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Pressurized High-Speed Development of Diazo Films

Abstract: The combination of a new high-speed process and developer unit which uses pressurized anhydrous ammonia gas offers a significant increase in the speed of developing diazo photomaterials. In addition to being up to 100 times faster than conventional ambient-pressure ammonia development processes, the new process and developer provide both flexibility and uniformity of sensitometric characteristics.

The unpleasant odor and corrosive character of ammonia gas required a means for positively sealing the film surface to the processing device and a means for disposing of residual ammonia gas remaining in the device at the end of the processing cycle. A developer platen, designed to meet these needs, also achieves uniform image development by utilizing the entering flow of ammonia gas to wash entrapped ambient air from the film surface and into a small reservoir. The process and its relatively simple hardware have been incorporated into an experimental photo-image converter to provide "on-line" input and output of photo-images from a random access image file. The process and a wash-type developer are used in the IBM 9950, 9954 and 9955 diazo aperture card copiers.

Introduction

Early in the development phase of an experimental photo-image converter, the need for a fast "on-line" method of developing diazo photomaterials became an important consideration. While some commercial reel-film ammonia developers provided reasonable throughput rates and enclosures for unpleasant corrosive and potentially toxic ammonia fumes, they did not offer practical application to the direct development of film chips and aperture cards. The aperture card developers did not have the required throughput rates, and their associated ammonia fume leakage suggested that "high-speed" adaptations, if feasible, would present problems for both human and machine environments. State-of-the-art diazo film development processes also required careful temperature and humidity control in order to obtain uniform results.

Investigations in our laboratory had shown that increased development speed could be obtained by using dry ammonia gas at pressures higher than atmospheric. To study the development process, an experimental developer was built. Tests demonstrated a significant increase in the speed of development at ammonia pressures of 30 to 90 psig.

Following the successful tests with the developer, engineering effort was directed toward optimum performance with minimum hardware, service and consumables cost. Optimum performance required reliable sealing of the developer platen to the film surface, minimum outgassing of ammonia into the machine and operator environment, and uniform image area development in the shortest possible processing time.

The experimental developer utilized an evacuation step to exhaust ambient air from the sealed platen prior to development, and a final evacuation step to purge the residual ammonia from the developer at the end of the development cycle. While the evacuation steps assured uniform development and minimum outgassing, a simpler hardware design was desired. An improvement in platen sealing was also sought since the metal-to-film seal in the experimental developer required high sealing forces to achieve a completely leak-free seal.

To meet these objectives a special film platen was designed and developed to accommodate the standard "Mil-D" 1.197″ × 1.615″ image field. It provided a reliable film-to-platen seal and a low-volume cavity that did not require evacuation to achieve uniform development and minimum outgassing at the end of the development cycle. Success of the low-volume nonevacuated platen design required the provision of a means to remove trapped and unmixed ambient air. This air was removed and "washed" into a small reservoir in the platen by the entering flow of ammonia gas; uniform development was thus achieved in minimum development time.

Before the description of the experimental work, a brief summary of diazo film materials and the basic ammonia development process will be given to provide a better understanding of the pressurized high-speed development of diazo films. This summary will be followed by a description of the state of the art for developing processes available at the time our studies were initiated.

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Diazo film materials and the ammonia development process

The image-forming process and the development process in a nonreversing diazo photomaterial are summarized as follows:

- The light-sensitive layer of a diazo film is made up of a diazo compound with a suitable coupler in a weak acid environment. The acid environment inhibits the chemical combination of the diazo compound and the dye-forming coupler. The dye eventually formed is much like the common azo dyes used for cloth.

- When the diazo compound is exposed to ultraviolet light, photodecomposition occurs, forming a colorless compound that will not react with the coupler. The mercury-vapor arc is effective as an exposure device because diazo compounds have their maximum sensitivities in a relatively narrow wavelength range (3700 to 4200 Å). The mercury arc has high-intensity output peaks at 3660, 4046 and 4358 Å. When a mask such as a microfilm image is placed between the mercury arc and a diazo film, a latent image is formed consisting of undecomposed and decomposed diazo compounds. The quantity of these compounds is a function of the relative exposure that the various film areas have had to the light source.

- After exposure to the light source, the diazo development process is used to enhance or convert the undecomposed yellow diazo image into a more usable and stable azo dye image. The color of the azo dye formed is primarily a function of the coupler or couplers used and secondarily of the diazo compound itself. Conventional development is accomplished by bringing ammonia gas (usually in the presence of moisture) into contact with the film surface. This ammonium hydroxide vapor neutralizes the weak-acid inhibitor. We do not know what the pH of the environment is, although it is probably greater than 7. In this environment, the coupler combines with the diazo compound to form the azo dye. The azo dye image is the resultant stable diazo photomaterial image.

State-of-the-art developing processes

Most of the commercially available diazo film developer units use either ammonia gas in the presence of water vapor or the vapor in equilibrium with a concentrated solution of ammonium hydroxide. The ammonia vapor is brought in contact with the sensitized surface of the diazo film in a development chamber or cavity within the equipment. Most of the equipment operates at ambient pressure using development temperatures of 130° to 140°F. "Complete" development is accomplished in 8 to 100 seconds, depending upon the operating temperature, humidity, ammonia concentration, and the coupling rate of the diazo photomaterial.

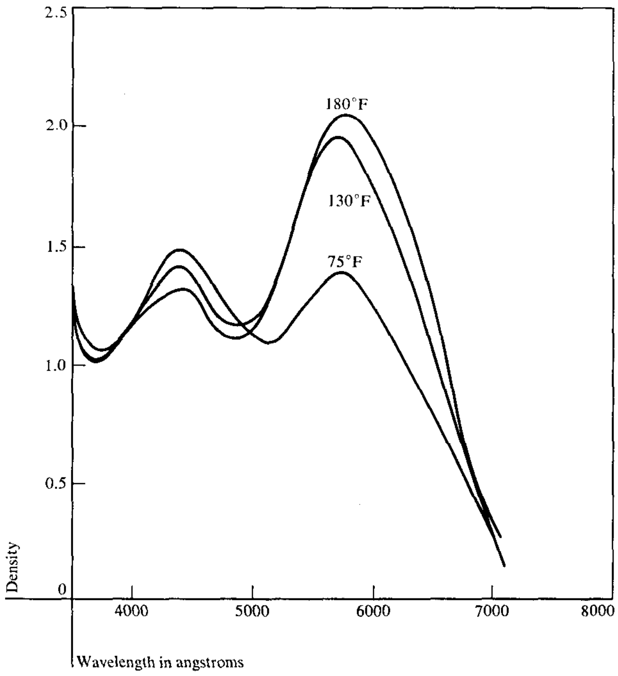


Figure 1 Density as a function of wavelength for a temperature-dependent diazo photomaterial developed at ambient pressure and three temperatures.

Uniformity of the dye in the developed diazo film depends on the uniformity of the various physical environmental conditions present in the development chamber during the process. Some of the modern diazo film materials are made by using multiple diazo compounds and/or multiple couplers to obtain special sensitometric properties in the resultant dye. The reaction rates involved in the coupling process of multiple diazos and/or couplers vary and can be highly temperature dependent.

Changes in development temperature or variation of temperature over the exposed film surface can significantly change the spectrophotometric characteristics of a number of commercial diazo photomaterials. Figure 1 shows an example of a well known commercial diazo film developed at three different temperatures. A yellow color is obtained at the low temperature, a greenish gray at the intermediate temperature, and a deep blue at 180°F. In this particular case the diazo film has a multiple coupler to obtain special spectrophotometric results. The coupling rates of the couplers vary with temperature and the contribution of each of the couples changes with the development temperature.[1]

If present conventional development techniques are used, the equipment designer is forced to provide very careful control of temperature and humidity. This control is necessary to assure a uniform film density and color and to minimize the tendency of some diazo films to "blush" or "bloom"* under specific development conditions. Experiments showed that some loss of resolution occurs when high development temperatures are accompanied with high moisture conditions. If the equipment is designed for room-temperature development, the development time is as long as 180 seconds for some films. All of these problems pointed to a definite need for a new and improved development process to make "on-line" diazo development feasible.

Early development work

Development time as a function of temperature was studied for several diazo materials. The decrease in development time with increased temperature was comparatively small. Moreover, serious spectrophotometric changes occurred in the resultant dye obtained in the film. Increase in development temperature was therefore not considered a practical approach.

In some of our early work, development time decreased when the diazo films were developed with dry ammonia gas at pressures slightly above normal atmospheric pressure. This fact led to the design of a small experimental developer platen and the design of several experiments to investigate the relationship of the time of development of a diazo film as a function of temperature and pressure.

The prototype developer

The initial experimental platen developer (Fig. 2) was a relatively simple device. It consisted of:

- A small cavity (a) which was evacuated by a vacuum pump and into which the "dry" ammonia gas (b) under pressure could be introduced,
- a metal seal surface around the cavity to which the film was sealed by pressure from a hard-rubber back-up platen (c), and
- a simple, manual clamping mechanism to urge the platen against the film.

A small bottle supplied the dry ammonia gas through a pressure regulator and gauge, with control provided by three two-way solenoid valves which were connected to the cavity. A timer controlled the duration between the opening of the ammonia valve and the opening of the vacuum solenoid valve. The ammonia valve was always closed prior to evacuation of the development chamber. The procedure for testing was as follows:

- The film to be developed was placed on the surface plate and clamped down with the hard rubber back-up platen (c).
- Solenoid valve (e) was closed.

* Blush and bloom refer to dust-like deposits appearing on the surface.

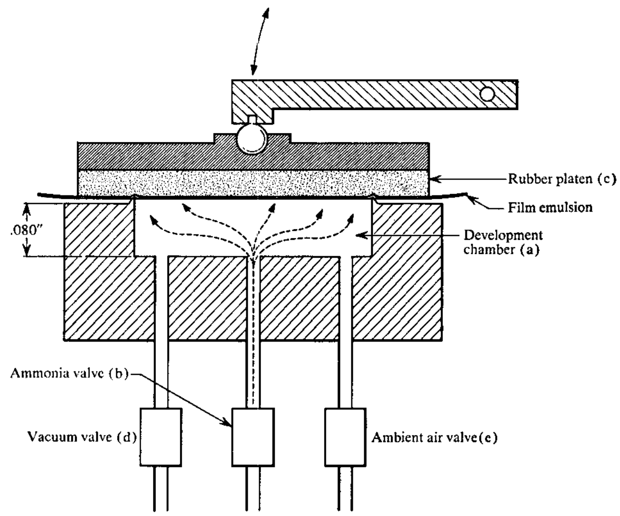


Figure 2 Diazo developer—initial experimental platen.

- The cavity (a) was evacuated and the solenoid valve (d) closed, sealing the cavity.
- The timer was actuated, opening a solenoid valve (b) and allowing the controlled-pressure dry ammonia gas to enter the cavity.
- After the timer had completed the development cycle, the ammonia solenoid (b) was closed, and the small amount of ammonia in the cavity was evacuated through the vacuum valve (d).
- Solenoid valve (e) was opened, introducing atmospheric pressure to cavity (a).

- *Experimental results*

The prototype platen was used to determine the time of development of a number of diazo films as a function of pressure. Development time for this work was defined as the time required to attain, in the diazo film under test, a density equal to $D_{\min} + 0.9(D_{\max} - D_{\min})$, where $D_{\max}$ = maximum density, and $D_{\min}$ = minimum density.

Figure 3 shows the relationship obtained for several of the films tested, where both the time of development and pressure (psia) are plotted in logarithmic scales. Analysis shows that time of development for these diazos was inversely proportional to the absolute pressure of the ammonia gas, to approximately the 2.4 power: $T = K/p^{2.4}$, where T = time of development, p = absolute pressure of ammonia, and K = constant. It was immediately obvious that this was the gain in development speed needed to make on-line diazo development a practical process. The curves of Fig. 3 are essentially parallel; slope variations on all the materials checked in the platen at this time showed no more than 0.2 to 0.3 variations. The data also showed a considerable variation in the development times of commercially available diazo films.

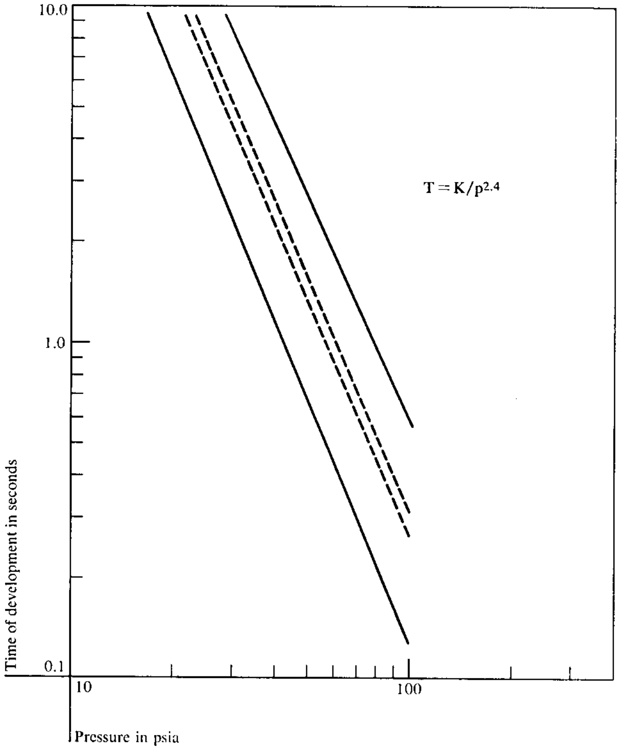


Figure 3 Time of development as a function of pressure of ammonia gas for several diazo films.

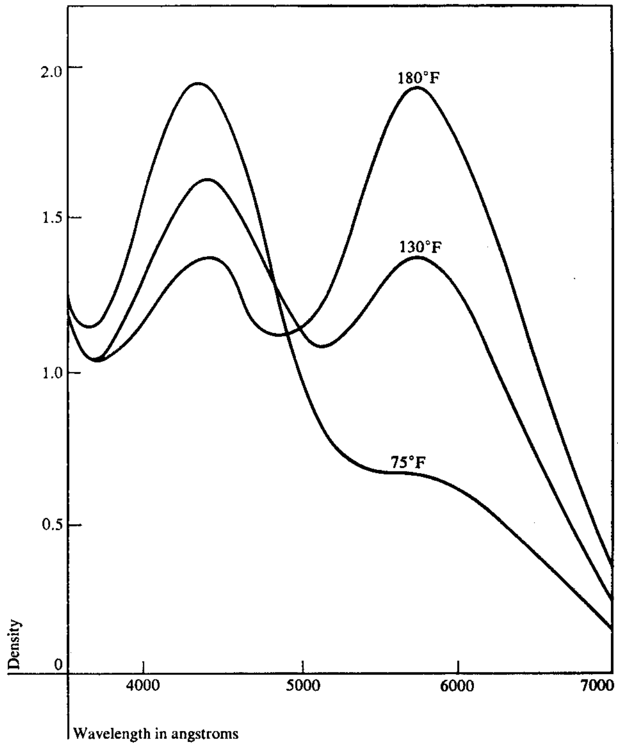
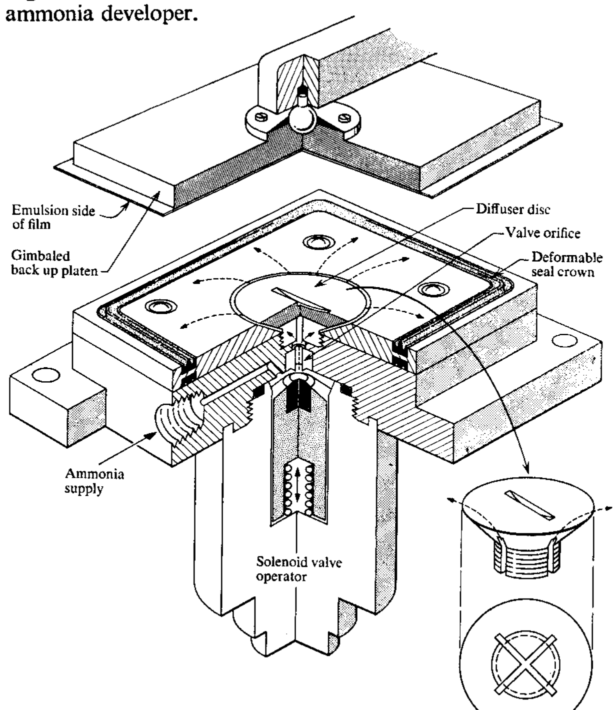


Figure 4 Density as a function of wavelength for a temperature-dependent diazo photomaterial developed at 84 psig and three temperatures.

As a first-order approximation, we might expect from Boyle's law to find an increase in speed with high-pressure development which would approximate the ratios of the pressures. Published tables show the vapor pressure of 28% aqua ammonia at room temperature (70°F) is about 13 psi absolute pressure. So, for a high-pressure development system using "dry" ammonia gas at 120 psi absolute pressure, the expected comparative speed of development would be approximately 120/13, or about 9 to 1. The high-pressure speed of development was as great as 100 times that which would reasonably be expected.

One possible explanation of the unexpected speed of development may be due to the effect reported by Weston and Bartlett.[2] They stated that the most active "coupling form" of a diazo compound occurs between the diazonium ion and the conjugate base of the coupler constituent. Optimum concentrations of diazonium ion and conjugate base of the coupler occur in the pH range of 4.5 to 9.5. In an aqueous surround, and above pH 9.5, the diazonium ion converts to the diazotate form. The diazotate reduces the coupling rate. The conditions of the high-pressure process allow the permeation of the film with alkaline ammonia in a nonaqueous surround, permitting the high rate of coupling to occur since the diazotate is not formed.

Figure 5 Initial machine prototype low volume nonevacuated ammonia developer.



• *Summary of process experiments*
The prototype developer demonstrated that speeds of development could be obtained on commercially available diazo films with moderate operating pressures in the time range of 0.07 to 0.70 sec, all practical on-line speeds.

The developer also demonstrated that very uniform spectrophotometric characteristics could be obtained using the high-pressure process. Density differences over the platen area varied no more than ± 0.02 density units for individual D_{max} readings on the several diazo materials tested from sample to sample. This density uniformity is better than that normally required by image systems and approximates the limitations of the film manufacturing process.

Further, the developer showed that the high-pressure development process could be used as a mechanism to obtain well-controlled wide variations in spectral density results in temperature-sensitive diazos when multiple couplers are used (Fig. 4). After this experimental work, serious consideration turned to the design of a working prototype developer mechanism for use in the system. The effects of pressure and temperature on spectrophotometric and sensitometric properties were further reported by Todd and Boone.[3]

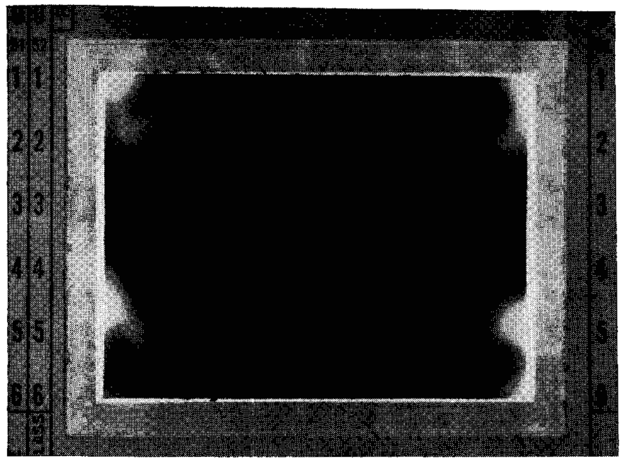


Figure 6 Nonuniform development caused by entrapped air—aperture card developed on initial machine prototype.

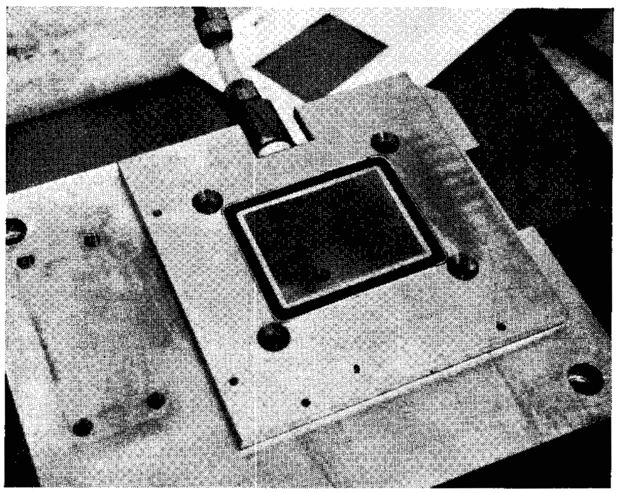
Impact of process on present state-of-the-art diazo photomaterials
The simple improvement in speed of development suggests new horizons in diazo photomaterials:

1. Couplers and diazo compounds which had previously been considered unuseable because of their slow coupling speeds may now be used in formulations. This should make possible more stable materials having longer shelf-life.

2. The use of new couplers may also open up the possibility of formulations that would prove to be more neutral spectrophotometrically.

3. Increased shelf life and more stable diazo films may improve the possibility of exposing and developing unused portions of a diazo film record.

Figure 7 Platen test robot.



Low-volume "wash" ammonia developer
The design of a machine prototype developer was started with the idea of simplifying the hardware and control requirements while providing reliable platen-to-film sealing, minimum ammonia consumption, minimum residual ammonia consumption, and minimum residual ammonia for disposal. This goal led to the decision of attempting to eliminate the evacuation steps. The initial prototype (Fig. 5) utilized a thin, low-consumption developer cavity with a diffuser designed to mix the pressurized ammonia gas and the ambient air trapped at the moment of film-to-platen sealing.

The seal in this platen was deformable elastomer crown of the Parker Gask-O-Seal ® type. The development cavity was provided by only partially compressing the 0.012″ high seal crown by the motion of the back-up platen. Reliable sealing of 90 psig gas pressure was provided by compressing the seal crown 0.003″ to 0.005″, leaving a developer cavity 0.009″ to 0.007″ high. Unfortunately, the relatively simple low-volume design suffered from air entrapment, as illustrated by the nonuniformity of development of the film shown in Fig. 6.

A search for a method of achieving uniform development in thin, nonevacuated cavities was initiated using the platen test robot, shown in Fig. 7. A number of different square diffuser plates designed to provide variations in cavity height and ammonia introduction geometry were

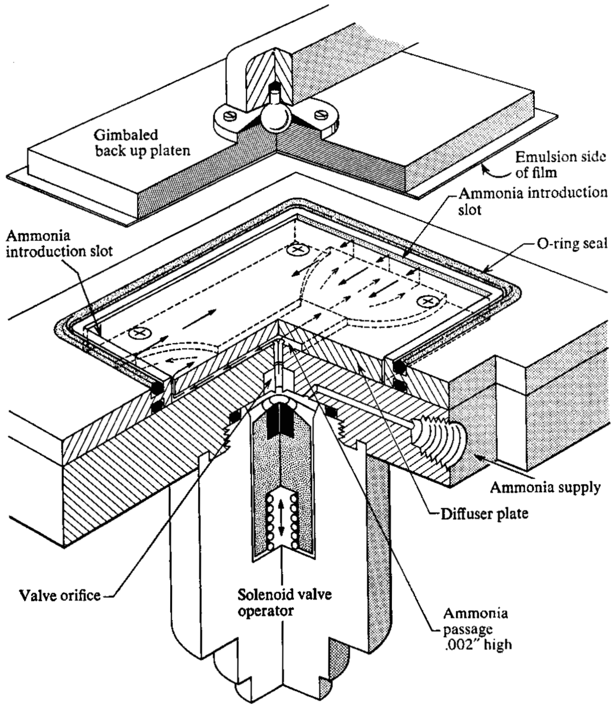


Figure 8 Diffuser plate to introduce ammonia at two opposed ends of image field.

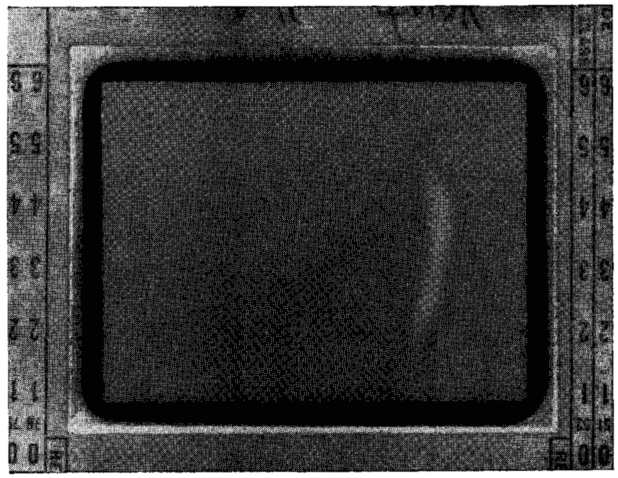
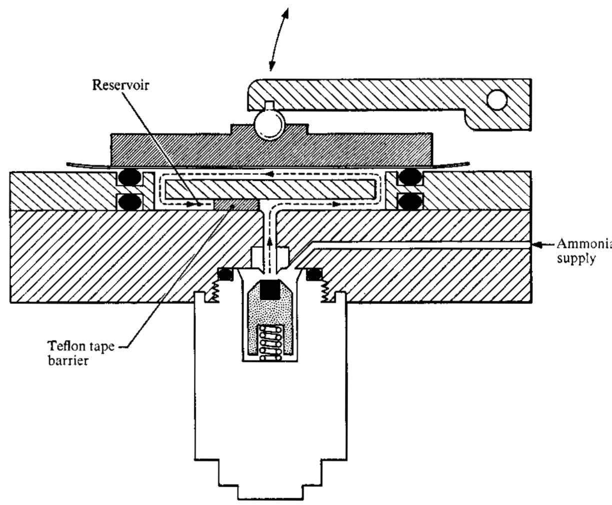


Figure 9 Undeveloped band across image caused by trapped ambient air positioned by two opposed flows of ammonia using diffuser of Figure 8.

Figure 10 Teflon tape barrier modification of Figure 8 diffuser to provide unidirectional ammonia flow and entrapped air reservoir.



built for insertion within the rectangular O-ring seal pattern of the robot. The initial approach was to devise a means for improving the mixing of trapped ambient air and the pressurized ammonia gas.

Tests with a diffuser (Fig. 8) designed to introduce the ammonia gas into the developer cavity through slots at opposite ends of the cavity resulted in the development pattern of Fig. 9. The narrow band of entrapped air resulting from the flow geometry suggested the concept of using the entering flow of ammonia to wash the entrapped air off the film surface into a small reservoir away from the image area.

This concept was first tried by using a simple modification of the diffuser in Fig. 8. A Teflon® tape barrier (Figs. 10 and 11) was placed under the diffuser to provide unidirectional ammonia flow across the developer cavity, with a thin reservoir cavity provided under the diffuser plate. The modification was successful; that is, an image was uniformly developed in a thin cavity without seal leakage or evacuation.

A single-piece platen was next developed. It incorporated a film-to-platen seal on its front surface and a reservoir seal on the rear surface. The developer cavity and reservoir cavities were provided by controlled compression of the front and rear surface seals.

The final seal configuration is a modified version of the original prototype Gask-O-Seal® design, with the seal crown positioned adjacent to the image area. Developer cavity height is controlled by the back-up platen motion, and reservoir height by a shim "picture frame."

A number of porting configurations were evaluated to provide uniform flow of ammonia across the entire sealed film area. The three-slot configuration shown in Fig. 12 proved satisfactory so long as the ammonia inlet valve orifice was symmetrically positioned. A vent valve for exhausting the developer to an absorber prior to opening the platen was added, as in Fig. 13; it introduced two new problems:

1. The asymmetric location of the ammonia valve orifice

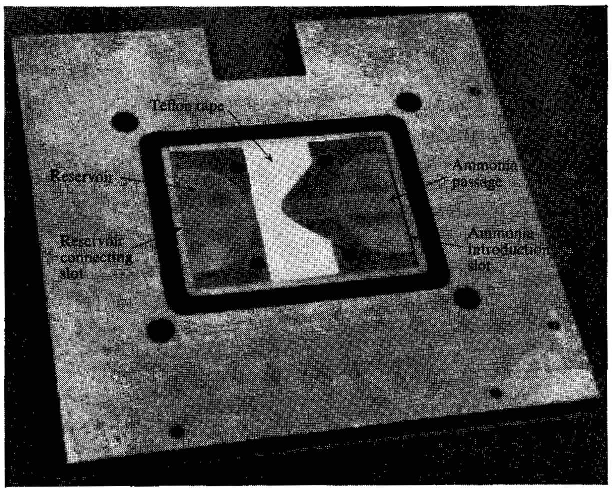


Figure 11 Rear view of modified diffuser plate with teflon tape barrier.

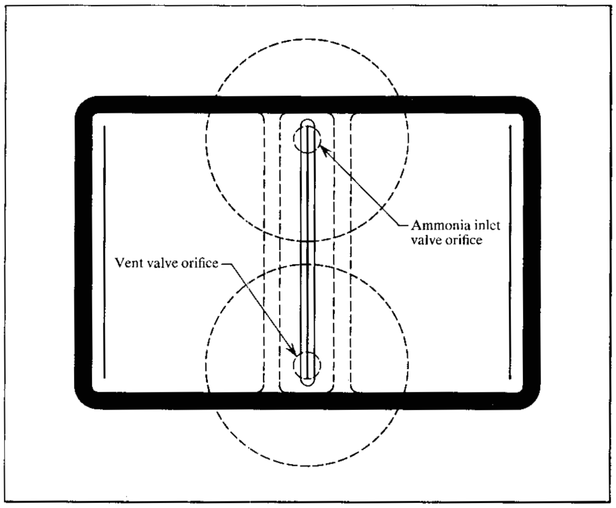
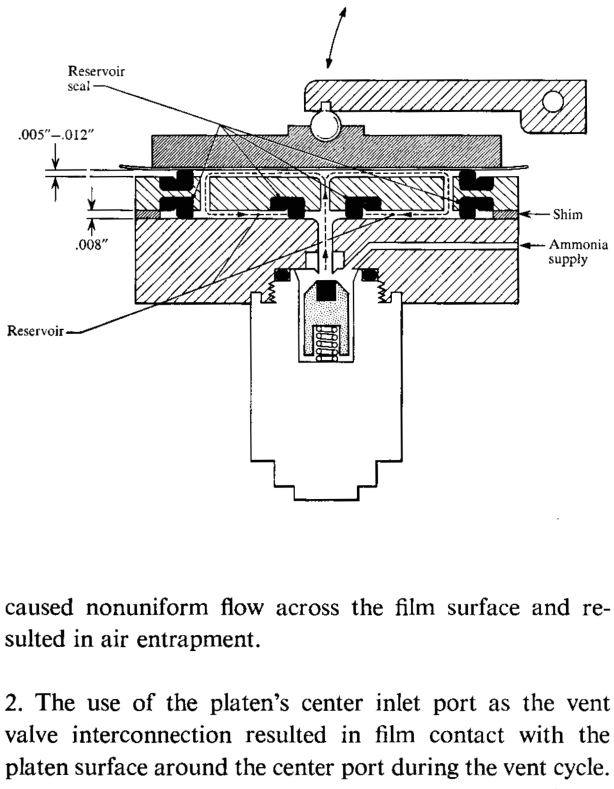


Figure 13 Three-slot wash-type developer with vent valve.

Figure 12 Three-slot wash-type developer platen.



caused nonuniform flow across the film surface and resulted in air entrapment.

2. The use of the platen's center inlet port as the vent valve interconnection resulted in film contact with the platen surface around the center port during the vent cycle. This film contact damaged the film and significantly increased the time required for venting the platen cavity to atmospheric pressure.

The inlet port was changed to a single central 0.060″ diameter opening. This porting arrangement re-established uniform flow across the film surface.

The tendency of the film to contact the platen surface was corrected by porting the vent valve to the reservoir cavity. In this configuration, the ammonia gas in the developer cavity was vented through the reservoir interconnecting ports adjacent to the seal area, the seal restraining the film from deflecting into contact with the platen surface.

The ammonia valve and vent valves were placed as close as possible to the development chamber to minimize ammonia consumption and to provide a rapid pressure rise at the platen inlet port. The valves are standard commercial solenoid operators and valve seats integrated into a special platen block. Individual two-way valves are utilized for inlet and vent to separate the platen inlet and vent ports and to avoid the "cross-over-loss" of ammonia to the vent port that would occur during valve transfer if a typical single three-way valve were used.

A subtle effect upon the wash flow capability of the platen was noted when the ammonia supply tubing was reduced from 0.026″ I.D. to 0.018″ I.D. The smaller tubing restricted the ammonia flow sufficiently to prevent a uniform wash action over the entire film surface, thus causing nonuniform development due to incomplete ambient air removal.

Figure 14 shows the final version of the developer platen. Reservoir interconnecting ports are three 0.030″ diameter holes at each end of the image field positioned in two chamfers in the platen surface. Chamfers serve to assure a "wash" flow of ammonia up to the seal area and permit the substitution of less costly drilled holes for the original slots. This design assures full development of the entire sealed film area and permits a single platen design to accommodate the standard IBM aperture card and the experimental film chip.

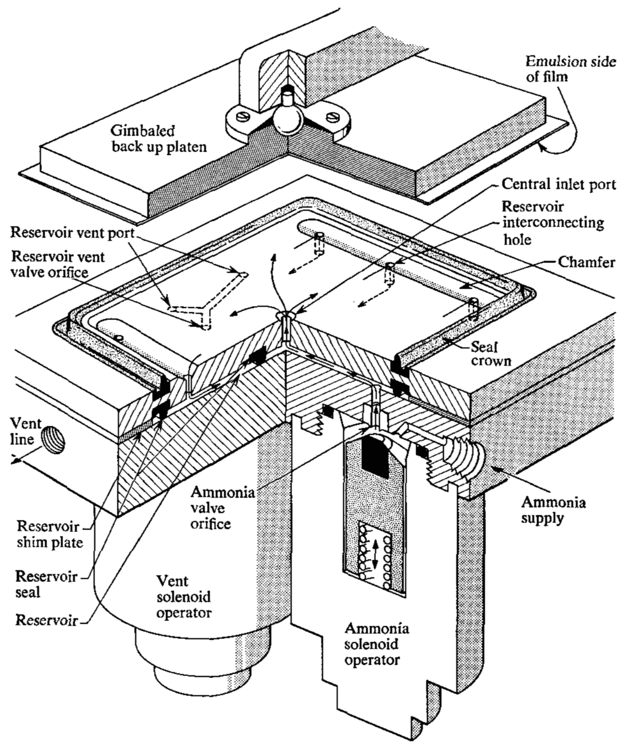


Figure 14 Final developer configuration.

Tests were made of a number of different reservoir volumes and cavity heights ranging from a cavity height of 0.002″ to 0.013″ and a reservoir height of 0.004″ to 0.015″. A cavity height of 0.005″ to 0.012″ with a reservoir height of 0.008″ was finally selected as an optimum combination. This combination assures uniform development in minimum time with a relatively low-volume cavity. Approximately 200,000 chips have been developed with a 2-lb bottle of ammonia gas.

The deformable elastomer platen seal has proven reliable over a wide range of compressed seal heights with over 1,000,000 cycles run on one seal. The addition of the vent valve to vent the residual ammonia pressure to an absorber prior to platen opening provides an odor-free system. The residual ammonia absorber used in the experimental image converter is a one-gallon throw-away bottle containing citric acid powder, bromothymole blue indicator and water. One bottle of absorber is required for 100,000 developer cycles.

Conclusion

The use of ammonia gas at pressures of approximately 90 psia has introduced development speeds up to 100 times faster than those previously possible with nonpressurized processes. Improved image uniformity and control of sensitometric results have also been shown to be characteristic of the process.

Accelerated development speeds permit the application of more stable, long-shelf-life (and typically slow developing) diazo films to image systems. The improved control of sensitometric characteristics inherent in the process will permit the design of new films with a wider range of selected sensitometric characteristics.

The evolution of a wash developer platen, designed for removal of trapped ambient air to assure uniform image development, has resulted in a simple developer device with reliable film-surface-to-platen sealing. Inherent in the design of the platen was the problem of finding an optimum flow pattern for introducing the ammonia into the developer cavity. This design provided uniform image development with minimum ammonia consumption.

Acknowledgments

H. S. Todd collaborated in the development of the high-pressure development process, and G. S. King was of valuable assistance in performing the many film material and development parameter evaluations required.

S. H. Mohr designed the initial machine prototype developer. N. K. Cooperrider and K. F. Strebel assisted in evaluating the performance of the wash developer platen, and C. P. Coolures designed the ammonia supply system and platen closure mechanism used in the experimental photo-image converter.

The Vestal Engineering Laboratory initiated a product development program for specific aperture card applications based upon the prototype work done in San Jose. This effort led to the IBM 9950 and 9954. The Endicott Development Laboratory developed the IBM 9955.

A wash type developer platen similar to the device described in this article was designed at Vestal by C. H. Hafer and C. A. Plante.

The citric acid type ammonia absorber was developed with the assistance of M. A. Kurlander.

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