographic films, both silver and diazo, change size with temperature and percent relative humidity (%RH). Although there are small differences between film types, most 0.18 mm (0.007") polyester photo tool films have these approximate coefficients of linear expansion: 0.00002/°C (0.00001/°F) and 0.000015/%RH.

At a constant relative humidity, film size increases as the temperature increases and decreases as temperature decreases. Film size also increases as humidity increases and decreases as humidity decreases. When the temperature changes, the film size changes in a few minutes. When the humidity changes, however, five to ten hours will be required for the film to reach its equilibrium size. It is important to know that effects of changes in temperature and relative humidity are cumulative.

The image is formed on the silver photo tool via a plotter. While the latent image on the film may be an exact replica from the plotter, once the film is processed and then used to expose resists or diazo photo tools, the physical dimensions are influenced by heat and humidity. Dimensional stability is an important process parameter for photo tools because of the trend to smaller line width. With line widths dropping below 0.004" (< 100 micron) any change in the image size is of potential concern. The science of dimensional stability is complex and frequently misunderstood. In the case of photo tools there are particular concerns for the silver halide original and a separate set of issues for the diazo copy. These issues include the film, processing factors, environmental issues and the conditions encountered during resist exposure.

Since the film does not adjust rapidly on changing ambient conditions it should be equilibrated at the temperature and humidity of use **at least** 24 hours in advance. Packaged film should be stored in the climate controlled work areas, both, the photo tool preparation area <u>and</u> the resist exposure area. It is strongly recommended that both have the same temperature and same relative humidity. For further details please refer to *"METODIAZ D-18, Product usage information".*





	203	254	305	356	406	457	508	559	610	914
-22 °C	-76	-97	-117	-135	-155	-173	-193	-213	-231	-348
-17 °C	-58	-71	-86	-102	-117	-130	-145	-160	-173	-262
-11 °C	-38	-48	-58	-69	-76	-86	-97	-107	-117	-173
-6 °C	-20	-25	-28	-33	-38	-43	-48	-53	-58	-86
-3 °C	-10	-13	-15	-18	-20	-23	-25	-25	-28	-43
0 °C	0	0	0	0	0	0	0	0	0	0
3 °C	10	13	15	18	20	23	25	25	28	43
6 °C	20	25	28	33	38	43	48	53	58	86
11 °C	38	48	58	69	76	86	97	107	117	173
17 °C	58	71	86	102	117	130	145	160	173	262
22 °C	76	97	117	135	155	173	193	213	231	348

Chart 2: Effects of temperature changes

	203	254	305	356	406	457	508	559	610	914
-40 %	-89	-112	-135	-158	-178	-201	-224	-246	-269	-401
-30 %	-66	-84	-112	-117	-142	-150	-168	-185	-201	-302
-20 %	-46	-56	-66	-79	-89	-102	-112	-122	-135	-201
-10 %	-23	-28	-33	-38	-46	-51	-56	-61	-66	-102
-5 %	-10	-15	-18	-20	-23	-25	-28	-31	-33	-51
0 %	0	0	0	0	0	0	0	0	0	0
5 %	10	15	18	20	23	25	28	31	33	51
10 %	23	28	33	38	46	51	56	61	66	102
20 %	46	56	66	79	89	102	112	122	135	201
30 %	66	84	112	117	142	150	168	185	201	302
40 %	89	112	135	158	178	201	224	246	269	401

Chart 3: Effects of humidity changes

To use the charts

Find the dimension being measured along the top of the chart (8 to 36 inches, interpolate for other dimensions). Drop down the vertical column under the selected dimension and intersect with the horizontal row designating the change in relative humidity from 50 % or change in temperature from the ambient conditions existing at the time of processing or other reference.

Example No. 1

16.0000" dimension. Film was processed directly from package which is preconditioned at 50 %RH. Subsequent use is in area with 70 %RH. Reference to chart shows dimension has expanded 3.5 mils to 16.0035".

Example No. 2

16.0000" dimension. Ambient film temperature at time of processing was 75 °F. Subsequent use in area of 65 °F indicates thermo contraction of -1.5 mils to 15.9985".

Important

Effects of changes in temperature and relative humidity are cumulative. If both conditions above applied, +3.5 mils expansion due to increase in RH is counteracted by -1.5 mils contraction due to temperature drop, making the final dimension change +2.0 mils to 16.0020".

Conditioning

It is critically important to condition all photo tool films prior to use. Without the conditioning dimensional stability will be a problem. Below is a chart that illustrates the time factors involved for conditioning 7 mil films. Note that in the first six minutes, if the film is moved from one environment to another, it will have changed 20 % of what it will eventually reach. The other chart shows that temperatures and humidities are necessary to maintain a certain growth or shrinkage specification.

The percentage specified in the following chart is the rate of equilibration. For example, the film has reached 45 % of equilibration in one hour. In then hours, the film is fully equilibrated for 7 mil (180 µm) film.

6 min	30 min	1 h	2 h	5 h	10 h
20 %	32 %	45 %	63 %	88 %	100 %

Chart 4: Rate of equilibration

Diazo is usually packed at 70 °F and 50 %RH. However, it is a good idea to unpack the film needed within the next 24 hours and allow it to acclimatise in the photo tool room before use. Make sure the film is protected from UV light which can cause premature exposure and hence diminish the density of the film. Special sleeves can be slipped over fluorescent lamps to reduce radiation in the UV range and help prevent inadvertent exposure. The presence of ammonia vapour is another source of trouble while acclimatising the film. Even a small amount of ammonia in the air can yellow the background (clear area) of diazo. This will increase the exposure times when the diazo is used to image photoresist. A hooded exhaust system is the popular way of isolating the unexposed diazo from ammonia and is essential in preparing clean photo tools. Diazo should be stored in a clean, dry place.

Environmental control

This chart relates to environmental control areas where film is used. This may require the installation of special air conditioning equipment. The chart may serve as a useful guide to the environmental control required with today's dimensionally stable films to stay within a given tolerance.

To hold ± 1 mil in	Hold temperature to	Hold RH to
10 "	± 7.0 F	± 9.0 %
20 "	± 3.5 F	± 4.5 %
30 "	± 2.0 F	± 3.0 %
40 "	± 2.0 F	± 2.0 %

Chart 5: Environmental control tolerance to achieve required dimensional stability

To maintain dimensional stability, the darkroom, photo tool storage and stencil exposure areas must be seen as a continuous space with controlled conditions of 21 * 1 °C and 45 to 50 %RH. The temperature of the glass in the exposure frame should be controlled. Exposure involves the use of high-powered lamps that are easily capable of raising the temperature of the glass, and thus the photo tool by as much as 8 to 10 °C. Radiational heating of the glass can be minimised by venting the lamp's exhaust fans, choosing stencil materials requiring minimum exposure and maximising the lamp-to-glass distance which has the secondary benefit of increasing exposure precision.

Exposure

A vacuum frame, a non-reflective backing and an UV-light source with 360 to 430 nm output are needed to expose diazo photo tools like METODIAZ D-18. Exposure units such as carbon arc, metal additive, xenon arc or high-intensity mercury vapour lamps are all acceptable. Underexposure leaves the background unclear with a high D_{min} and tends to lengthen the exposure time when the diazo photo tool is used to image the photoresist. Overexposure can cause line width changes and diffuse edges.

A Stouffer 21-step wedge is the most common technique for establishing the correct exposure time. Place the step wedge between the master and the unexposed sheet of diazo so it is under a clear portion of the master. The emulsion side of the step wedge must have contact to the emulsion side of the diazo film. Adjust the exposure for "a clear step 2, haze on step 3" which means the second step should vanish with just a hint of the third step still visible. An exposure of step 3 or even 4 may be used to clean out slight imperfections in the original artwork.

The length of the exposure depends on the size of the light source used. For example a 5.0 kW light source requires approximately 25 s of exposure, a 3.5 kW light source requires 1 min, and a 900 W light source requires 4 min of exposure.

It is essential to properly adjust the height of the light source. The closer the light source is placed to the film the more light and heat reaches the film and the shorter is the exposure time. With the light source placed to close to the film the exposure may not be uniform and shadowing of the traces can occur at the perimeters of the sheet of film. A good rule of thumb is to place the light source no lower than ¾ the length of the diagonal across the image plane.

Integrators

Once the proper exposure value is established it is essential that this total energy value will be maintained sheet after sheet. Since the power line voltages fluctuate and light supplied by the light source diminishes very gradually with time the only way to make sure the value will be retained is with an integrator.

This is an instrument that employs a light sensor mounted on the exposure plane or sometimes in the light source itself. It measures the total amount of energy in Joules and shuts the light off when the proper amount of light has been transmitted to the film. The total amount of light, regardless of any variation in the light intensity, is automatically shortened or lengthened accordingly so the total energy is constant shot after shot.

Vacuum frames

The black board placed in the vacuum frame plays several important roles:

- It is slightly matted so that no light is reflected back through the film which could blur the trace images.
- It helps to minimise the distortion by the dimpled rubber bladder which presses against the board to draw down the master and copy together.

The uniform formation of the Newton Rings on the glass surface of the exposure unit is a good way to confirm that intimate contact between the master and unexposed film has been achieved. Entrapped air pockets cannot always be detected and will cause blurred traces from poor contact. Lengthening the vacuum drawdown time will help to ensure that there is no entrapped air. Also, cut your film to the same size as the master so that there is no tendency for the master to push outward on the film margins and entrap air.

Development

Diazo films like METODIAZ D-18 are most commonly developed in an ammonia developer operating with aqueous ammonia in the range 23 to 29 % (23 to 26° Baumé) with a chamber temperature of approximately 150 °F (65 °C). A conventional diazo developer can be used for processing. Maximum density (D_{max}) is usually achieved in one pass through a properly adjusted developer. The amber image colour can make it difficult to visually verify full development. For this reason we recommend that METODIAZ D-18 is passed through the developer twice to assure complete development. You cannot overdevelop a diazo print. Your METODIAZ D-18 print can be used immediately after processing, no other finishing is required. Despite this we recommend to allow the processed film to equilibrate for minimum 5 hours after development.

Helpful Hints for proper Development

- Make sure your developer unit is operating at suggested development temperature (approx 150 °F, 65 °C). Too much heat can cause the film to stick and become dimensionally stretched. On the other hand a developer that is too cold can cause incomplete development and low blocking density. Use temperature strips fastened to the emulsion side of the diazo film to check that the temperature is in the recommended range.
- Use fresh ammonia in the range 22 to 24° Baumé. Aqueous ammonia can loose strength as it sits in a polypropylene container/bottle. Use a hydrometer (such as NH_3-Tester, ASMETEC-Code107283) if you wish to check concentration.
- In low concentrations ammonia is a harmless substance. Humans can detect levels as low as 5 to 10 ppm. This sensitivity means that individuals retreat from levels higher than 20 ppm. Ammonia concentrations higher than 50 ppm are the lower limit for health concerns. Most diazo developers have provision for venting. A vented processor with reasonable room air flow should not be a source of objectionable odours.
- If you have an UV reading densitometer check the density after one development pass and then re-check after a second pass. If the two readings are within a few points of each other than you may not need to double pass your diazo photo tool.

Degree Baumé

Degree Baumé is related to the concentration or specific gravity of the ammonia in water solution (ammonium hydroxide) by the formula:

Degree Baumé = (140/specific gravity) - 130

where Specific gravity is those of ammonium hydroxide solution. In turn the specific gravity is related to the volume of water (Vol. W) added to the volume of ammonia (Volume A) by the relationship:

Specific gravity = (Vol. A x 38 + Vol. W x 62,4) / (Vol. A + Vol. W) x 62

where density of ammonia at 70 °F is 38 lbs/cu.ft and density of water is 62,4 lbs/cu.ft.

Baumé	Specific Gravity	% NH_3	Baumé	Specific Gravity	% NH_3
10,00	1,0000	0,00	20,00	0,9333	17,76
10,25	0,9982	0,04	20,25	0,9318	18,24
10,50	0,9964	0,80	20,50	0,9302	18,72
10,75	0,9947	1,21	20,75	0,9287	19,20
11,00	0,9929	1,62	21,00	0,9272	19,68
11,25	0,9912	2,04	21,25	0,9256	20,16
11,50	0,9894	2,46	21,50	0,9241	20,64
11,75	0,9876	2,88	21,75	0,9226	21,12
12,00	0,9859	3,30	22,00	0,9211	21,60
12,25	0,9842	3,73	22,25	0,9195	22,08
12,50	0,9825	4,16	22,50	0,9180	22,56
12,75	0,9807	4,59	22,75	0,9165	23,04
13,00	0,9790	5,02	23,00	0,9150	23,52
13,25	0,9773	5,45	23,25	0,9135	24,01
13,50	0,9756	5,88	23,50	0,9121	24,50
13,75	0,9738	6,31	23,75	0,9106	24,99
14,00	0,9721	6,74	24,00	0,9091	25,48
14,25	0,9705	7,17	24,25	0,9076	25,97
14,50	0,9687	7,61	24,50	0,9062	26,46
14,75	0,9670	8,05	24,75	0,9047	26,95
15,00	0,9653	8,49	25,00	0,9032	27,44
15,25	0,9636	8,93	25,25	0,9018	27,93
15,50	0,9619	9,38	25,50	0,9003	28,42
15,75	0,9602	9,83	25,75	0,8989	28,91
16,00	0,9589	10,28	26,00	0,8974	29,40
16,25	0,9573	10,73	26,25	0,8960	29,89
16,50	0,9556	11,18	26,50	0,8945	30,38
16,75	0,9540	11,64	26,75	0,8931	30,87
17,00	0,9524	12,10	27,00	0,8917	31,36
17,25	0,9508	12,56	27,25	0,8903	31,85
17,50	0,9492	13,02	27,50	0,8889	32,34
17,75	0,9475	13,49	27,75	0,8875	32,83
18,00	0,9459	13,96	28,00	0,8861	33,32
18,25	0,9444	14,43	28,25	0,8847	33,81
18,50	0,9428	14,90	28,50	0,8833	34,30
18,75	0,9412	15,37	28,75	0,8819	34,79
19,00	0,9396	15,84	29,00	0,8805	35,28
19,25	0,9380	16,32			
19,50	0,9365	16,80			
19,75	0,9349	17,28			

Table 6: Degree Baumé vs. % NH_3

New Diazo

Dry-film solder masks require long exposures to properly expose the resist material. When long runs are being exposed the diazo must be able to maintain its density (D_{max}) over repeated exposures without degrading the film's UV blocking power. Higher-density films are now available for such applications. Many new liquid photo-imageable solder masks employ solvents such as glycol-ether. If the diazo is not specially formulated these solvents can bleach the emulsion on the diazo film surface. Special diazos have been developed which can withstand such corrosive chemicals.

Daily Start-Up

It is important that all of your diazo processing equipment is checked every morning to make sure that nothing has changed from the previous day. Diazo, being a photo system just like silver halide films, should be checked for any variations. It is important that your equipment is warmed up for 30 minutes before being used to create the proper processing conditions without fluctuation.

Materials needed

- Silver target master similar to the type of work
- Stouffer 21-step wedge sensitivity guide
- Temperature tapes 140 to 180 °F (60 to 80°C)
- Check ammonia degree Baumé to be 23 or more (use hydrometer)
- A piece of unexposed diazo film

Exposure

Take a raw piece of diazo film and place the silver target master on it, emulsion to emulsion. Put the step wedge outside of the target film, emulsion to emulsion. Expose the film at normal time.

Developing

Check ammonia with a hydrometer.

Attach a temperature tape to the exposed diazo film and run the film through the processor in normal manner. The temperature readings should be in a range of 140 °F to 160 °F (60 to 70 °C).

Check D_{min} and D_{max} with your densitometer (important: densitometer warm-up at least 30 minutes!). The densitometer must be calibrated using zero adjustment and once a week using the calibration wedges.

METODIAZ D-18 Family
Diazo Films in the PCB Industry

METODIAZ D-18 diazo films offer the microelectronic industry positive working products with superior resolution for photo tool production in normal room light. These films offer a number of unique features to increase productivity, improve photo tool quality and reduce production costs.

- The visual see-through of the image aids registration
- The actinic density can be used to expose dry resists as well as liquid resists.
- The matte surface of the emulsion side allows faster drawdown before exposure, eliminates Newton rings and provides channels to avoid nitrogen gas entrapment during exposure.
- The durable polyester base stands up to repeated handling and aging.
- The stable 178 micron polyester base offers superior dimensional stability.
- The METODIAZ D-18 series provides a hard image layer without compromising sensitometry
- METODIAZ D-18 (standard film) for general purpose offers low matte emulsion side for superior resolution.
- METODIAZ D-18-L (light amber) makes visual registration even easier and develops slightly faster.
- METODIAZ D-18 and METODIAZ D-18-M employ a hardened, crosslinked image.
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The METODIAZ D-18 family has balanced the key performance factors: imaging parameters, surface durability and dimensional stability. We believe excellence in these disciplines is essential for a world class photo tool.

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