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J. W. BOONE ET AL

3,411,906

DIAZO DEVELOPMENT PROCESS

Filed May 25, 1964

2 Sheets-Sheet 1

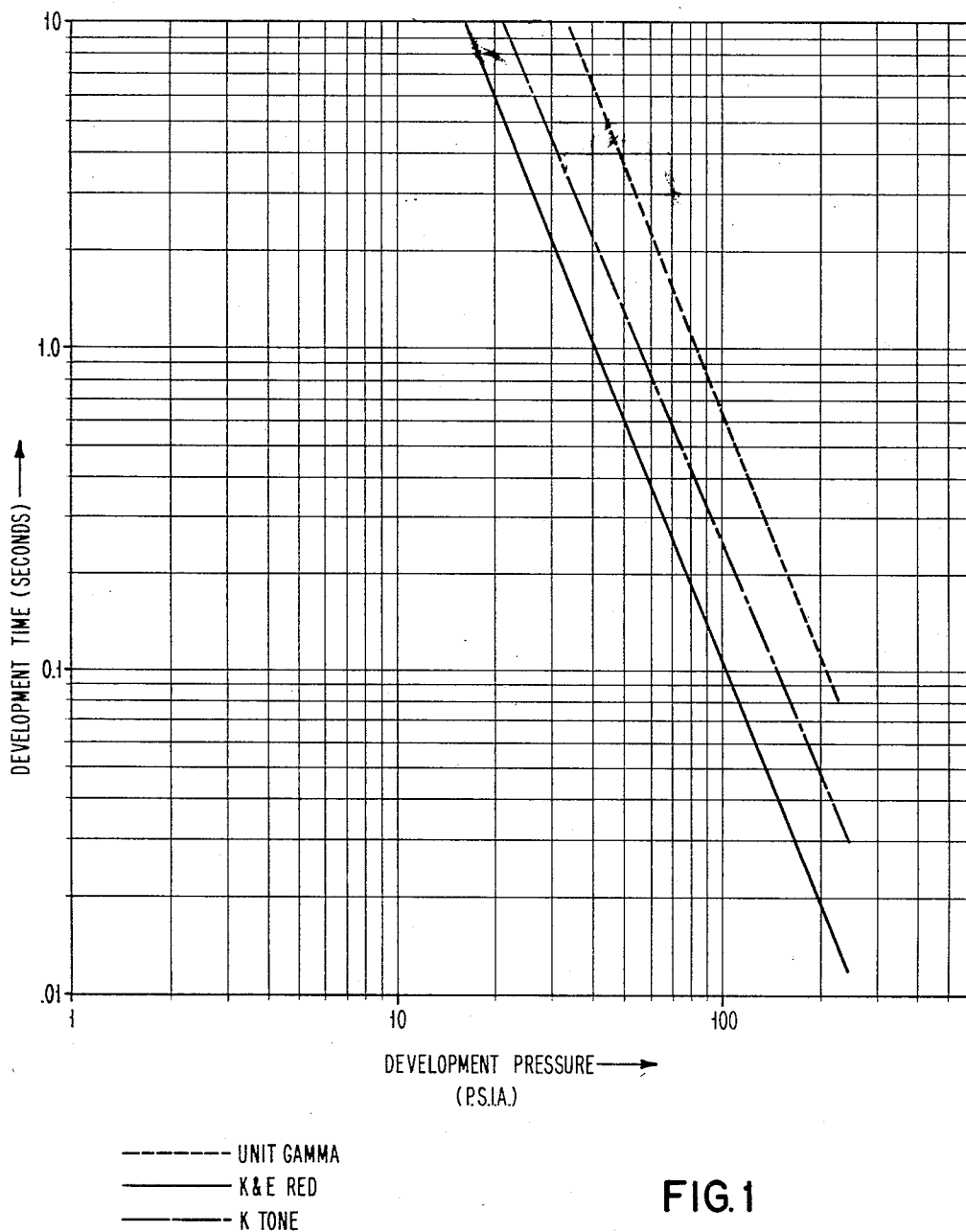


FIG. 1

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2 Sheets-Sheet 2

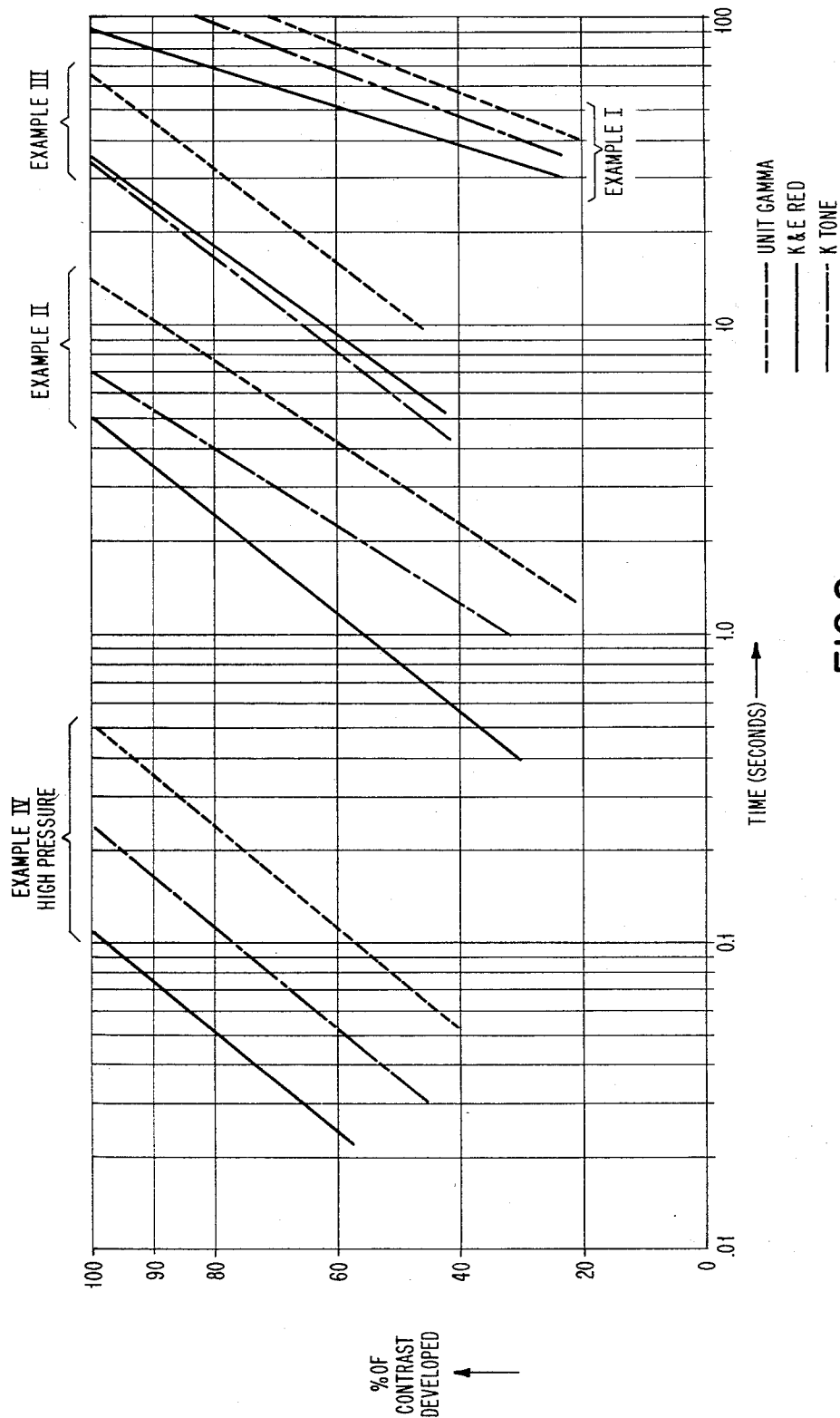


FIG.2

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3,411,906

DIAZO DEVELOPMENT PROCESS

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11 Claims. (Cl. 96—49)

ABSTRACT OF THE DISCLOSURE

A method of developing photosensitive materials, such as diazotype films and papers, with ammonia at high pressures thereby reducing significantly the development time. For example, a commercial diazotype film was developed to 90% contrast in less than 0.1 second by contacting the film with anhydrous ammonia at about 90 p.s.i.a.

This invention relates to an improved process for the development of ammonia process diazotype films and papers. The process to be described is especially suitable for the development of diazotype films. It is in this connection that the invention finds its greatest use, since the technological importance of these latter materials has arisen almost explosively owing to their extremely high intrinsic resolution capability. Our invention is especially significant in the mechanized production of diazo film duplicates of either silver or diazo film originals. Such film duplicates commonly occur as the analogue storage section of a so-called aperture card, that is to say, a punched tabulating card in which a section of the card has been removed and replaced with a piece of light-sensitive film. With document miniaturization technology approaching the point where the ability to resolve 1000 lines/mm. is becoming essential, diazo films are a first choice in such applications. Heretofore, however, the use of such diazo film aperture cards has been limited to so-called "off-line" applications since the ammonia developing process as heretofore practiced has been too slow and problem-ridden to make practical its use in an "on-line" information storing and disseminating system.

It is an object of this invention to provide a developing process for two component diazo films and papers which operates at speeds several orders of magnitude higher than heretofore possible.

It is a further object of this invention to provide a developing process for diazo photomaterials which can operate at ambient temperatures, that is to say, temperatures around 70° F., and with very simple devices.

Still another object of this invention is to provide a process which operates at extremely high efficiency insofar as usage of ammonia is concerned so that the ammonia handling problems heretofore associated with the so-called two component diazo process are substantially eliminated.

Another object of this invention is to provide a developing process in which variations in color and sensitometric response owing to unavoidable changes in development conditions are essentially eliminated.

Finally, it is an object of this invention to provide a development process which retains all of the intrinsic high resolution capability of the diazo process.

As an aid in understanding and appreciating our invention, we review below the technology of ammonia development of two component diazo films and papers as it is currently practiced, and some of the problems associated with present ammonia developing technology.

For many years diazo papers were overwhelmingly more important to the manufacturer than were diazo films, and, in fact, diazo films were not invented until several

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years after the introduction of diazo sensitized papers. Historically, then, the ammonia developing process was largely adapted to the needs of diazo papers. The ammonia developing process as it evolved employed aqua ammonia as a source of ammonia. The usual present day commercial white print machine contains a chamber in which is located a tray or other container which can be heated. The chamber usually contains other auxiliary heating elements. Aqua ammonia at some 20 to 25% concentration is dripped into the heated container where substantially all of the ammonia, together with a considerable proportion of the water-solvent, is vaporized. Diazo paper or film is brought into contact with the hot, moist ammonia fumes by sliding the paper across perforations in the chamber or in some cases, by direct introduction of the film or paper into the chamber itself through sealing rolls. Insofar as the development of paper is concerned, considerable experience indicates that a certain degree of moisture is quite essential in suitably developing diazo papers. It would appear that the actual dye-forming reaction takes place in a water-ammonia liquid medium. Heat likewise aids the development of films and papers with aqua ammonia.

If an attempt is made to develop films and papers at ambient temperatures, the development is extremely slow, the shades obtained are non-typical, and thus the process is entirely unsatisfactory. While modern commercial white print machines can expose diazo papers at speeds in excess of 100 feet per minute, the ability of such machines to fully develop diazo paper at these speeds falls rather short of perfection. Thus, in critical work, a second pass through the ammonia chamber is usually required in order to insure that all of the diazo has coupled to form dye and in many cases, three or more passes at printing speed velocity may be needed. This failure to develop at printing speed velocity, of course, subtracts considerably from the value to be gained from the use of high speed exposing equipment and/or the use of higher speed diazo sensitized papers.

A number of other difficulties obtain in connection with the presently used developing system which employs hot vapors of aqua ammonia for development. For instance, many diazo products contain several couplers and/or several diazos in order to secure the desired color or, in some cases, the desired sensitometric response. For example, a black developing paper is usually secured by the inclusion of at least two couplers in the sensitizing formulation; in order to secure neutral shades along the entire sensitometric curve, three couplers are frequently employed. In practice, the actual shades obtained are found to depend to a very great degree on the actual conditions of development. Thus, a "hot, dry" developing environment is prone to produce blue prints, while a "cool, moist" environment tends to yield yellow-brown hues. This effect is not unexpected since the activation energy for coupling can be expected to vary from diazo-coupler pair to diazo-coupler pair and a variability in relative coupling rates with temperature is unavoidable.

Further, as noted earlier, a proportion of moisture has been found essential in developing diazo paper; the velocity of development depends critically on the amount of water present. Thus, too low a proportion of water leads to poor development and off-color shades, while too high a proportion of water leads to sodden prints, dye bleed, streaking, paper cockling and false colors.

It will be recognized that the sensitivity of the aqua ammonia developing process poses a severe problem. Maintaining strictly predetermined conditions at varying speeds and printing loads imposes a severe burden on the machine designer, while providing diazo printing materials passably insensitive to developing conditions is a problem which the diazo chemist has not yet solved.

It should be noted that the foregoing problems are not eliminated if one turns to the so-called "one-component" or semi-moist process. To cite a single objection to the semi-moist process, this process cannot be satisfactorily adapted to the ultra-high speed operation envisaged because of paper drying problems. Resolution requirements completely eliminate moist developing diazo films owing to slight dye bleed during development.

The difficulties sketched here in connection with paper products (to the development of which the aqua ammonia process has been optimized, insofar as this is possible) are magnified somewhat when one turns to "dry developing" diazo film products. These diazo films, typically, comprise a suitable transparent base, frequently a tough, dimensionally stable, polyester film, to which has been bonded, e.g., by subbing, a resin matrix suitable for diazo sensitization. Sensitization is normally done by the use of a solvent-sensitizing component containing mixture. Cellulose acetate is typical of a suitable sensitizing layer. In view of the water-resistant characteristics of typical diazo film matrices, it is not surprising that difficulty ensues when aqua ammonia is employed. In addition to certain of the developing difficulties mentioned for paper, new difficulties arise, such as a tendency for the film to bluish and haze under certain conditions of moisture and heat and a marked slowing down of the development rate owing to the difficulty in securing a rapid penetration of the layer by the ammonia-water mixture. Furthermore, water-induced curl, always a major difficulty with paper, can become uncontrollable with certain types of films.

Finally, a major source of difficulty with the development procedures currently employed, is a loss of resolution owing to diazo diffusion during the relatively slow development process. As noted earlier, photomaterial technology is approaching the point where the ability to resolve 1000 lines/mm. is becoming essential. In order to accomplish this high resolution, it is fundamental that the image pattern laid down by light be preserved during subsequent processing steps. This implies that the motion of the imaging species during development can be only a few hundred molecular diameters. Clearly, in the case of the diazo film process, it is essential that the developing process be aimed at minimizing diazo diffusion; that is, that the diazo must be immobilized by dye formation as rapidly as possible. It is well known that diffusion rates are increased by an increase in temperature so that low temperature development is desirable. Further, it is necessary that an effective quantity of the developer composition be infused as rapidly as possible to the full depth of the resin matrix bearing the diazo image. The ammonia-water developer system is clearly not adapted to the attainment of these objectives, and, in fact, severe degradation of image resolution owing to diazo diffusion can be demonstrated in diazo systems in which heat during development is the prime factor in securing satisfactory image development.

It should now be clear that current aqua ammonia development technology is fundamentally deficient. These shortcomings become decisive in film systems in which the ultimate in resolution is required. We have devised means by which the development of both diazo films and papers may be carried out at ambient temperatures instead of the elevated temperatures hitherto used. In spite of the fact that we may employ low temperature conditions at which a lowering of development rate would be expected, we achieve an increase in development rate of the order of hundreds of times that possible with aqua ammonia under the same conditions. With our system, development is so nearly instantaneous that in combination with the relatively low temperatures employed, substantially no diazo diffusion occurs before the diazo is immobilized by dye formation. Further, with our system, an essentially constant temperature is possible so that relative coupling rates remain constant.

Films and papers formulated for development by our

new system exhibit a hitherto unattainable fidelity of tonal response. Since the speed of our process makes it feasible to design our developing apparatus for constant development time rather than the variable development time inevitable with "synchronized" machines, haze, blotch and curl in films are substantially reduced or eliminated. The sensitometric and color fidelity, the extreme rapidity of development and the very high efficiency with which ammonia is used make our process especially compatible with existing accounting and computing machinery so that "on-line" processing of aperture card and aperture card duplicates becomes practical for the first time with ammonia developing systems.

Without being limited to the foregoing hypothesis, we propose that we attain the foregoing useful objectives by introducing a liquid ammonia environment as a reaction solvent for our system. In our process we use essentially pure ammonia gas at a pressure sufficiently high that condensation of the gas can be expected to occur throughout the molecular pores of the matrix, be it film or paper. Our coupling reaction is thus deemed to occur in a surround of liquid ammonia solvent instead of an aqua ammonia surround.

It is well known that liquid ammonia is a solvent of astonishing properties and that the rates of many reactions are very decidedly higher in liquid ammonia than in water. One of our preferred methods for carrying out development by our improved process involves sandwiching a piece of film or paper between two closely fitting surfaces so that very little dead space or volume remains. We provide suitable gasketing means to contain the material to be developed. We may first exhaust the air around the sample so that diffusion of the developing gas is unimpeded by the presence of air. This process avoids contamination of ammonia by air as well, since we (in some cases) prefer to reuse the ammonia. We then provide means for introducing ammonia at slightly above ambient saturation pressure (usually from about 90 to 120 p.s.i. absolute) for a dwell time measured in fractions of a second (usually about 0.1 second suffices), followed by essentially instantaneous removal of the trace of ammonia exterior to the film or paper, either by pumping or by flushing the chamber into a vessel containing an ammonia absorbent.

Our process is so efficient that almost no excess ammonia remains, so that venting or disposal by other means is very easy. Our entire developing process at room temperature thus requires only some 0.2 second. This should be contrasted with a time of several minutes required for full development by means of some prior art aqua ammonia devices at the same temperature.

As an alternative to development in a substantial vacuum, our invention may also be practiced by the use of high pressure ammonia in the presence of air. Preferably, a developing chamber having a relatively small volume of air is employed, and high pressure ammonia is introduced therein in a manner similar to that described above for vacuum development. We have found that perfectly satisfactory development occurs, even in the presence of air. We have further found that the only substantial difference between developing in a vacuum and developing in the presence of air is that when developing in the presence of air, the pressure of the developing ammonia should be increased by approximately the amount of atmospheric pressure, i.e., 15 pounds per square inch, to obtain development in the same time as that achievable by vacuum development.

It is, of course, well known that the rate of a chemical process may frequently be enhanced by an increase in the concentration of a catalyst for the reaction or an increase in concentration of one of the reacting components. It should be noted, however, that quite apart from its other advantages, the increase in development rate afforded by our process is considerably greater than would be predicted on a simple first order pressure basis. We attribute this to the fact that under our processing

conditions, the coupling reaction is occurring in liquid ammonia solvent.

The following examples show the improved development times available with our invention compared with different commercially available diazo development machines. In all of the examples, three different types of commercially available diazo film were tested. These films were identified as: "K&E Red," manufactured by the Keuffel and Esser Company; "K Tone," manufactured by the Technifax Corporation; "Unit Gamma," manufactured by General Aniline and Film Company.

EXAMPLE I

In this example, apparatus similar to that described in U.S. Patent 2,948,208 was employed to test the three different types of diazo film. This apparatus includes a central cylinder around which the film sample to be developed is disposed. This cylinder is surrounded by an outer wall to form the development chamber, and heating means are provided to maintain the developing chamber at an elevated temperature of approximately 135° F. A measured amount (4 oz.) of 28% ammonia was poured into the bottom of the cylinder and the temperature allowed to come up to operating temperature. Samples of each of the three types of diazo film were inserted around the warmed central cylinder. A stop watch was started at the instant the film sample was introduced into the developing chamber. Several samples of each type of film were so treated, each separate sample being exposed to the ammonia fumes for a different length of time, as indicated in Table I below. At the conclusion of the allotted development time for each sample, the stop watch was stopped and the sample removed from the development chambers.

The degree of development of each sample was determined by densitometry, and the results are listed in Table I below in terms of the percentage of contrast developed. We have defined "complete development" as:

90% ($D_{\max} - D_{\min}$) + $D_{\min}$ or 90% of maximum contrast possible.

where $D_{\max}$ is the maximum or completely developed density of the film, and

$D_{\min}$ is the base or background density of the film prior to development.

We chose the figure of 90% rather than 100% to represent complete development because the timer required for 100% development is indefinite since at that point the slope of a density vs. time plot is zero. In the table below, the "Percent of Contrast Developed" is the percentage of complete development (as defined above) achieved for that film sample in the development time specified.

TABLE I.—MATERIAL

K Tone		Unit Gamma		K&E Red	
Dev. Time, Sec.	Percent Contrast Devel.	Dev. Time, Sec.	Percent Contrast Devel.	Dev. Time, Sec.	Percent Contrast Devel.
5	3.1	5	1.2	5	4.8
10	3.6	10	1.8	10	7.2
15	6.7	15	2.3	15	11.2
20	12.9	20	3.5	20	15.2
30	17.0	30	11.7	30	22.8
40	30.0	40	22.8	40	40.8
50	43.8	50	35.6	50	57.6
60	46.4	60	43.4	60	72.0
75	65.4	75	49.1	75	87.3
90	75.8	90	62.0	90	95.2
105	83.5	105	74.3		
120	92.8	120	84.3		

Samples of each of the specified types of diazo film were then run in a commercially available Ozamatic white print machine, Model 23500, manufactured and sold by the Ozalid Division of General Aniline and Film Corporation. This machine employs an aqua ammonia environment at an elevated temperature. These film sample were developed at varying belt speeds to yield different development times. The data from this machine is listed below in Table II.

TABLE II.—MATERIAL

K Tone		Unit Gamma		K&E Red	
Dev. Time, Sec.	Percent Contrast Devel.	Dev. Time, Sec.	Percent Contrast Devel.	Dev. Time, Sec.	Percent Contrast Devel.
				.95	54.5
1.04	34.5	1.04	16.5	1.04	59.0
				1.15	58.0
				1.30	63.0
1.50	50.0			1.50	70.0
				1.73	74.0
2.10	56.0	2.10	28.0	2.10	80.0
2.10	65.5			2.60	83.0
3.5	80.0	3.5	44.5	3.5	91.0
4.2	85.0	4.2	52.0		
5.2	92.5	5.2	62.0	5.2	98.0
6.5	97.0	6.5	70.0		
7.4	"100.0"	7.4	81.0		
		8.7	87.0		
		10.4	91.0	10.4	"100.00"
		11.5	95.0		
		13.0	96.0		
		14.9	99.0		

EXAMPLE III

Samples of each of the above diazo films were developed in a commercially available diazo film developing machine. The Uniprinter, Model 086, manufactured by Minnesota Mining and Manufacturing Company. This machine employs a warm aqua ammonia environment at a developing area temperature of approximately 135° F., as discussed above in connection with the prior art machines. The data from this machine is indicated below in Table III.

TABLE III.—MATERIAL

K Tone		Unit Gamma		K&E Red	
Dev. Time, Sec.	Percent Contrast Devel.	Dev. Time, Sec.	Percent Contrast Devel.	Dev. Time, Sec.	Percent Contrast Devel.
2	32.1	5	37.5	5	47.3
3	37.8	10	49.2	7	52.2
5	44.5	15	57.5	10	59.5
7	58.5	20	68.8	12	66.0
10	64.2	30	78.5	15	76.6
12	71.5	40	87.8	20	82.2
15	76.8	50	93.0	25	87.3
20	84.0	60	97.0	30	97.0
25	91.2	75	97.8		
30	96.4	90	"100.0"		

EXAMPLE IV

A single sample of each of the different films above invention. This apparatus included means for the essentially instantaneous addition of ammonia to a chamber at a pressure slightly below the saturation pressure of liquid ammonia at room temperature (70° F.). As indicated above, the sample chamber had a very small volume formed by sandwiching the sample between two closely fitting surfaces so that very little dead space or volume remained. After removal of the air from around the sample, ammonia was admitted to the chamber under control of fast acting mechanical valving means which permitted dwell times for the ammonia gas in the developing chamber of 0.05 sec. and above.

After this exposure to ammonia, the sample space was exhausted of ammonia, air admitted to the developing chamber and the sample removed. Different pressures of ammonia were employed, and the resulting development times are plotted in the graphs of FIG. 1 as a function of the development pressure.

From FIG. 1, it will be seen that our invention produced complete development in remarkably short times, and that at a development pressure of only 100 p.s.i.a., the fastest film was completely developed in 0.1 second.

As indicated above, our invention is equally effective in diazo developing in the presence of air. When development occurs in the presence of air, the only significant change is that the pressure of the developing ammonia should be increased by the amount of atmospheric pressure to attain complete development in the same time as under vacuum conditions. Thus, the graphs of FIG. 1 apply

equally well to development in the presence of air except that the pressure valves should be increased by approximately 15 p.s.i. Or, putting it another way, the graphs of FIG. 1 apply to development in the presence of air if the pressure plot on the axis of abscissa is considered gage pressure rather than absolute pressure.

A summary of the results of the above tests listed in Examples I-IV is shown in the graphs of FIG. 2. In FIG. 2 the data from Examples I-IV is plotted in terms of the percentage of contrast developed in the film as a function of time.

The graphs of FIG. 2 clearly indicate the superiority of the present invention in terms of development time. It will be seen that even the fastest of the prior art machines (Example II), with the fastest film, required approximately 3.4 seconds to reach 90% development; whereas, the technique of the present invention, operating at a pressure of 120 p.s.i. absolute, developed this same film sample to 90% development in 0.07 of a second, a factor of improvement in development time of almost fifty over the fastest prior art machine. Further, the method of the present invention produced 90% of complete development for even the slowest of the films tested in 0.40 second, a factor of improvement in developing speed of more than 8 over the fastest prior art machine with the fastest film. It should be understood that the fastest prior art machine tested, the machine of Example II, is primarily a paper developing machine and we found that it did not yield satisfactory density uniformity because the grid pattern of the screen belt is transferred to the film in the development process.

From FIG. 2 it will further be seen that the other two prior art machines which are designed for film development and which do develop film satisfactorily were considerably slower than our process. The fastest of these two machines, utilizing the fastest of the three films tested, produced a development time 328 times slower than our process. The slower of the two machines approached a time of 80 seconds for developing the fastest diazo film, a time which is more than a thousand times greater than the development time in accordance with the present invention for that same film.

In terms of the quality of the resulting developed film samples, several of the materials showed marked hue differences when developed in the prior art apparatus of Example I and when developed in the prior art machine of Example II under the conditions described. Very uniform density results were obtained using the high pressure development process of this invention. Density differences were no greater than the normal variation (.02 density) one might expect due to coating of the diazo material itself. In the cases where the dye hues were comparable, samples processed by our new method and the machines of Examples I, II, and III were comparable in density.

Based on the foregoing data, we took 80 seconds as a conservative lower limit for full development under the conditions noted for the tube developer of Example I operating at somewhat above ambient temperature conditions. Reference to published tables for the vapor pressure of 28% aqua ammonia at room temperature gives a figure of about 13 p.s.i. absolute pressure. The absolute pressure of ammonia in our high pressure experiment was about 120 p.s.i. Disregarding the fact that the aqua ammonia experiment was conducted at substantially above room temperature (135° F.), where its rate is somewhat increased over that to be expected at room temperature, we would expect as a first order approximation to find an increase in rate in the high pressure experiment to aqua ammonia experiment in the ratio of 120/13 or about 9 to 1. We find, however, by actual experiment the wholly unexpected increase in ratio of 80 sec. to 0.07 sec. or approximately 1000 to 1. To put the result succinctly, the high pressure rate is nearly 100 times that which would reasonably be expected.

As noted heretofore, we are inclined to attribute this to the fact that under our process, coupling occurs in a liquid ammonia surrounded within the molecular pores of the film matrix. Still another factor which contributes to the enormous and unexpected increase in coupling rate may be the realization in our invention of an effect reported by R. Wistar and P. D. Bartlett "Kinetics and Mechanism of the Coupling of Diazonium Salts With Aromatic Amines in Buffer Solution," *Journal of American Chemical Society*, vol. 63, pp. 413-417, 1941. This article demonstrated that the most active "coupling form" of a diazo compound occurs between the diazonium ion and the conjugate base of the coupler constituent. These species are usually at an optimum concentration in the pH range of 4.5 to 9.5. Above a pH of 9.5, the coupling rate is reduced because of the conversion of the diazonium ion to the diazotate in aqueous media. We believe that under the conditions of our high pressure process the permeation of the film with alkaline ammonia is essentially a non-aqueous surround permits highly alkaline conditions and, therefore, a high rate of coupling to ensue without the formation of diazotate.

The usable ammonia pressure range according to our invention is quite broad. The minimum pressure should be significantly in excess of the ambient pressure of the diazo material so as to produce a significant increase in the development speed. From the curves in FIG. 1 it will be seen that a pressure of approximately 90 p.s.i. absolute produced development of all film samples in less than one second at room temperature. It will be further noted from the curves in FIG. 1 that even an absolute pressure of 50 pounds produced development of all film samples in times which were less than or equal to those required for the fastest prior art device (Example II).

Similarly, the upper pressure limit usable in our invention is determined by a number of practical factors, such as gross condensation of liquid ammonia on the film surface at excessively high ammonia pressures. Preferably the maximum ammonia pressure employed in developing in accordance with the present invention does not exceed the partial saturation pressure of ammonia at the particular temperature being employed, to avoid gross condensation of ammonia on the film sample upon exposure to the ammonia. In terms of the temperature range for the ammonia, although we have found ambient or room temperature (about 70° F.) to be a particularly convenient one, we believe a temperature range from about 40° F. to about 212° F. to be practical. In this connection, if ammonia temperatures in excess of room temperature are employed, it is useful to warm the developing chamber containing the diazo material to approximately the same temperature as the ammonia to eliminate or reduce the condensation problem. At temperatures which exceed 212° F. by a significant amount, the pressure of ammonia is quite high, increasing the problem of handling the high pressure ammonia.

A further consideration in connection with such high pressure ammonia is the necessity of accurately controlling the development time, to produce complete development of the film without producing any undesired chemical reaction on the film from over-exposure to ammonia at these pressures. Our calculations indicate that a temperature of 212° F., with a corresponding pressure of ammonia of 908 p.s.i. absolute, 90% development of a diazo film would occur in the order of 0.35 millisecond. Thus, such pressures may be employed in our invention if suitable means are provided to limit the time of contact of the diazo film with the ammonia to this short period. It will be appreciated that in a batch or discrete sample developing system, the mechanical problems of valving and the like to achieve such a short development time would be considerable. However, if the diazo material is in strip form and is driven past a developing station at a suitable speed, exposure and development times of this order may be achieved.

From the logarithmic plot (FIG. 1) of the values obtained according to the present invention, the unexpected variation of development time with pressure is clearly evident. By careful analysis of the data obtained in these experiments, we have found that the development time T appears to follow a predictable relationship for all diazo films tested. This relationship can be expressed as follows:

$$T = K/P^n$$

where

T is the development time in seconds,
 P is the pressure in pounds per square inch absolute,
 n is a number between 2.0 and 3.0, and
 K is a constant of the particular film.

We have found that the exponent n varies with different films, apparently depending on the particular substrate and the film properties involved. However, in all of the samples we have tested, we have found n to lie between a value of 2.0 and 3.0.

All of the experiments performed in accordance with our invention were carried out using anhydrous ammonia gas, because of its commercial availability and cost, but there is no reason to limit the disclosure invention to the use of pure anhydrous ammonia. Mixtures of anhydrous ammonia with other gases and water vapor would also be useful in carrying out the development process, and the invention should not in any way be limited to ammonia gas alone.

What we claim is:

1. A method for developing images on light-sensitive diazotype materials comprising:

the steps of contacting said diazotype material with substantially anhydrous ammonia at a pressure between about 50 and 1000 pounds per square inch gage in the presence of air and water vapor.

2. The method of claim 1 wherein the pressure is between about 90 and 120 pounds per square inch gage.

3. A method for developing images on light-sensitive diazotype materials comprising:

the step of contacting said diazotype material with substantially anhydrous ammonia at a pressure between about 50 and about 1000 pounds per square inch absolute.

4. The method of claim 3 wherein the pressure is between about 90 and 120 pounds per square inch absolute.

5. A method for developing images on light-sensitive diazotype materials comprising:

the step of contacting said diazotype material with substantially anhydrous ammonia, in an atmosphere substantially free of air, at a pressure of from about 50 to about 1000 pounds per square inch absolute.

6. The method of claim 5 wherein the pressure is between about 90 and 120 pounds per square inch absolute.

7. The method of claim 6 in which prior to contacting said diazotype material with said ammonia the diazotype material is in a substantial vacuum.

8. A method for developing images on light-sensitive diazotype materials comprising:

the step of contacting said diazotype material with substantially anhydrous ammonia at a pressure of from about 50 to about 100 p.s.i.a., said pressure not to exceed the partial saturation pressure of ammonia at the temperature employed, said temperature to be in the range from about 40° F. to about 212° F.

9. The method of claim 8 in which prior to contacting said diazotype material with said ammonia the diazotype material is in an evacuated atmosphere.

10. A method for developing images on light-sensitive diazotype materials comprising the steps of:

placing said diazotype material in an evacuated atmosphere.

contacting said diazotype material in said evacuated atmosphere with substantially anhydrous ammonia at a pressure of from about 50 to about 1000 p.s.i.a., and

removing the excess ammonia from said evacuated atmosphere in the vicinity of said diazotype material.

11. The method of claim 10 wherein the pressure is between about 90 and 120 pounds per square inch absolute.

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NORMAN G. TORCHIN, *Primary Examiner*.

C. BOWERS, *Assistant Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,411,906

November 19, 1968

John W. Boone et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 27, "penertation" should read -- penetration --. Column 4, line 9, "compartible" should read -- compatible --. Column 5, line 1, "liquid" should read -- liquid --; line 7, "avialable" should read -- available --; line 52, "sepcified" should read -- specified --; before line 67, insert -- EXAMPLE II --; line 68, "avialable" should read -- available --; line 73, "sample" should read -- samples --. Column 6, line 45, after "above" insert -- was developed in apparatus according to the present --. Column 8, line 19, "is" should read -- in --; line 42, "tempearture" should read -- temperature --.

Signed and sealed this 26th day of August 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents