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(71) Applicant: **MINNESOTA MINING AND MANUFACTURING COMPANY**
3M Center
Saint Paul, Minnesota 55101(US)

(72) Inventor: **Swan, David Walter**
Minnesota 3M Research Limited Pinnacles
Harlow Essex(GB)

(72) Inventor: **Hellings, Thomas David Grinter**
Minnesota 3M Research Limited Pinnacles
Harlow Essex(GB)

(74) Representative: **Bowman, Paul Alan et al,**
LLOYD WISE, TREGEAR & CO. Norman House 105-109 Strand
London WC2R OAE(GB)

(54) The development of lithographic films.

(57) A lithographic development process in which a lithographic film (6) is contacted separately and in either order with two aqueous baths:

bath (A) containing a developing agent and having a pH of from 2.5 to 7.0 such that development will not occur when the film is contacted solely with the bath, and

bath (B) having a pH of at least 9 such that when the film is contacted with the baths development will occur, the bath (A) and/or bath (B) containing one or more contrast controlling agents in an amount of from 0.002 g/l to 10.0 g/l.

Suitable contrast controlling agents are certain types of antifoggant compounds, for example 5-nitroindazole, 6-nitrobenzimidazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5,6-dinitrobenzimidazole and benzotriazole.

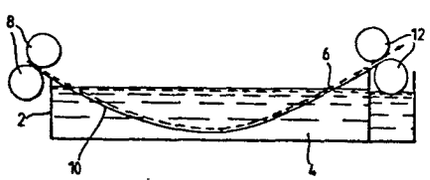

Fig.1.

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THE DEVELOPMENT OF LITHOGRAPHIC FILMS

This invention relates to the development of lithographic films.

When producing continuous tone images for mechanical printing purposes in, for example, newspapers, it is normal practice to make a half-tone photographic intermediate on which tonal gradation is represented by dots of differing sizes. The quality of the final print and the length of life of the printing plate are closely connected with the shape and the spectral quality of these dots.

Very high edge contrast is required for the dots whereby areas at the edge of a dot are developed to full density while areas adjacent to the edge of a dot are not developed or only developed to a very low density. The higher the edge contrast the higher the quality of the final printed work.

In order to achieve these very high edge contrasts special so-called "lith developers" are used. These developers are believed to operate by an autocatalytic action due to a local high concentration of the oxidation products of the developing agent which can build up as a result of low sulphite ion concentrations. Accordingly, such lith developers have very low sulphite concentrations.

When such developers are at a high pH as required for development, they are unfortunately very susceptible

to aerial oxidation. Accordingly, their life is very short once they become exposed to the atmosphere and very careful control is required for their replenishment.

Another disadvantage with known lith developers is that the development times through normal processing machines or by hand development in trays of the developer are between 1½ and 3 minutes. For many purposes such times are unacceptably long and it is only possible to accept such long times for the very highest quality work.

Accordingly, if the problem of aerial oxidation can be avoided or to a large extent reduced and the development time can be speeded up without significant loss of the high edge contrast required this would be an advantage. It is therefore an object of this invention to provide such a development process.

Therefore according to the present invention there is provided a lithographic development process in which a lithographic film is contacted separately and in either order with two aqueous baths:

bath (A) containing a developing agent and having a pH of from 2.5 to 7.0 such that development will not occur when the film is contacted solely with the bath, and

bath (B) having a pH of at least 9 such that when the film is contacted with the baths development will occur,

the bath (A) and/or bath (B) containing one or more contrast controlling agents (as defined herein) in an amount of from 0.002 g/l to 10.0 g/l.

The bath containing the developer is at a relatively low pH and therefore it will remain relatively stable upon exposure to air thereby avoiding the problems of instability for the bath. Further, provided the film is contacted first with that bath and then with the bath of high pH, no development products are formed in that bath and so it merely needs topping up to replace developing agent which is absorbed and removed by the film. This also reduces significantly waste of chemicals since the only developer used is that removed from the bath containing it, and avoids pollution problems in dispensing of exhausted or oxidised developer. The bath which is at a high pH can also be stable since it need not contain any chemicals which are subject to decomposition.

Provided the pH of the high pH bath is sufficiently high, the development time can be fast, the presence of the contrast controlling agent retaining high edge contrast for the dots at fast development times.

After contact with the first bath, the surface of the film is preferably wiped clear of excess developer before contact with the other bath. The film is preferably

contacted initially with the bath containing the developing agent followed by contact with the bath of high pH.

The contrast controlling agents used in the invention are certain organic antifoggant compounds. Organic antifoggant compounds are well known and are described, for example, in the Theory of the Photographic Process, Mees and James, 3rd Edition, page 344. In order to select those antifoggant compounds which are useful as contrast controlling agents in the process of the invention the following test has been devised. Firstly, an available lithographic film must be qualified as suitable for use in the test and secondly a candidate antifoggant compound is tested using a qualified film to ascertain whether it is suitable for use as a contrast controlling agent.

(i) Qualification of lithographic film

The following solutions are prepared:

Solution A

hydroquinone	25.0 g
sodium metabisulphite	3.4 g
sodium sulphite	1.0 g
potassium nitrate	20.0 g
triethylene glycol	40.0 g
Water to	200.0 g

Solution B

potassium bromide	0.75 g
sodium sulphite	5.0 g
potassium carbonate	40.0 g
water to	220.0 g

10 ml of solution A is mixed with 40ml of solution B to produce a developer of pH 11.0 which is placed in a covered test tube in a water bath at 40°C.

Strips of the chosen lith film are exposed in a sensitometer to a lamp (colour temperature 2850°K) with a daylight correction filter and using a 0 to 4.0 density units continuous neutral tone wedge for 10 seconds, choosing the exposure intensity to obtain measurable sensitometric results.

One such strip is developed in the developer for 20 seconds followed by conventional fixing, washing and drying. This is repeated with a series of strips after successive additions to the developer of a solution of 5-mercapto-1-phenyltetrazole in polyethylene glycol 200. The number of strips and concentration of 5-mercapto-1-phenyltetrazole solution is chosen to be such that a maximum value of contrast can be determined and such that prospective contrast controlling agents can be dissolved in polyethylene glycol 200 at the same concentration.

The fog density and the slope of the straight line between densities of 0.1 and 2.5 above fog on the characteristic curve (this is termed the contrast, θ) is measured. The maximum value, θ_s, and its attendant fog value Dmin is recorded. If $\theta_s > 2.0$ and Dmin < 0.06 the film may be used for testing. If not, another lith film having these parameters must be found. Since the contrast is very sensitive to slight changes in developer composition and development conditions it is desirable to eliminate any of these errors by expressing the maximum contrast θ_s as a ratio with the contrast recorded for zero addition (θ_o). This ratio will be referred to as R_s.

(ii) Testing of antifoggant compound

A suitably qualified lith film is subjected to a series of development tests as described above but with the exception that a polyethylene glycol 200 solution of a candidate organic antifoggant compound is added to the developer in place of the 5-mercapto-1-phenyl tetrazole. The concentration of the antifoggant solution should be the same as that of the 5-mercapto-1-phenyl tetrazole used for the film qualification. The θ and Dmin values are measured as before and are recorded and R values calculated.

Antifoggant compounds useful as contrast controlling agents in this invention are those which exhibit antifoggant properties in the test developer with the test film, i.e. Dmin must be ≤ 0.06 at an R value ($\frac{\theta}{\theta_o}$) greater than R_s of the film which is used. The term contrast controlling agent used herein refers to such compounds.

Test Results

(1) Using 3M QA IV lith film the following results were obtained with increasing quantities of 1% solution of 5-mercapto-1-phenyl-tetrazole in polyethylene glycol 200.

Volume added (ml) to 50 ml of test developer	Dmin	θ	R
0	0.08	3.10	1.00
0.3	0.05	3.10	1.00
0.7	0.05	3.41	1.10
1.7	0.05	3.60	1.16
2.7	0.05	3.79	1.22
4.7	0.05	3.80	1.23
5.7	0.05	3.90	1.26
10.0	0.05	1.30	0.46

These data give $\theta_s = 3.9$ and Dmin = 0.05, thus qualifying the film. The value of $R_s = 1.26$.

The following antifoggants were tested as contrast controlling agents at 1% concentration.

(a) 5-nitroindazole

Volume added (ml/l)	Dmin	R
1	0.05	1.045
2	0.04	1.210
4	0.04	2.060

Since $R > R_s$ at a Dmin < 0.06, 5-nitroindazole passes the test as a contrast controlling agent.

(b) 6-nitrobenzimidazole

Volume added (ml/l)	Dmin	R
1	0.05	0.965
8	0.05	0.986
32	0.05	1.160
64	0.05	1.360
128	0.05	1.160

Since $R > R_s$ at a Dmin < 0.06, 6-nitrobenzimidazole passes the test as a contrast controlling agent.

(c) 2-methyl-6-nitro-benzothiazole

Volume added (ml/l)	Dmin	R
2	0.05	0.985
4	0.05	0.990
8	0.05	0.997
16	0.05	1.050
32	0.06	1.040

At this level the antifoggant precipitated. Since $R < R_s$ this material does not qualify as a contrast controlling agent in accordance with the invention.

(d) 2-methyl-5-nitro-benzoxazole

Volume added (ml/l)	Dmin	R
2	0.06	1.00
4	0.04	0.99
8	0.04	0.96
16	0.07	0.98
64 (precipitated)	0.06	0.97

Since $R < R_s$ this is not a contrast controlling agent in accordance with the invention.

(e) 5-methyl-benzotriazole

Volume added (ml/l)	Dmin	R
2	0.08	0.97
4	0.07	1.00
8	0.06	1.02
16	0.05	1.07
32	0.05	1.15
64	0.05	1.33
128	0.04	0.75

Since $R > R_s$ at a Dmin < 0.06 this qualifies as a contrast controlling agent.

(2) Using 3M QA IV lith film the following results were obtained with increasing quantities of 3% solution of 5-mercapto-1-phenyl tetrazole in polyethylene glycol 200.

Volume added (ml) to 50 ml of test developer	Dmin	θ	R
0	0.07	3.10	1.00
0.5	0.05	3.47	1.12
1.0	0.05	3.70	1.19
1.5	0.05	3.72	1.20
2.0	0.05	3.63	1.17
2.5	0.05	3.29	1.06
3.0	0.05	2.30	0.74

This gives θ_s = 3.72 and Dmin = 0.05 which qualifies the film. R_s = 1.20.

The following antifoggants were tested as contrast controlling agent at 3% concentration of polyethylene glycol 200.

(a) 5-methylbenzotriazole

Volume added (ml/l)	Dmin	R
4	0.08	1.06
8	0.05	1.16
12	0.04	1.30
16	0.05	1.35
20	0.05	0.93

Since R > R_s at a Dmin < 0.06 this qualifies as a contrast controlling agent agreeing with the test at the 1% level.

(b) 5-nitrobenzotriazole

Volume added (ml/l)	Dmin	R
4	0.05	1.03
8	0.04	1.08
12	0.05	1.10
16	0.05	1.16
20	0.04	1.24
24	0.04	1.36
28	0.04	1.44
32	0.05	1.62
36	0.04	1.22
40	0.04	0.94
44	0.09	0.23

Since $R > R_s$ at a Dmin < 0.06 this is a contrast controlling agent.

(c) benzimidazole

Volume added (ml/l)	Dmin	R
10	0.06	0.99
15	0.07	1.02
35	0.08	1.05
50	0.09	1.09
70	0.11	1.12

Although R was increasing, the value of Dmin also increased so that this compound fails to qualify as a contrast controlling agent in accordance with the invention.

(3) Using 3M QA IV lith film the following results were obtained with increasing quantities of 8% solution of 5-mercapto-1-phenyl tetrazole in polyethylene glycol 200.

Volume added (ml) to 50 ml of test developer	Dmin	θ	R
0	0.06	3.00	1.00
0.1	0.05	3.33	1.11
0.4	0.05	3.51	1.17
0.6	0.04	3.69	1.23
0.8	0.04	2.43	0.81

Since θ_s = 3.69 and Dmin = 0.04 the film can be used with this concentration. R_s = 1.23.

The following antifoggants were tested as contrast controlling agents at 8% concentration.

(a) 5,6-dinitrobenzimidazole

Volume added (ml/l)	Dmin	R
0.5	0.08	1.04
1.0	0.07	1.07
2.0	0.07	1.09
4.0	0.07	1.07
8.0	0.03	1.09
16.0	0.04	2.33
32.0	0.04	6.80

Since $R > R_s$ at a Dmin < 0.06 this passes the test as a contrast controlling agent.

(b) 3,5-dinitrobenzoic acid

Volume added (ml/l)	Dmin	R
0.5	0.05	0.98
1.0	0.05	0.93
2.0	0.06	0.97
4.0	0.06	0.99
8.0	0.05	0.95
16.0	0.06	0.94
32.0	0.09	1.01
64.0	0.09	0.96
128.0	0.17	1.10

This showed increasing fog and $R < R_s$. This material is not a contrast controlling agent in accordance with the invention.

(c) benzotriazole

Volume added (ml/l)	Dmin	R
8	0.04	1.04
16	0.05	1.09
32	0.05	1.78

Since $R > R_s$ at a Dmin < 0.06 this qualifies as a contrast controlling agent in accordance with the invention.

Thus, suitable compounds for use as contrast controlling agents in the process and baths of the invention include 5-nitroindazole, 6-nitrobenzimidazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5,6-dinitrobenzimidazole and benzotriazole.

The contrast controlling agents may be present in either the low pH bath containing developer or in the high pH bath in an amount of 0.002 g/l to 10.0 g/l. The incorporation of even quite small amounts of contrast controlling agent gives improvement in contrast. The amount of contrast controlling agent is preferably selected to give the maximum increase in contrast which is highly desirable to give the high edge contrast

required for good dot quality. Generally it has been found that when the amount of each contrast controlling agent exceeds a certain value (specific to the particular compound) there is a dramatic increase in contrast as illustrated hereinafter in Example 1.

The two-bath development system used in the invention may include the conventional reagents used for lithographic development, e.g. buffer, solvent for developer, antioxidant, etc. Antifoggant compounds which are not contrast controlling agents in accordance with the above test may also be included.

For example, bath (A) containing hydroquinone developer may include a solvent such as triethylene or diethylene glycol, a buffer, antioxidant such as sodium sulphite and a gelatin swelling controller such as potassium nitrate, potassium citrate or sodium sulphate. The pH of the bath is in the range 2.5 to 7 in order to prevent any development occuring in the bath. The contrast controlling agents may be included in the bath in an amount of 0.002 g/l to 10.0 g/l.

The bath (B) has a high pH greater than 9 and generally in the range 11 to 13, the exact pH being selected according to the particular contrast controlling agent used. When a film which has previously been immersed in the bath of developing agent is immersed in bath (B) acid is produced in the regions of the silver halide grains during development and acid which was absorbed into the emulsion may also be released, thereby tending to reduce the pH in the localised regions at the film surface. This localised change in pH may deleteriously affect the kinetics of the development process leading to inferior quality in the product particularly when the halftone dots are close together. Thus, it is important that a sufficiently high pH is maintained in the region of the film during development. This may readily be achieved by using large amounts of

a strong base in bath (B), e.g. potassium hydroxide, or by the presence of a buffer, e.g. potassium carbonate and sodium bicarbonate. The bath (B) preferably includes a contrast controlling agent in an amount in the range 0.002 g/l to 10.0 g/l. Other components which may be present in bath (B) include sodium sulphite as a dot controlling agent buffered with a sulphite buffer, e.g. triethanolamine and sodium formaldehyde bisulphite, and polyethylene glycol as a solvent for the contrast controlling agent.

Generally the baths of the invention comprise the following components the contrast controlling agents being present in either or both baths:

Bath A

Component	Range	Preferred
developing agent, e.g. hydroquinone	50 to 170 g/l	100 to 150 g/l
antioxidant, e.g. sodium metabisulphite	10 to 35 g/l	13 to 30 g/l
contrast controlling agents	0.002 to 10 g/l	
water	to 1 litre	
pH	2.5 to 7.0	5.0 to 6.5.

Additional solvents may be required for the developing agent and/or contrast controlling agent. Gelatin swelling controller agents may also be included.

Bath B

Component	Range	Preferred
alkali to establish pH,	>9	10.9 to 12.5
e.g. potassium carbonate	130 to 240 g/l	160 to 220 g/l
or potassium hydroxide	50 to 200 g/l	70 to 150 g/l
sulphite	5 to 35 g/l	
contrast controlling agent	0.002 to 10 g/l	
water	to 1 litre	

Antifoggant compounds (0.002 to 10 g/l), dot controlling agents, e.g. sodium sulphite (5 to 35 g/l, preferably 20 to 30 g/l) buffered with a sulphite buffer, e.g. triethanolamine and/or sodium formaldehyde bisulphite, and solvent for the contrast controlling agent may be present.

Examples of bath formulations are as follows:

Bath A	Range/l	Preferred/l
hydroquinone	100 to 175 g	125 g
sodium sulphite	0 to 10 g	6 g
sodium metabisulphite	13 to 20 g	17.2 g
potassium nitrate	0 to 120 g	100 g
triethylene glycol	120 to 300 g	200 g
pH	5 to 7	6.5

Bath B

potassium bromide	1.5 to 20 g	5 g
sodium sulphite	18 to 22 g	18 g
sodium formaldehyde bisulphite	18 to 22 g	18 g
triethanolamine	0 to 80 g	50 g

potassium carbonate	195 to 205 g	200 g
polyethylene glycol 200	50 to 70 g	50 g
1% solution of 5-nitro-indazole in polyethylene glycol 200	10 to 12.5 ml	11.5 ml
pH	>9	12.5.

Alternative formulations include:

Bath A	Range/l	Preferred/l
hydroquinone	100 to 175 g	145 g
polyethylene glycol 200	0 to 80 ml	60 ml
triethylene glycol	120 to 300 g	120 g
sodium metabisulphite	10 to 40 g	30 g
sodium acetate	1 to 5 g	2 g
1% solution of 5-nitro-indazole in polyethylene glycol 200	0 to 20 ml	9 ml

Bath B		
potassium carbonate	170 to 220 g	200 g
potassium bromide	0 to 20 g	5 g
sodium sulphite	18 to 35 g	30 g
sodium bicarbonate	10 to 30 g	to pH 11.3
1% solution of 5-nitro-indazole in polyethylene glycol 200	0 to 20 ml	
polyethylene glycol 200	0 to 150 g	80 g.

In Bath A simple dilution has been investigated and over the concentration range indicated (+10% to -30%) the action of the developer is substantially unchanged both in developing activity and half-tone dot quality. Developer activity is only marginally affected by reducing concentration by 50% but the dot quality then suffers.

It has been found that the requirements of a processing machine for use with the two-bath developer system of the invention differ from those of conventional rapid access processing. Most rapid access processing machines have three processing stages, namely develop, fix and wash, and then would normally be followed by a drying stage. Generally, the total time through the processor is 90 to 120 seconds. In some machines where the film is passed through shallow trays rather than roller stacks, the agitation is low and one stage of washing is found to be inadequate. A second wash stage is therefore included giving a four-bath machine.

The two-bath development system for use in the invention conveniently requires four baths:

1) a first bath containing developer at low pH,
2) a high pH bath,
3) fix, and
4) wash.

The conventional designs for four bath machines are quite suitable for the first, third and fourth stages but it has been found that special requirements in bath B are necessary which are not found on any commercially available machine.

The main reason for these differences lies in the different way of development from the conventional technique. With a single bath developer, efforts are made by means of agitation to maintain the solution at the film/developer interface in motion to aid diffusion of development products from the film into the bulk and to replace these with fresh developing agents. The agitation may be provided by rollers and liquid motion round the bath, and in some processors higher rates of fluid flow are deliberately introduced in order to avoid undesirable effects resulting from the build-up of oxidation products on or close to the surface which can be "dragged" from areas of high development to areas of

less development. This gives changes in dot size which are not exposure controlled, and therefore undesirable. Removal of "bromide drag" adjacency effects is a highly desirable feature of any processor; and it has been found that the two-bath development gives much lower adjacency effects than conventional lith processors.

Thus in conventional lith development (approx. 1½ minutes), or even in rapid access chemistry where lith development is not obtained, the film/solution interface is in an equilibrium situation with respect to developers and oxidation products.

The two-bath developer system used in the invention does not function in this way. There is no development in bath A, only absorption. In bath B solution there are no developing agents, and the total development relies on the developer already in the film. Agitation at the surface of the film in bath B is therefore kept to a minimum in order to avoid washing developer out of the film before it has had a chance to develop silver halide. If rollers are used to transport the film through bath B, the agitation at the surface resulting from contact between roller and emulsion layer is enough to give low density of development and a non-uniform development as well.

Thus, one requirement of the machine is that in bath B no rollers nor any other object come in contact with the surface of the film until the development is substantially complete, i.e. until the film has passed through most of the bath and preferably has emerged from the bath.

It has also been found that the initial stage of contact of the film with the bath B solution is very critical if uniform development is to be achieved, which is essential for good half-tones, and this results in two further requirements for the processor.

First, the film must be wiped clean on the surface after coming out of bath A and before entering bath B. If the surface layer of bath A on the film is uneven as it enters bath B the rate of diffusion and rate of rise of pH within the film is not uniform and this shows up as uneven final development.

Second, the motion of the film through the surface of bath B must be uniform along the entire length of the film. This is not easily obtained as the tail of the film on leaving the squeegee rollers just before bath (B) often flicks or curls. Any jerky motion at all gives bands of uneven development across the film.

It has been found that the passage of the film through the bath can generate waves on the surface of the processing solution which results in lines of uneven development which are believed to occur due to the waves hitting the film as it enters the processing solution. The liquid-film interface at the point of entry into the bath is particularly critical and it is important to ensure that every part of the film is subjected to the same conditions on entry into the processing solution in order to achieve even development.

Suitable apparatus for use in the processing of photographic film includes a bath for a processing liquid, conveying means for conveying a photographic film through the processing liquid contained in the bath and means for guiding the film through the bath, said conveying means and guiding means being constructed and arranged so that the motion of the entire length of the film from entry to exit into and out of the processing liquid is uniform and there is no contact by any object with the emulsion surface of the photographic film until the film has passed substantially through the processing liquid.

The apparatus may be constructed and arranged so that the film is immersed

in the bath by being continuously moved along a smooth curved guide in the bath with nip rollers positioned before and after the guide so that all parts of the sheet of film follow a smooth path in and out of the bath without any discontinuity in the direction of motion. The nip rollers at the beginning are sufficiently compressible to give good surface wiping. The rollers are arranged so that the nips of the rollers are aligned with the surface of the guide to enable the film to pass smoothly through the nip of the first rollers onto the guide and to pass smoothly from the guide through the nips of the second set of rollers. The film is processed emulsion side up to avoid any contact of the emulsion with any surface during passage through the second bath. As an alternative to driving the film onto the guide by a pair of rollers it is possible to use film guides carefully aligned to bring the leading edge of the film to the guide surface. However, these guides must not extend into the solution where they might touch the emulsion surface during development.

In order to reduce the generation of waves on the surface of the processing solution, the apparatus is preferably provided with a cover which rests upon the surface of the processing solution, the cover being provided with two slits for the entry and exit of the film into and out of the processing solution. The cover is preferably provided with baffles which project down into the processing solution to prevent the generation of disturbances, such as eddy currents, through the solution. In this way it is possible to obtain uniform conditions for the passage of the entire length of the film through the processing solution.

The viscosity of the processing solution may be adjusted to reduce the propensity of the liquid to generate waves and disturbances. Generally, the viscosity of the solution is adjusted to the range 5 to 20 cP (at 40°C), preferably in the range 15 to 20 cP. The viscosity of the processing solution may be adjusted by the addition of sodium carboxymethyl cellulose or a similar compound in order to thicken the solution.

The invention will now be illustrated with reference to the accompanying drawings, in which:

Figure 1 represents apparatus for conveying the film through the second processing bath,

Figure 2 represents a modified version of the apparatus of Figure 1, and

Figure 3 represents a plot of density against relative log, exposure obtained from the tests disclosed in Example 1.

Figure 1 shows a second bath 2 containing the high pH solution 4. The film 6 is fed via a pair of squeegee rollers 8 which wipe the surface of the film through the bath, emulsion side upwards, along film guide 10. The shape of the film guide is the natural line taken by the film travelling through the solution, this guide shape, which is probably a catenary, provides a smooth jerk free passage through the bath. The film

guide and the rollers 8 and 12 are aligned so that the direction of the film passing through the nips of the rollers is exactly along the surface of the guide.

Figure 2 shows a modified version of the apparatus of Figure 1 in which the rollers 12 are mounted vertically. In order to ensure that the film undergoes a smooth passage on exit from the bath a bar 14 is provided at the exit of the solution to restrict the backward movement of a loop which always forms as the film enters the nip between the rollers. The formation of the loop is illustrated at 16.

The apparatus shown in Figures 1 and 2 may be provided with a cover positioned on the surface of the processing solution, which is provided with two slits for the entry and exit of the film. Preferably, the cover is provided with downwardly projecting baffles which extend to just above the surface of the film.

The invention will now be described by the following Examples.

Example 1

Bath A

Hydroquinone	15 g
Triethylene glycol	30 g
Sodium sulphite	3 g
Buffered to pH 5 with sodium acetate and acetic acid	
Water to	100 ml

Bath B

Potassium hydroxide	7 g
Sodium sulphite	0.5 g
Polyethylene glycol 200	15 g
Water to	100 ml

Kodalith Ortho 3 film was exposed to a continuous neutral wedge and processed in the above solutions at 45°C. The time in bath A was 20 seconds after which excess surface liquid was removed with wiper blades. The film was then immersed in bath B for 5 seconds during which development occurred. A stop bath of dilute acetic acid arrested development, and the film was fixed, washed and dried in the usual way.

Curve A in Figure 3 shows the type of characteristic curve obtained. The fog is very high, and the value of γ low. γ is a measure of the steepest slope on the

curve, and for curve A this would be about 5. Adding 0.1 gm of 6-nitrobenzimidazole to bath A and processing an exposed strip of film as before resulted in a curve B in Figure 3. The effect of the 6-nitrobenzimidazole is seen to be that of a traditional antifoggant, giving a reduced fog, a loss of speed and a reduction in Dmax. Further addition of antifoggant continued to reduce speed, fog and density until, in the present example, at about 0.5 gm of 6-nitrobenzimidazole there was a dramatic change in the shape of the characteristic curve to that of curve C in Figure 3. The fog is 0.04, and a region of exceptionally high γ(>30) has appeared. Further addition of 6-nitrobenzimidazole to 1 g does not lead to any further large change in Dmax, but increases the density range over which this high contrast occurs by cutting back the development to higher exposures as shown in curve D in Figure

Example 2

This Example shows the tolerance to bath B time which the contrast controlling agent imparts under most ferocious conditions.

Bath A

Potassium metabisulphite	3.0 g
Hydroquinone	15 g
Triethylene glycol	30 g

6-nitrobenzimidazole	0.8 g
Potassium hydrogen phthalate	2 g
pH to 2.5 with HCl	
Water to	100 ml

Bath B

Potassium hydroxide	15 g
Polyethylene glycol 200	15 g
Sodium sulphite	1 g
Water to	100 ml

3M Type QA IV lith film was exposed to a continuous wedge and processed in the above solutions at 45°C. The time in bath A was 15 seconds. After various times in bath B the film was fixed, washed and dried.

Bath 2 time (sec)	Fog	Rel. Log Speed	Dmax	γ
15	0.04	1.45	>7	>30
30	0.04	2.0	>7	>30
60	1.6	1.4	>7	-

After 30 seconds the fog level had not increased, and even after 60 seconds the fog was only 1.6.

The remarkable effect of the 6-nitrobenzimidazole is more clearly appreciated when it is realised that a piece of unexposed film put directly onto bath B which is slightly contaminated by carry-over from bath A of

previous tests, gave a fog of 2.0 in less than 10 seconds.

Example 3

The very high γ observed in this 2 bath system was not confined to 6-nitrobenzimidazole as the contrast controlling agent. Neither was it necessary to have the contrast controlling agent in bath A only, for under certain conditions it is advantageous to have the contrast controlling agent in both baths or only in bath B. This feature is illustrated in this Example.

Bath A

ethylene glycol	30 g
hydroquinone	12.5 g
potassium metabisulphite	3 g
water to	100 ml

Bath B

potassium carbonate	13 g
potassium metabisulphite	1 g
polyethylene glycol 200	15 g
water to	100 ml

pH was adjusted to required level with glacial acetic acid or sodium hydroxide solution.

Contrast controlling agent/antifoggant was added to either bath as reported in the following Table. The solutions were used at 45°C.

3M lith film was exposed to a continuous wedge on a Kodak 101 sensitometer and half-tone images were exposed by contact exposure through a similar wedge and a Kodak 133 line magenta negative contact screen.

The film was immersed in bath A for 10 seconds, and then excess solution was removed with wiper blades. The film was then immersed in bath B for 15 seconds, after which it was fixed, washed and dried in the usual way.

Dot quality for 50% dots was assessed visually, rating between 1 for excellent and 6 for poor.

The following Table reports the amounts of agents used in each bath and the results.

Contrast controlling agent/antifoggant in bath A	Contrast controlling agent/antifoggant in bath B	Quantity of agent in bath A mg/100 ml	Quantity of agent in bath B mg/100 ml	Bath B pH	Fog	γ	50% dot quality
none	none	-	-	10.9	0.26	10	>6
5-nitroindazole	5-nitroindazole	12.75	25	10.9	0.04	28	2
5-methylbenzotriazole	5-methylbenzotriazole	12.75	12.75	10.9	0.05	13	3.5
6-nitrobenzimidazole	5-nitrobenzotriazole	50	50	10.9	0.04	30	2
5-nitroindazole	5-nitrobenzotriazole	12.75	50	10.9	0.04	35	3.5
5-nitro-2-methylbenzoxazole	5-nitroindazole	50	25	10.9	0.06	35	3.5
2-methyl-6-nitrobenzothiazole	5-nitroindazole	50	25	10.9	0.07	52	3.0
5,6-dinitrobenzimidazole	5-nitroindazole	50	12.5	10.9	0.04	52	3.0
none	5-nitroindazole	-	50	10.9	0.04	35	3.0

The tests show in each case how the presence of the contrast controlling agents gives increase γ and improved dot quality, and how the quantity of contrast controlling agent required for this invention is greatly reduced at lower pH levels of bath B. The results also indicate that the presence of antifoggants other than the contrast controlling agent may be tolerated.

Example 4

The same beneficial effect of very high contrast is obtained with potassium bromide included in bath B.

Bath A

hydroquinone	12.5 g
sodium metabisulphite	2 g
polyethylene glycol 200	2 ml
ethylene glycol	30 g
5-nitroindazole	1 mg
water to	100 ml

Bath B

5-nitroindazole	5 mg
potassium bromide	0.25 g
sodium sulphite	2.5 g
polyethylene glycol 200	4 ml
potassium carbonate	20 g
acetic acid to pH 10.9	
water to 100 ml	

3M Type QA IV lith film was exposed to a continuous wedge and to a half-tone dot screen, and the strips

processed in the above solutions at 40°C. The time in bath A was 20 seconds and the time in bath B was also 20 seconds. Fixing, washing and drying were carried out normally.

The continuous wedge showed a fog level of 0.03 and a γ in excess of 25, while the dots were of good quality, suitable for half-tone work.

Example 5

The second bath may be applied as a thin layer, in which case the solution would not be re-used but totally lost by washing off.

Bath A

Ethylene glycol	30 g
Potassium metabisulphite	3 g
Hydroquinone	12.5 g
Water to	100 ml

Bath B

Potassium bromide	0.25 g
Potassium metabisulphite	1.0 g
Potassium carbonate	13 g
Polyethylene glycol 200	2 ml
5-nitroindazole	6 mg
3% aqueous solution of sodium carboxymethyl-cellulose	40 g
Water to	100 ml

pH to 12.0 with sodium hydroxide.

The solution temperature was 45°C in each case.

3M lith film was exposed to a half-tone image and immersed in bath A for 15 seconds. After wiping excess solution from the surface, the film was placed between two sheets of polyester film joined along an edge to form a spreader sheet. Bath B was spread evenly over the film surface by pouring the solution between the polyester layers close to the joined edge and then pulling through a pre-adjusted slit. After 25 seconds the film was removed, bath B washed off, and then fixed, washed and dried as usual. Excellent half-tone dots were obtained, high contrast and low fog being exhibited.

Example 6

The following baths were prepared:

Bath A

hydroquinone	125 g
triethylene glycol	120 g
polyethylene glycol 200	50 g
sodium metabisulphite	17 g
sodium acetate	1.6 g
water to 1 litre	
pH	5.7

Bath B

potassium carbonate	180 g
sodium sulphite	30 g
sodium bicarbonate	20.5 g
potassium bromide	2.5 g
0.1% 5-nitroindazole in polyethylene glycol 200	80 ml
water to 1 litre	
pH	11.4

3M Type QA IV lith film was exposed to a half-tone image and immersed in Bath A for 15 to 20 seconds at 25 to 40°C. After wiping excess solution from the surface the film was immersed in Bath B for 15 to 20 seconds at 40°C. The film was then fixed, washed and dried in the normal manner. Excellent half-tone dots were obtained, high contrast and low fog was exhibited.

Example 7

The conditions of Example 6 were repeated except that 5,6-dinitrobenzimidazole (80 ml of 8% w/w solution in polyethylene glycol 200) was used in place of the 1% 5-nitroindazole solution in polyethylene glycol 200. 3M Type QA IV film after development gave a contrast value (θ) of 5.56 and a Dmin value of 0.04, illustrating the effectiveness of this compound which passed the qualifying test.

Example 8

The conditions of Example 6 were repeated except that 3,5-dinitrobenzoic acid (80 ml of 8% w/w solution in polyethylene glycol 200) was used in place of the 1% 5-nitroindazole solution in polyethylene glycol 200. 3M Type QA IV film after development gave a contrast value (θ) of 2.66 and a fog level of 0.36, and was ineffective as a contrast controlling agent. This compound failed the qualifying test.

Example 9

Developing baths were made up as in Example 6 except that the 5-nitroindazole solution in polyethylene glycol 200 in bath B was replaced by 20 ml of 3% 5-methylbenzotriazole in polyethylene glycol 200. 3M QA IV film after development gave a contrast value (θ) of 9.4 and a Dmin of 0.04. Half-tone dots were of good quality. This compound passed the qualifying test.

Example 10

The conditions of Example 6 were repeated except that the 5-nitroindazole solution was replaced by 60 ml of 3% 5-nitrobenzotriazole in polyethylene glycol 200. 3M QA IV film after development gave a contrast value (θ) of 9.6 and a Dmin of 0.04. Half-tone dots were of good quality. This compound passed the qualifying test.

Example 11

The conditions of Example 6 were repeated except that the 5-nitroindazole solution was replaced by 60 ml of 3% benzotriazole in polyethylene glycol 200. 3M QA IV film after development gave a contrast value (θ) of 9.7 and a Dmin of 0.05. The half-tone dots were of good quality. This compound passed the qualifying test.

Example 12

The conditions of Example 6 were repeated except that the 5-nitroindazole solution was replaced by 60ml of 3% benzimidazole solution in polyethylene glycol 200. 3M QA IV film after development gave a contrast value (θ) of 3.31 and a Dmin of 0.05. With no benzimidazole solution added the contrast was 3.4 and Dmin 0.05. Half-tone quality was poor, being unaffected by the addition of the benzimidazole solution. A repeat test with 140 ml addition of 3% benzimidazole gave a contrast of 3.9 and a Dmin of 0.14. This compound is therefore ineffective as a contrast controlling agent. It also failed the qualifying test.

Example 13

Effect of buffer capacity on Bath B

The significance of the ability of Bath B to maintain the pH at the region of the film during the development process was assessed by the following tests.

Bath A

hydroquinone	12.5 g
sodium metabisulphite	2.0 g
triethylene glycol	12.0 g
polyethylene glycol 200	5 ml
water to 100 ml	
pH adjusted with 10N sodium hydroxide	5.5

Bath B

potassium bromide	0.25 g
sodium sulphate	2.5 g
polyethylene glycol 200	6 ml

0.1% 5-nitroindazole in polyethylene glycol 200	8 ml
potassium carbonate (1) 18 g, (2) 20g, (3) 22 g	
pH adjusted with acetic acid in each case to 11.4	
water to 100 ml	

Using standard exposures and 3M QA IV film the following data was obtained (20 seconds in each bath at 40°C).

potassium carbonate (g)	Dmax	Speed (relative log E units)
18	3.15	1.0
20	3.58	1.21
22	3.75	1.39

This shows that speed increases by about 0.2 relative log exposure units for every 2 g of potassium carbonate, even though the pH was the same in each case.

The effect was further substantiated by the following experiment.

Bath A

hydroquinone	12.5 g
triethylene glycol	12.0 g
polyethylene glycol 200	5 ml
sodium metabisulphite	1.7 g
sodium acetate	0.16 g
water to 100 ml	
pH	5.7

Bath B

polyethylene glycol 200	8 ml
sodium sulphite	3.0 g
potassium bromide	0.25 g
0.1% 5-nitroindazole in polyethylene glycol 200	8 ml
potassium carbonate	20.0 g
water to 100 ml	

(1) pH adjusted by 2.5 g sodium bicarbonate to 11.3

(2) pH adjusted by acetic acid to 11.3

The results of developing 3M Type QA IV film for 20 seconds in each bath at 40°C were:

	fog	Dmax	Speed	contrast
(1)	0.04	3.72	1.26	6.50
(2)	0.04	3.63	1.07	6.35

In this case, although the original level of potassium carbonate was 20 g in each bath B, the use of sodium bicarbonate to adjust the pH rather than acetic acid gave a speed increase of ∿0.2 and a reduction in dot quality.

Recognising that:

$$2CH_3COOH + K_2CO_3 \longrightarrow 2CH_3COOK + CO_2 + H_2O,$$

the use of acetic acid for pH control would reduce the carbonate level to 18 g which agreed with the earlier test where 2 g change in potassium carbonate changed

speed with 0.2. Bath B was then reformulated with only 18 g of potassium carbonate and the pH adjusted with sodium bicarbonate. The result was the same as that found with the 20 g level adjusted with acetic acid.

Examples 1 and 2 which contain a strong base but no buffer provide excellent results. Thus whilst it is important for bath B to maintain the desired pH at the surface of the film it is not essential that the bath contains a buffer to maintain the pH.

CLAIMS

1. A lithographic development process characterised in that a lithographic film is contacted separately and in either order with two aqueous baths:

bath (A) containing a developing agent and having a pH of from about 2.5 to about 7.0 such that development will not occur when the film is contacted solely with the bath, and

bath (B) having a pH of at least 9 such that when the film is contacted with the baths development will occur,

the bath (A) and/or the bath (B) containing one or more contrast controlling agents (as defined herein) in an amount of from about 0.002 g/l to about 10.0 g/l.

2. A process as claimed in Claim 1 characterised in that the contrast controlling agent is selected from the group consisting of 5-nitroindazole, 6-nitrobenzimidazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5,6-dinitrobenzimidazole and benzotriazole.

3. A process as claimed in Claim 1 or Claim 2 characterised in that the film is contacted with bath (A) prior to bath (B) and bath (B) includes a contrast controlling agent.

4. A process as claimed in any preceding claim characterised in that bath (B) includes 5 to 35 g/l of a sulphite.

5. A process as claimed in Claim 1 characterised in that the film is first contacted with bath (A) comprising:

hydroquinone	100 to 175 g/l
sodium sulphite	0 to 10 g/l
sodium metabisulphite	13 to 20 g/l
potassium nitrate	0 to 120 g/l
triethylene glycol	120 to 300 g/l
pH	5 to 7,

and thereafter contacted with bath (B) comprising:

potassium bromide	1.5 to 20 g/l
sodium sulphite	18 to 22 g/l
sodium formaldehyde bisulphite	18 to 22 g/l
triethanolamine	0 to 80 g/l
potassium carbonate	195 to 205 g/l
polyethylene glycol 200	50 to 70 g/l
1% solution of 5-nitroindazole in polyethylene glycol 200	10 to 12.5 ml
pH	12.4 to 12.7.

6. A process as claimed in Claim 1 characterised in that the film is first contacted with bath (A) comprising:

hydroquinone	100 to 175 g/l
polyethylene glycol 200	0 to 80 ml/l
triethylene glycol	120 to 300 g/l

sodium metabisulphite	10 to 40 g/l
sodium acetate	1 to 5 g/l
1% solution of 5-nitroindazole in polyethylene glycol 200	0 to 20 ml/l

and thereafter contacted with bath (B) comprising:

potassium carbonate	170 to 200 g/l
potassium bromide	0 to 20 g/l
sodium sulphite	18 to 35 g/l
sodium bicarbonate	10 to 30 g/l
1% solution of 5-nitroindazole in polyethylene glycol 200	0 to 150 g/l.

7. A two bath developer system characterised by the combination of:

bath (A) containing a developing agent and having a pH of from about 2.5 to about 7.0 such that development will not occur when the film is contacted solely with the bath, and

bath (B) having a pH of at least about 9 such that when the film is contacted with the bath development will occur,

the bath (A) and/or bath (B) containing one or more contrast controlling agents (as defined herein) in an amount of from about 0.002 g/l to about 10.0 g/l.

8. A two bath developer system as claimed in Claim 7 characterised in that the contrast controlling agent is

selected from the group consisting of 5-nitroindazole, 6-nitrobenzimidazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5,6-dinitrobenzimidazole and benzotriazole.

9. A two bath developer system as claimed in Claim 7 or Claim 8 characterised in that bath (B) includes a contrast controlling agent and from 5 to 35 g/l of a sulphite.

10. A two bath developer system characterised in that bath (A) comprises:

hydroquinone	100 to 175 g/l
sodium sulphite	0 to 10 g/l
sodium metabisulphite	13 to 20 g/l
potassium nitrate	0 to 120 g/l
triethylene glycol	120 to 300 g/l
pH	5 to 7,

and bath (B) comprises:

potassium bromide	1.5 to 20 g/l
sodium sulphite	18 to 22 g/l
sodium formaldehyde bisulphite	18 to 22 g/l
triethanolamine	0 to 80 g/l
potassium carbonate	195 to 205 g/l
polyethylene glycol 200	50 to 70 g/l
1% solution of 5-nitroindazole in polyethylene glycol 200	10 to 12.5 ml
pH	12.4 to 12.7.

11. A two bath developer system as claimed in Claim 7 characterised in that bath (A) comprises:

hydroquinone	100 to 175 g/l
polyethylene glycol 200	0 to 80 ml/l
triethylene glycol	120 to 300 g/l
sodium metabisulphite	10 to 40 g/l
sodium acetate	1 to 5 g/l
1% solution of 5-nitroindazole in polyethylene glycol 200	0 to 20 ml/l

and bath (B) comprises:

potassium carbonate	170 to 220 g/l
potassium bromide	0 to 20 g/l
sodium sulphite	18 to 35 g/l
sodium bicarbonate	10 to 30 g/l
1% solution of 5-nitroindazole in polyethylene glycol 200	0 to 150 g/l.

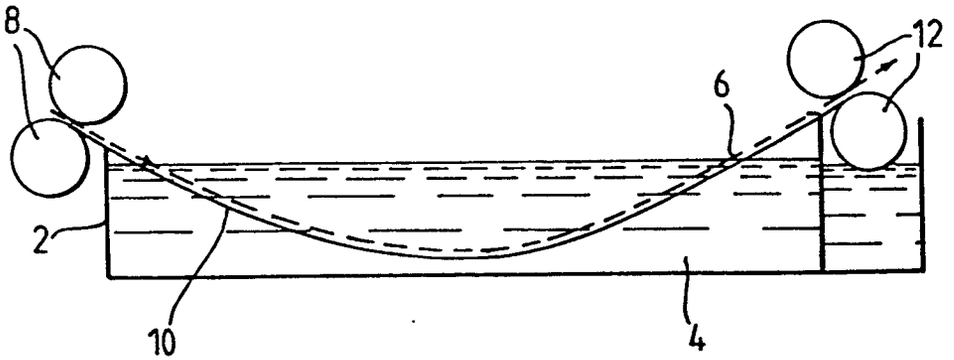


Fig.1.

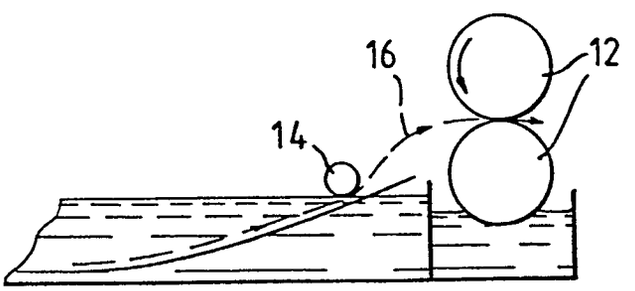
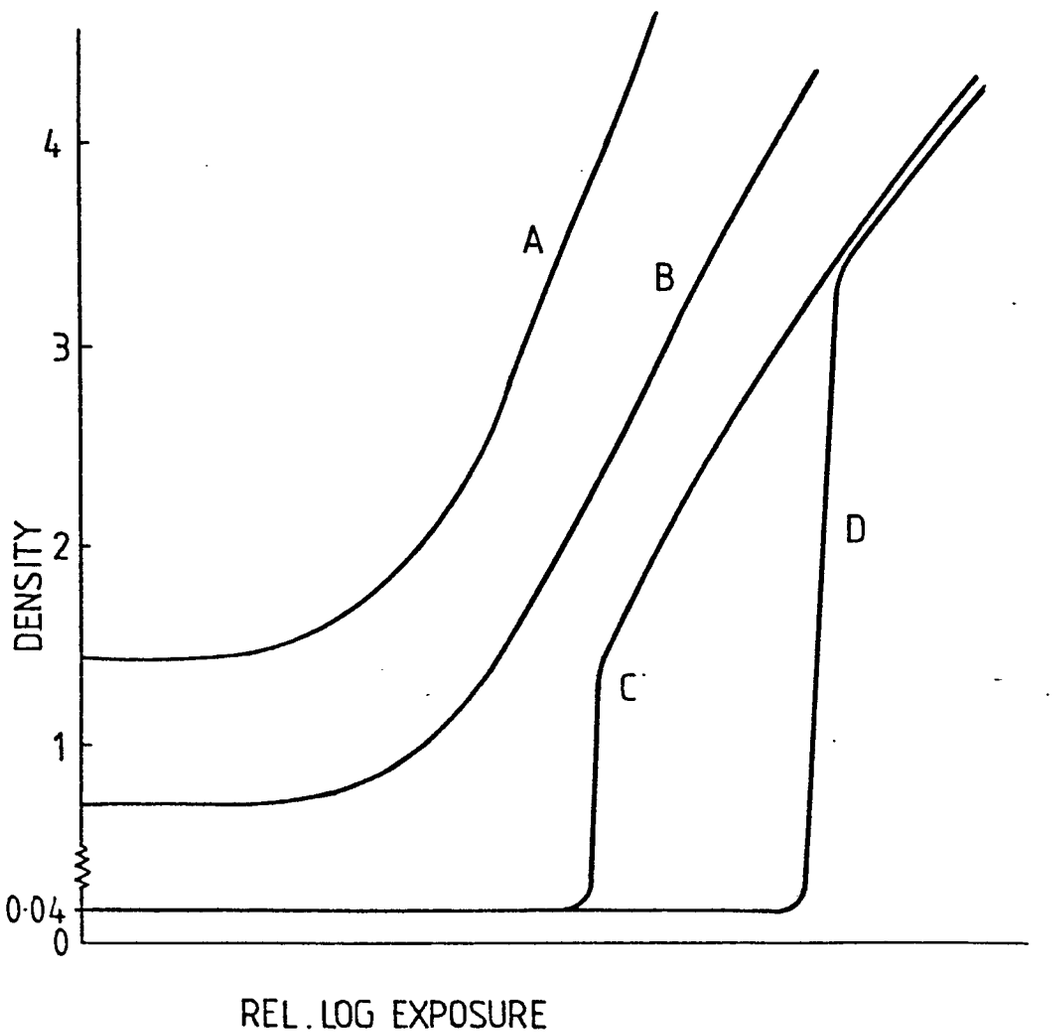


Fig.2.

Fig.3.



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EUROPEAN SEARCH REPORT

Application number
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.³)
X	GB - A - 1 469 763 (MINNESOTA MINING AND MANUFACTURING COMPANY) + Totality; especially examples 2,7,8 + ----	1,2,7,8	G 03 F 7/06 G 03 C 5/26 G 03 C 5/30

TECHNICAL FIELDS SEARCHED (Int. Cl.³)

G 03 F
G 03 C

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	19-02-1981	SALTEN