

# REPORT

### The developing process in the application of photoimageable solder resists

 The ecology, economic efficiency and process reliability of aqueous-alkaline and polyalcohol developable systems

> Dipl.-Ing. Markus Wieler Dipl.-Ing. Tilman Sehlen

**Ref. No. 140E, supplemented and revised version** issued September 2004

# The developing process in the application of photoimageable solder resists

#### Contents

1.	Introduction1		
2.	Examination of the developer fluids from a safety technology point of view1		
2.1	Aqueous-alkaline developer solutions1		
2.2	Polyalcohols as developer fluids		
	2.2.1	Butylcarbitol	
	2.2.2 2.2.3	Carbitol.	
3.		γ-Butyrolactone I aspects - disposal/recycling of the developer solution	
<b>3.</b> 3.1			
-	Recovery and discharge of loaded soda solution		
3.2	, ,	of polyalcohols	
	3.2.1 3.2.2	Internal recycling	
	3.2.3	Water Management Act (WHG)	
4.	Economic	examination of the developer fluids	
4.1	Alkaline developers; material and preparation costs		
4.2	Material and preparation costs of polyalcohol developers8		
	4.2.1	External recycling costs	
	4.2.2	Internal recycling costs	
5.	Process re	eliability	10
5.1	Examination of polyalcohols from a process technology point of view		
5.2	Examination of the aqueous-alkaline development method from a process engineering point of view11		
5.3	Copper border coverage		11
5.4	Development from plated-through holes		
5.5	Transition zone developer - water rinse		
5.6	Methods for the process control of aqueous-alkaline developer modules1		13
	5.6.1 5.6.2 5.6.3	Measurement of the developer concentration by titration Measurement of the developer loading (gravimetric determination) Measurement of the developer loading (photometric determination)	14
6.			
7.	Literature		15



#### 1. Introduction

Within the scope of processing photoimageable solder resists, particularly in the process step "development", economic efficiency, process reliability and environmental compatibility are becoming more and more significant.

This topic certainly supplies subject matter for comprehensive treatises so that the following statements and observations can definitely not lay claim to completeness. The subject of environmental compatibility in particular is extremely complex and has to be examined within the scope of the entire field of pcb production and the related ecological questions. Special "trouble sources" are the legislation that is in a permanent state of flux and the rapid development of new processes of the environmental protection technology.

The basic principles for the following statements regarding the development process and the resulting questions are the application technology experiences which LACKWERKE PETERS have gathered in many years of partnership cooperation with users of the aqueous-alkaline solder resists of the series' Elpemer<sup>®</sup> 2467 as well as of the polyalcohol developable series Elpemer<sup>®</sup> 2469.

## 2. Examination of the developer fluids from a safety technology point of view

#### 2.1 Aqueous-alkaline developer solutions

As a rule, a solution of about 1 % sodium or potassium carbonate is used for the development of photoimageable aqueous-alkaline developable solder resists. The production and handling of this developer solution do not require any measures exceeding those of normal care. The developer fluid as such does not hold any loading or danger potential for the users.

The waste water treatment of the developer solution and the elimination of the lacquer resist, however, create a different situation: The handling of precipitation chemicals that are added as hazardous matter in controlled quantities is unavoidable when aqueous-alkaline developer fluids are used. In addition, the inseparable lacquer resist and the acidification for precipitation purposes cause a quite substantial saline loading of the waste water which results in water pollution.

#### 2.2 Polyalcohols as developer fluids

#### 2.2.1 Butylcarbitol

Mainly butylcarbitol (BDG, CAS No.: 112-34-5, IUPAC Name: 2-(2-Butoxyethoxy)ethanol) is used as a developer for the solder resists of the series Elpemer<sup>®</sup> 2469: its principal safety technology data are listed below:

i.

Physical and safety technology data:		
Boiling point (at 1013 mbar)	230 °C [446 °F]	
Vapour pressure (at 20 °C [68 °F])	0.003 kPa	
Flash point	+ 105 °C [221 °F]	
Density at 20 °C [68 °F] (DIN 51 757)	0.95 g/cm³	
Odour	slightly fruity	
Ignition temperature	204 °C [399.2 °F]	
EU-VOC guideline (1999/13/EC)	no VOC	
Transport regulations:		
GGVSE/ADR/RID	non-hazardous substance	
IATA/DGR	non-hazardous substance	
GGVSee/IMDG-Code	non-hazardous substance	
Health protection and safety standards at work:		
Hazardous substance regulation	listed substance	
Hazardous symbol	Xi = irritant	
Hazard advice (R phrases)	R 36*	
Safety recommendations (S phrases)	S 24-26**	
MAK value	100 mg/m³	
Toxicology data:		
LD <sub>50</sub> oral (rat)	6600 mg/kg	
Environmental compatibility:		
Water hazard class	WGK 1 (list)	
Storage instructions:		
VbF hazardous class (abolished)	not applicable	
Storage class (VCI concept)	10	

#### Table 1

- \* R 36 = Irritating to eyes
- \*\* S 24 = Avoid contact with skin
- \*\* S 26 = In case of contact with eyes, rinse immediately with plenty of water and seek medical advice

Table no. 1 clearly indicates that butylcarbitol features very favourable safety technology data. The extremely low vapour pressure results in a very low room air loading so that the TLV value can practically not be reached at the usual processing temperatures of 20 °C [68 °F]; all the more since the actual development is performed in largely encapsulated systems so that the room air loading by butylcarbitol vapours is negligible.

#### 2.2.2 Carbitol

Besides butylcarbitol, also carbitol (EDG, CAS No.: 111-90-0, IUPAC Name: 2-(2-Ethoxyethoxy)-ethanol) can be employed as a developer for the solder resists of the series Elpemer<sup>®</sup> 2469; its most important safety technology data are listed below:

Physical and safety technology data:		
Boiling point (at 1013 mbar)	196 - 205 °C [384.8 – 401 °F]	
Vapour pressure (at 20 °C [68 °F])	0.013 kPa	
Flash point	+ 94 °C [201.2 °F]	
Density at 20 °C [68 °F] (DIN 51 757)	0.99 g/cm³	
Odour	fruity	
Ignition temperature	190 °C [374 °F]	
EU-VOC guideline (1999/13/EC)	VOC	
Transport regulations:		
GGVSE/ADR/RID	non-hazardous substance	
IATA/DGR	non-hazardous substance	
GGVSee/IMDG-Code	non-hazardous substance	
Health protection and safety standards at work:		
Hazardous substance regulation	-	
Hazard symbol	not subject to identification	
Hazard advice (R phrases)	-	
Safety recommendations (S phrases)	-	
MAK value	not listed	
Toxicology data:		
LD <sub>50</sub> oral (rat)	5540 mg/kg	
Environmental compatibility:		
Water hazard class	WGK 1	
Storage instructions:		
VbF hazardous class (abolished)	not applicable	
Storage class (VCI concept)	10	

#### Table 2

From a safety technology point of view, carbitol is similar to the positive characteristics of butylcarbitol. The vapour pressure is almost as low as that of butylcarbitol which also results in an extremely low room air loading.

#### 2.2.3 γ-Butyrolactone

The  $\gamma$ -butyrolactone (GBL, CAS No.: 96-48-0, IUPAC Name: Dihydro-2(3H)-furanon) that is sometimes used for polyalcohol developable lacquer systems can - theoretically - also be employed as a developer for the solder resists of the series Elpemer<sup>®</sup> 2469. The most important safety technology data are listed below:

Í

Physical and safety technology data:		
Boiling point (at 1013 mbar)	204 - 206 °C [399.2–402.8 °F]	
Vapour pressure (at 20 °C [68 °F])	0.04 kPa	
Flash point	+ 100 °C [212 °F]	
Density at 20 °C [68 °F] (DIN 51 757)	1.13 g/cm³	
Odour	mild	
Ignition temperature	455 °C [851 °F]	
EU-VOC guideline (1999/13/EC)	VOC	
Transport regulation:		
GGVSE/ADR/RID	non-hazardous substance	
IATA/DGR	non-hazardous substance	
GGVSee/IMDG-Code	non-hazardous substance	
Health protection and safety standards at work:		
Hazardous substance regulation	-	
Hazard symbol	Xn = harmful to health	
Hazard advice (R phrases)	R 22, 36*	
Safety recommendations (S phrases)	S 26, 45**	
MAK value	not listed	
Toxicology data:		
LD <sub>50</sub> oral (rat))	1580 mg/kg	
Environmental compatibility:		
water hazard class	WGK 1	
Storage instructions:		
VbF hazardous class (abolished)	not applicable	
Storage class (VCI concept)	10	

#### Table 3

- \* R 22 = Harmful when swallowed
- \* R 36 = Irritating to eyes
- \*\* S 26 = In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
- \*\* S 45 = In case of accident or if you feel unwell, seek medical advice immediately (show label where possible)

This table clearly proves that  $\gamma$ -butyrolactone has definitely less favourable safety technology features than butylcarbitol and carbitol. The vapour pressure of 0.04 KPa at 20 °C [68 °F] is much higher than with butylcarbitol and carbitol. Although no TLV value is stated for  $\gamma$ -butyrolactone, the hazard symbol  $X_n$  = harmful and the by far more critical toxicological value (LD<sub>50</sub>) emphasize the less favourable properties of  $\gamma$ -butyrolactone from a safety technology point of view.

The high solvency and the resulting high aggressiveness of this developer fluid lead to a definitely higher undercut, particularly with thicker lacquer coats and fine lands. For these reasons, we cannot recommend  $\gamma$ -butyrolactone as a developer fluid and even advise against its use.

# 3. Ecological aspects - disposal/recycling of the developer solution

Regardless of which developer medium is used, the solution that is loaded with broken-off solder resist must be recovered by all means; this process is described below. Furthermore, we draw your attention to our Technical Information sheet TI 15/110 "The EU-VOC regulation – Content and consequences for the pcb industry".

#### 3.1 Recovery and discharge of loaded soda solution

The approx. 1 % sodium carbonate solution that is loaded with dissolved or suspended resist and also with special defoamants (causes relatively high COD values) (COD = chemical oxygen demand) is, as a rule, fed to a common waste water treatment together with other alkaline developer and stripper solutions that are incurred in the pcb production. A usual method in this process is the mixing of the entire solution with concentrated hydrochloric or sulphuric acids, ferric-III-chloride as well as certain polyalcohols as a flocculant. The solved resists are largely precipitated from this acidly set solution as solid organic components. After sedimentation of the solids, the solution is mixed with calcium hydroxide (Ca[OH]<sub>2</sub>) and thus neutralized (pH 7 - 8). Subsequently, the suspension is filtered through filter presses, the sediment is disposed as hazardous waste and the watery solution discharged as waste water. Even now, the observance of the COD limit values in force constitutes a considerable problem and can - in some cases - only be accomplished by expensive additional treatments (ultrafiltration or similar).

Besides the high COD value caused by organic contaminations, a substantial saline load (sodium carbonate, acid and calcium hydroxide) is led into the waste water circulation.

#### 3.2 Recycling of polyalcohols

Polyalcohols are recyclable solvents that can be recovered in a high purity by vacuum distillation and reused without any loss of quality. Merely the solved solder resist is incurred as distillation sludge so that, in this case, the hazardous waste disposal is reduced to an absolute minimum (no flocculation agents, etc.). The recovery of the loaded developer solution can be effected either on the spot by the user (internally) or by specialized recycling companies (externally).

#### 3.2.1 Internal recycling

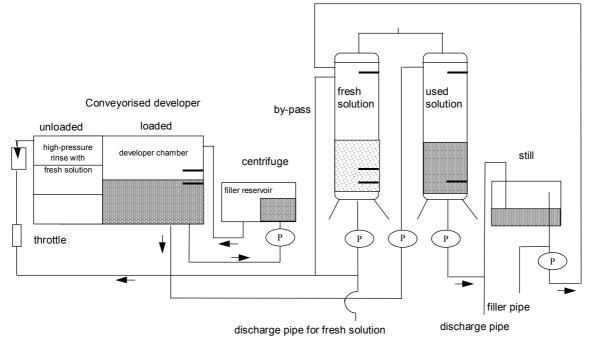


Fig. 1: Schematic representation

The flow chart shows a process diagram in which - according to the board through-put rate - pre-set quantities of loaded developer are taken from the first development chamber and automatically fed to the distillation unit. The distillate is then returned to the final developer chamber (in front of the rinsing zone). The individual developer chambers are interconnected by means of a cascade system. This results in a largely automated cleaning cycle which - in conjunction with the integrated filler centrifuge - reduces the service downtimes of the unit to an absolute minimum. In addition, the use of a filler centrifuge reduces the cost of the still and reduces the cost of distillation.

#### 3.2.2 External recycling

The substantial investment costs for a vacuum distillation unit induce particularly small and medium-sized production companies to order external distillation enterprises which then take the responsibility for all recycling and disposal activities. In this case, however, the user has to provide corresponding temporary storage facilities for loaded developer solution. The following is a diagram of the external recycling process:

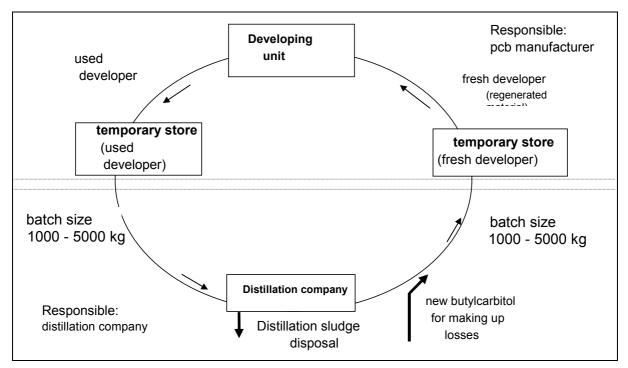


Fig 2: External recycling of polyalcohols

#### 3.2.3 Water Management Act (WHG)

Following the development of the printed circuit boards in polyalcohol, the pcbs proceed into the water rinsing zone of the development unit (conveyorised developer). During the transition of the printed circuit boards into the rinsing zone, a certain quantity of polyalcohol is dragged into the rinsing water. At first sight, this seems to create a waste water problem. Numerous investigations have proved, however, that the polyalcohols butylcarbitol, carbitol and  $\gamma$ -butyrolactone described in item 2.2 are easily decomposed by micro-organisms in the waste water and can practically no longer be traced after a relatively short period of time. The following data substantiate this:

	butylcarbitol	carbitol	γ-butyrolactone
Degree of elimination per Zahn-Wellens (OECD 302 B)	> 70%	> 70%	> 70%
Rating of the elimination ability from the water	easily eliminated	easily eliminated	easily eliminated
Acute fish toxicity	> 1000 mg/l, 48 h leuciscus idus	> 1000 mg/l, 48 h goldorphus	220 – 460 mg/l, 96h leuciscus idus
Bacteria EC <sub>10</sub>	1170 mg/l, 18 h	> 4000 mg/l	> 10000 mg/l
Daphnia EC50	3300 mg/l, 24 h	> 10 g/l, 24 h	> 500 mg/l

#### Table 4

The waste water loading by the polyalcohols listed is relatively low and only temporary so that the Water Management Authorities are not expected to object to the discharge in such a low concentration as it may occur in the rinsing water of conveyorised developers (70 - 140 ppm).

#### 4. Economic examination of the developer fluids

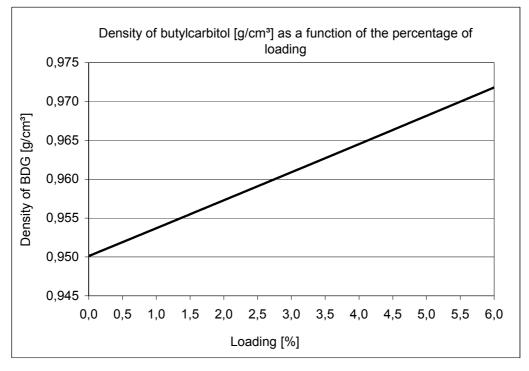
#### 4.1 Alkaline developers; material and preparation costs

The material costs for the production of a usually 1 % aqueous sodium carbonate solution are very low and - in view of the process costs - practically negligible. On the other hand, it is hardly possible to calculate the resulting costs of the necessary waste water treatment of the loaded developer solution with respect to their share in the solder resist development because, as a rule, all alkaline resist-loaded waste waters incurred in production are subjected to a joint treatment. Owing to the certainly increasing waste water charges, it is expected, however, that the economic viability of aqueous-alkaline development processes will have to be scrutinized time and again in future.

#### 4.2 Material and preparation costs of polyalcohol developers

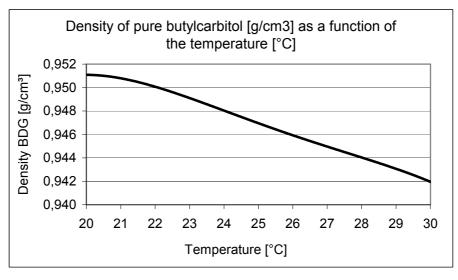
As far as the use of polyalcohols as the developer medium is concerned, quite accurate figures are available so that a comprehensible costing can be effected. The decisive factor in this case is the usable degree of loading of the developer; i.e. how many grams of dry lacquer can be dissolved per kilogram or litre, respectively, of polyalcohol, maintaining a perfect process reliability. Many years of practical experience have proved that a safe production, irrespective of whether butylcarbitol or carbitol is used as the developer fluid, is guaranteed up to a loading degree of 5 % of solids.

In the case of butylcarbitol, the degree of loading is directly correlated with the specific gravity of the developer solution so that this process parameter can be very easily controlled by means of a determination of the specific gravity. The dependency of the specific gravity on the loading of the butylcarbitol is illustrated in the following diagram:





Should the measuring temperature deviate from 20 °C [68 °F], this fact has to be considered in the determination of the specific gravity. The following diagram illustrates the temperature - specific gravity curve of pure butylcarbitol:





The consumption of butylcarbitol can be calculated as follows:

Calculation parameters	quantity of wet lacquer applied	100 g/m²
	dry matter of lacquer after predrying (64 % solids content)	64 g/m²
	Percentage share of area to be developed (average value)	10 %
This results in a lacquer quantity to	6.4 g/m²	
With a 5 % loading, this results in	128.00 g/m²	

Thus, about <u>**256**</u> g of butylcarbitol are required for 1  $m^2$  of printed circuit board coated on both sides.

#### 4.2.1 External recycling costs

Corresponding quotations from successfully operating recycling companies can furnish a perspective of the actual cost that the pcb manufacturer will incur. The following is a brief calculation of a renowned recycling company:

#### Butylcarbitol recovery costs

Quantity supplied 1000 I		
Distillation cost excluding lump-sum for freight	540.00€	
Residue disposal (abt. 5 % = 50 l)	0.38 €/I	19.00€
Barrel scrapping (5 pcs. à 200 l)	10.00 €/St.	50.00€
New barrel	79.00€	
Total costs for 950 I of redistillate (yield abt. 95 %)	688.00€	
Costs per litre of redistilled butylcarbitol	0.72 <b>€</b> /I	
Balancing of distillation loss (50 I butylcarbitol new)	40.00€	
Total costs for redistillation including distillation loss	728.00€	
This results in cost per litre of	0.73 €/I	
or cost per kg: (0.73 €/l divided by 0.95 kg/l [density	0.77 €/kg	

This results in the following cost calculation:

#### 077 €/kg x 0.256 kg/m² = <u>€ 0.20 / m²</u>

This means that costs of  $\in$  0.20 are incurred for the butylcarbitol development of 1 m<sup>2</sup> of pcb coated on both sides.

We draw your attention to the fact, however, that depending on the pcb layout and coating process, deviating calculation parameters will be obtained that may lead to different results.

With the other developing media, the costs of redistillation are almost on the same level. However, differences result as far as the balancing of the distillation losses is concerned.

	BDG	EDG	GBL
cost/kg (new)*	0.80 <b>€</b> /I	1.20 €/I	3.00 €/I
*Price per: August 2004			

Table 5

#### 4.2.2 Internal recycling costs

The cost advantages of internal recycling cannot be estimated in generally applicable terms because they largely depend on the production capacity. One can generally say that the higher the consumption of butylcarbitol, the more profitable the investment in one's own vacuum distillation system including peripheral units.

#### 5. **Process reliability**

Irrespective of whether the development is aqueous-alkaline or polyalcohol, the decisive factor for reliability in the development process is the plant technology employed.

A cascade system (for instance, triple cascade) has proved to be a success, both in the development area proper and in the rinsing zone. With a fully continuous plant operation, the dosing of fresh developer solution/fresh water is always effected from the last chamber seen in transport direction while a corresponding quantity is pumped off from the first chamber. In order to achieve an optimum process reliability, the length of the development section should not be less than 1.5 m. With much shorter units, the conveyor speed of the printed circuit boards has to be reduced to such an extent that fluctuations that can hardly be avoided at a slow speed result in partly considerable variations of the actual development periods.

The correct length ratio of development and rinsing zone is another important parameter. It should be at 2 : 1 to 3 : 1. Rinsing zones that are too short can lead to unnecessary long development times because, for an adequate rinsing result, the conveyor speed of the plant has to be reduced more than would be required for the actual development. The correct dimensioning of the dryer behind the rinsing zone not only depends on the length but mainly on the performance of the drying module. It has to be taken into consideration that, depending on the pcb thickness and the minimum hole diameter, it is more difficult to dry certain layouts than, for instance, standard sizes.

#### 5.1 Examination of polyalcohols from a process technology point of view

The development in polyalcohols is a physical dissolution process. The lacquer that was tackcured in the predrying process and not exposed in the exposure process is returned to dissolution. In this process, the dissolving velocity depends on the developer fluid used, the temperature and the loading of the fluid. Development processes in polyalcohol should be performed relatively cold (up to 26 °C [78.8 °F]max.) because the development proceeds quickly even at low temperatures and higher temperatures lead to a greater aggressiveness of the medium. This will increase the undercut which is detrimental to the stability, particularly of very fine lacquer structures. In order to stop the development process, the development process is immediately followed by water rinsing.

Quite recently, our application technology department and PETERS RESEARCH tested the possibilities of using carbitol as a developer medium for the lacquer systems of the series Elpemer<sup>®</sup> 2469 with excellent results.

It was the target of these tests to achieve a capacity increase of the developer with a renowned German pcb manufacturer by replacing butylcarbitol by carbitol. For this purpose, PETERS RESEARCH performed thorough preliminary tests at laboratory and technical college level. These test results proved that regarding the development velocity of the series 2469, carbitol definitely outperformed butylcarbitol. For instance, the development time could be reduced by about 25 % without having to change the exposure times or observing a lower quality free development. Merely the sensitivity of the lacquer in the high-pressure pump zone is somewhat higher when carbitol is used; this can be controlled without any problems, however, by a corresponding adjustment of the spray pressure. Furthermore, in case of triple development slightly longer holding times may be necessary after the first development in order to stabilize the coating sufficiently.

Also, when looking at the undercut it was found that the development in carbitol is comparatively more favourable. Regarding the realization of 150  $\mu$ m lands, an undercut of max. 10  $\mu$ m was measured which, in this case, means a reduction by more than 30 %.

These promising results were confirmed in a pilot project lasting several days with one of our customers in a production environment. The development velocity was increased from 2.8 to 3.5 m/min, using a developer temperature of 26 °C [78.8 °F] and a spray pressure in the developer zone of 4 - 5 bar [58 – 72.5 PSI].

On account of these excellent results, some manufacturers of printed circuit boards have meanwhile decided to employ carbitol as the developer medium.

Wherever maximum capacity utilization is in great demand, the developer fluid carbitol can make an important contribution.

### 5.2 Examination of the aqueous-alkaline development method from a process engineering point of view

The term "aqueous-alkaline" development is widespread but generally not correct. According to the simplified reaction scheme

## $\begin{array}{r} 2 \ R \ \text{-} \ \text{COOH} \ + \ \text{Na}_2 \text{CO}_3 \ \rightarrow \ 2 \ R \ \text{-} \ \text{COONa} \ + \ \text{H}_2 \text{O} \ + \ \text{CO}_2 \\ R \ \text{=} \ \text{resin residue} \end{array}$

a chemical conversion of the carboxylic groups (-COOH), a certain number of which is contained in the resin of the lacquer system, with soda into a water soluble salt takes place in this process. This salt is dissolved in water and rinsed off. Again, the speed of development is largely dependent on the temperature of the developed medium. In order to achieve complete development results and acceptable development velocities, the operating temperatures are, as a rule, >  $30^{\circ}$  C [ $86^{\circ}$ F] because the reaction speed is too low at temperatures below that value. Water rinsing is necessary in order to stop the development process.

In the development process, some fundamental parameters are independent of the development medium and should be observed by all means in order to increase the process reliability.

#### 5.3 Copper border coverage

The process step development is meant to remove the solder resist from those areas of the printed circuit board that were covered by the artwork in the exposure process. As a rule, the pcb edge is exposed completely because otherwise the loading of the developer would

increase unnecessarily fast and a free developed edge would inevitably also be treated in subsequent processes (Hot Air Levelling, electroless Ni/Au, etc.); in the long run, this would cause considerable costs owing to additional material consumption.

Attention must be paid to the fact that the exposure or non-exposure of the edge is effected unambiguously. Edges that are not covered lightfast can create considerable problems. Lacquer that is not fully exposed in these areas does not have sufficient stability in the development process owing to inadequate polymerization. A "lacquer smear" will develop that is absorbed by the transport rollers and squeegee rollers of the developer and can be stamped on to subsequent printed circuit boards. If these lacquer components are stamped on to free developed areas that are perhaps tinned later on and these pcbs thus contaminated are final cured thermally, (microscopically small) areas develop that are unwettable for subsequent processes. Incorrectly coated pcbs should not be washed in the developer because, on the one hand, the loading of the development medium would increase unnecessarily fast and, on the other hand, the transport system of the developer would become badly contaminated by these activities.

#### 5.4 Development from plated-through holes

When coating printed circuit boards in the curtain-coating process, more lacquer is deposited in bores and plated-through holes than in other application processes; these deposits must be removed. In order to ensure a complete free development of these holes, high spray pressures (abt. 4 bar) and flat cone nozzles are applied.

The nozzles should be inclined at an angle of about 60° to the printed circuit board so that the developing medium can attack the lacquer in the plated-through holes as long as possible and with a high pressure. These development conditions inevitably create a certain degree of undercut because this fixing of the development time is oriented towards the free development of the plated-through holes. Structures such as ink dams are thus developed for a longer period than necessary which may lead to reduced stabilities.

The above considerations apply to holes of > 0.4 mm. Different conditions apply to smaller diameters because, irrespective of the application method, such holes are more or less completely filled with lacquer. In order to achieve full development in this case, a frequent change of the developing medium at the spot to be developed must be ensured. However, this cannot be realized without problems in the case of clogged holes. The solution could be approached as follows:

In the first third of the development process, the plated-through holes should first be sprayed at high pressure and with vertical nozzles in order to permeate the ink and guarantee a subsequent flow through the holes.

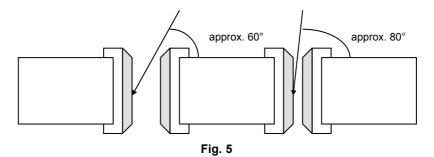


Fig. 5 illustrates the influence of the spray angle on the development process. With larger holes, a smaller angle should be chosen in order ro remove lacquer even from the centre of the plated-through holes. However, the smaller the hole diameter, the more effective a larger angle for the removal of lacquer from this area.

After the ink in the plated-through holes has been permeated, a good flow through the holes for complete removal of the lacquer has to be ensured.

Initial tests by various manufacturers of printed circuit boards have proved that the number of spray nozzles applied must be substantially increased in order to equally ensure full free development with further decreasing diameters. A certain number of these nozzles must then be adjusted in such a manner that the permeability of the lacquer-filled holes is reached. The other nozzles should remain set at an angle of about 60° in order to also enable the free development of larger plated-through holes and, particularly, slots. Promising results were also achieved with wave nozzles that render a good flow through even small plated-through holes possible.

#### 5.5 Transition zone developer - water rinse

The transition between development zone and water rinse is regarded as a very critical area in the overall process of development. It is obvious that no developer medium should be dragged into the rinsing zone. For this reason, squeegee rollers and/or air knives are used in the transition zone. Since partially dissolved resist residues exist between the lacquer edges of the coating, same can be squeezed out of the coating together with the excess developer medium by means of the squeegee roller. If these residues get stuck on the squeegee rollers, this can also result in a stamping effect which would contaminate subsequent printed circuit boards, and wetting in later processes is no longer guaranteed. In order to avoid making mistakes at this point, the squeegee rollers should never run dry but always be moistened with the corresponding medium.

The squeegee rollers at the inlet of the water rinse are particularly critical. The rollers should be sprayed with water in such a manner that a "puddle" forms on the printed circuit boards entering the water zone that would remove or wash off lacquer particles that may have dissolved.

By means of these measures, electroless Ni/Au wetting problems caused by squeegee rollers running dry were eliminated in many cases and rework and rejets, respectively, reduced to a minimum.

#### 5.6 Methods for the process control of aqueous-alkaline developer modules

As a rule, for the process control of aqueous-alkaline developer equipment a titration of the developer solution against 0.1-molare hydrochloric acid (HCI) with methylorange as an indicator solution is performed. Less widespread, but in principle also suitable for process control purposes is a photometric analysis of the developer loading.

Basically, the following methods are suitable for process control:

#### 5.6.1 Measurement of the developer concentration by titration

Reagents:

+ 0.1 N HCI

+ Methylorange or pH electrode

Method:

10.0 ml of the developer solution are thinned with 50 ml deionised water and subsequently titrated with 0.1 molar hydrochloric acid against methylorange or with the help of a pH electrode up to pH 7.0.

#### Calculation of result:

Consumption (in ml) of 0.1 N HCl x 0.053 = % sodium carbonate (g/100)

The sodium carbonate concentration must definitely not fall below 1%!

#### 5.6.2 Measurement of the developer loading (gravimetric determination)

#### Reagents:

+ 10% hydrochloric acid (HCl)

#### Method:

The hydrochloric acid is added to 100 ml of the developer solution until the solder resist contained in the developer solution flocculates. Subsequently, the acid solution is filtered through previously weighed dry filter and then dried at 105  $^{\circ}$ C [221  $^{\circ}$ F].

Calculation of result:

Weighed lacquer quantity x = g/l solder resist loading of the developer solution

The loading of the developer solution with solder resist must not exceed 8.0 g/l!

#### 5.6.3 Measurement of the developer loading (photometric determination)

In order to faciliate the determination of the developer loading by means of a photometre, a calibration curve must first be generated. By means of comparison measurements to this calibration curve later the current loading of the developer solution can be determined very quickly.

Method:

Previously, weighed plates of base material (tara) are coated and predried with a defined wet ink weight. The weight of the dried ink layer is determined by means of renewed weighing. The test pcbs are then solved in a beaker with a predefined quantity of developer solution. In this way solutions with different loading concentrations between 1 and 8 g/l are made and subsequently the transmission of the solutions is measured with a photometer. The more solutions are registered for the calibration curve the more exact the later measurement results.

The loading of the developer solution with solder resist must not exceed 8.0 g/l!

#### 6. Summary

The advantages and disadvantages of either aqueous-alkaline or polyalcohol developer media are discussed controversially. The continuously increasing waste water charges play an important part in the examination of the economic viability of the various processes and presumably lead to an increasing share of the polyalcohol developable resists, not least in the Asiatic area where aqueous-alkaline developable systems are traditionally used because a distinct tightening of the environment legislation is expected there.

A comparison of the dielectric properties inevitably leads to the conclusion that the polyalcohol developable systems are somewhat more favourable although some of the aqueous-alkaline systems have shown a definite inprovement over the past few years. Quite a number of end users, however, still explicitly stipulate the use of polyalcohol developable lacquer systems in the case of printed circuit boards for particularly critical applications (life preserving and military electronics, etc.).

From a process technology point of view, however, the aqueous-alkaline developable lacquer systems have some advantages. For example, the plain development time in the soda development is definitely shorter than with alcoholic development processes. Since the aqueous-alkaline development is based on a chemical conversion of carboxylic groups of the lacquer system, the risk of an overdevelopment of such lacquer systems is much lower than with polyalcohol developable systems with which the structuring of the solder resist is achieved by a purely physical dissolution process.

#### 7. Literature

- /1/ G. Korsten: Photoimageable solder masks, "Leiterplatte 86", Vol. 1, Carl-Hanser-Verlag, D-Munich, 1986
- /2/ K. Maurischat: Liquid photoimageable solder resists, "Leiterplatte 88", Vol. 1, Carl-Hanser-Verlag, D-Munich, 1988
- /3/ W. Peters: Photoimageable solder resists in circuit printing, IS+L, 2/86, Publishers: "Der Siebdruck", D-Lübeck
- /4/ W. Peters: Photosensitive solder resists and their application procedures trends, problems and solutions - Lecture held on the occasion of the specialist conference "Principles and industrial application of photo resists, "Haus der Technik", D-Essen 1988
- /5/ A. Weis/J. Jahn: State-of-the-art in pcb exposure, IS+L, 6/1986, Publishers: "Der Siebdruck", D-Lübeck
- /6/ Roth: Carcinogenic substances, Wiss. Verlagsgesellschaft, D-Stuttgart, 1988
- /7/ S. Kramer: Photoimageable solder resists optimising the processing, Lecture held on the occasion of the Printed Circuit World Convention VII, Basle, Switzerland, May 21. - 24., 1996
- /8/ M. Wieler: The application of photoimageable solder resists in vertical, double-sided screen printing - Comparison of this process with curtain-coating technology, Paper presented at a panel discussion of the Association of Former Graduates of the Technical College for Metal Design, Metal and Plating Technology, D-Solingen, on January 28,1997 in D-Solingen
- /9/ Dr. Meyer: Technical Information sheet TI 15/110: The EU-VOC regulation Contents and consequences for the pcb industry –