APPENDIX
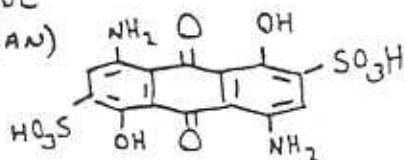
Dye Transfer Dyes
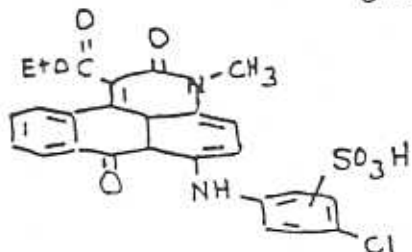
Current

AC 2500C
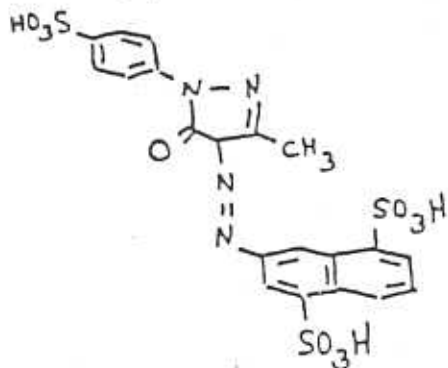(CYAN)

Erio fast cyanine

Copper phthalocyanine
tetrasulfonic acid
tetrasodium salt

MM 2500 (MAGENTA)

Brilliant Alizarin light
red I B

MY 2500 A (YELLOW)

Taylor yellow
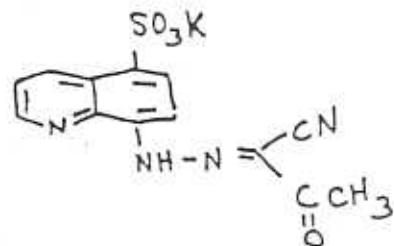
Metalized yellow

Z 465 - 114 S E

C. BARD, 12/84

DYES for

Imbibition Printing

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THE widespread use of imbibition color printing processes by the amateur wanting a few prints and by the professional producing a large volume of color prints indicates the wide adaptability of such processes. The growth of this type of color printing has not, however, been accompanied by any factual literature on dyes—one of the most important features of such systems. The dyes in use are generally sold commercially for the purpose and the printer simply follows instructions without realizing the nature of the problems or the type of coloring matter that he is using. This paper will discuss the problems of the choice and preparation of a satisfactory set of dyes for three color printing.

Imbibition printing processes fall into two distinct classes, those employing a relief image of gelatin, and those making use of differential dye absorption. In the latter case, the printing matrix is smooth, the dye image being due to the differential affinity of certain dyes for unhardened gelatin in a film containing both hardened and unhardened gelatin. This type of imbibition process has been largely superseded by relief printing in which the dye transferred is proportional to the gelatin thickness of the relief matrix. In this paper, we wish to discuss dyes that are applicable to the latter method of imbibition printing. On the choice of dyes rests not only the picture's existence, but also its color, stability, sharpness and gradation.
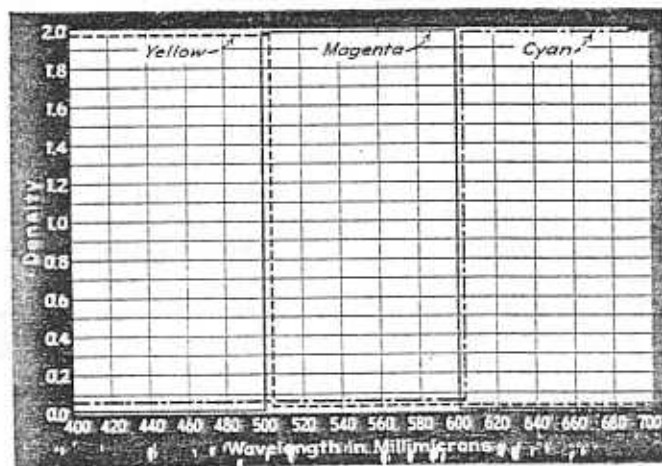

Fig.1 Reflection density curves for an ideal set of tricolor dyes for imbibition printing methods of color photography

Dyes added to water do not dissolve but become minutely dispersed throughout the solvent forming what is known as suspensoids. Solutions of this type are typical colloids. The solid dye particles suspended in water become charged electrically due to the potential difference at the interface between the solid, dyes, and the liquid. Since all of the dye particles in suspension have like charges, they are repelled from each other and are prevented from coalescing into particles which are large enough to precipitate.[1]

When the charges of the dye particles are removed as by the addition of a solution of acid, base, or salt which dissociates into ions of opposite charge, the dye precipitates out. Electrophoresis affords further evidence of the charge on the suspended dye particle. If an electric current is passed through solutions containing the basic dye, methylene blue, and another containing the acid dye, aniline blue, the basic dye
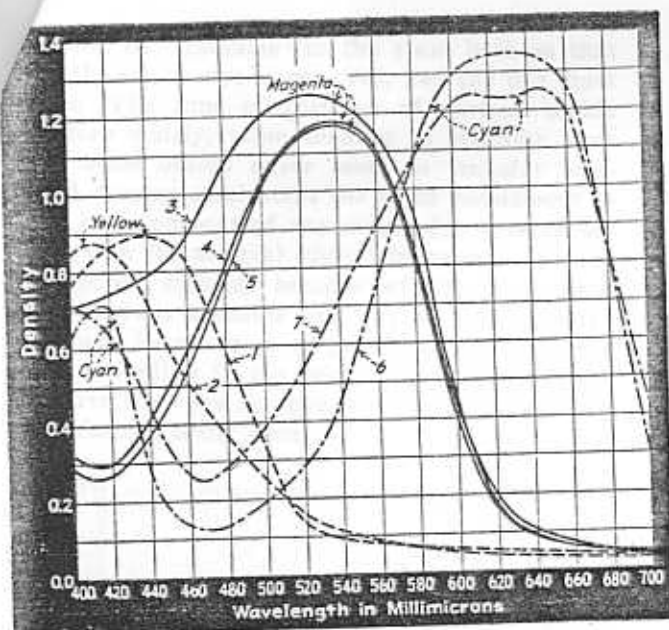
Fig. 2 Reflection density curves of seven typical dyes commonly employed in color photography. Curves 1 and 2 represent typical yellow dyes; curves 3, 4, and 5, give data on typical magenta dyes, while curves 6 and 7 are for commonly available cyan dyes
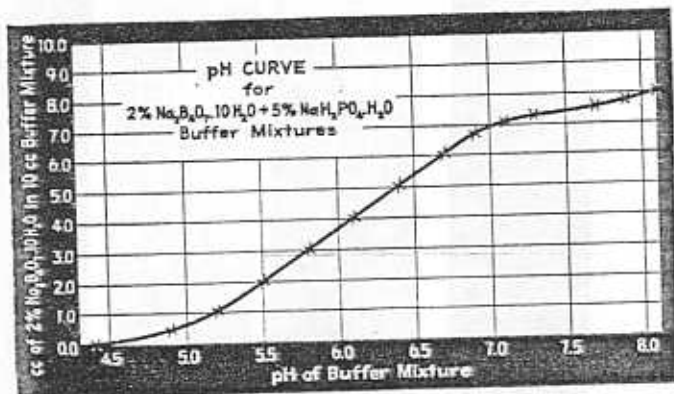

Fig. 3 pH curve showing the relation between concentration of borax in buffer solution and the pH of the buffer mixture

will migrate to the negative pole showing that it carries a positive charge while the acid dye migrates to the positive pole showing that it carries a negative charge.[3]

Factors Involved in Dye Choices

The dyes used for relief imbibition printing belong to the large class of synthetic dyestuffs called acid dyes. These dyes are salts of colored compounds containing acid groups. They will stain gelatin directly and most of the acid dyes are somewhat faster to light than basic dyes.[2] Among the acid dyes a choice must be made among hundreds of dyes that might satisfy the requirements. The chief factors to be considered are (1) hue, (2) fastness to light, (3) color balance, (4) transfer time, (5) equilibrium, and (6) miscellaneous factors. These are discussed below.

Hue. The dyes chosen must be as nearly complementary to the separation filter colors as possible. In Fig. 1 are plotted the ideal dye hue characteristics on a density-wavelength basis. Curves of several commonly used imbibition dyes are shown in Fig. 2, all of which are plotted for a reflection density of 0.85±0.10. The dyed sample is measured in a densitometer through the complementary filter, e.g. the magenta dye patch is measured with a green filter. The departures from the ideals are rather large but some of these dyes are the best obtainable colors. The magenta dye should only deposit green densities on the print, the cyan only red densities and the yellow only blue densities. Figure 2 clearly shows that all these magentas deposit appreciable blue densities, which they should not. The curves also show that the dyes differ widely among themselves; both curves 3 and 4 are commonly used imbibition dyes. It is evident from the curves that magenta dye No. 4 (Eastman Kodak washoff relief B dye) has the better color of these two. With the exception of No. 4 magenta, we have not found any dyes marketed for imbibition printing that approach the correct hue, all being decidedly too red. The cyans are more alike as a class but all deposit unwanted blue and green densities. The yellows in Fig. 2, while not perfect, are fairly satisfactory. There are many usable yellows although choices can be made; for example, yellow dye No. 1 is superior to No. 2 which has a lower average blue density and a higher green density, the cut-off between the blue and green being more abrupt for dye No. 1.

Light Fastness. Another requirement, probably more essential for paper prints than for transparency films which are only viewed occasionally, is that they do not fade appreciably with a reasonable exposure to light. The acid dyes differ markedly among themselves as to light fastness. In Fig. 2 are shown two cyans widely sold for color printing. Cyan No. 6 is of a somewhat superior hue, but is not so stable under sunlight exposure as No. 7, which fades and changes color quite rapidly. Of the usable acid dyes, those of the Anthraquinone class are the most stable under exposure to daylight. Fortunately, some dyes of this class which satisfy the requirements as to color or hue are available.

Color Balance. A set of three dyes that are well balanced as to hue must be chosen even though the exact hues which are desired are not obtainable. For example, a magenta that is on the red side and an orange-yellow should not be used together, as the general tone of the picture will be shifted noticeably. So far as possible the dyes chosen should also balance as to light fastness. A combination of a stable magenta and yellow with an unstable cyan will show a noticeable change upon exposure to light sooner than a print made with a set of three equally unstable colors. The dyes should be of similar solubility so that, with proper manipulation, equal densities can be obtained from a given gelatin relief. Such a situation will make possible a close approach to dye contrast balance so that, for example, equal increments of acid added to each dye bath will increase the dye absorption equally. This is not essential but makes manipulation simpler in practice.

Transfer Time. After being "stopped" in an acid rinse bath, the dyes must transfer to the gelatin surface which is to become the final print. The three

...ors must be "insoluble" in the rinse bath so that .one of the image dye is removed, i.e., the dye must not bleed. The time of transfer of various usable dyes differs widely, some tending to transfer very rapidly, while others never seem to transfer completely. A fundamental point for print consistency is that the same amount of any single dye (preferably all the dye in the matrix) should transfer each time from a given matrix, because of the long time interval between transfer and drying, the transfer times should be as short as possible to prevent the dyes from bleeding in the gelatin print. The shorter the transfer time the sharper will be the final print, all other factors being equal.
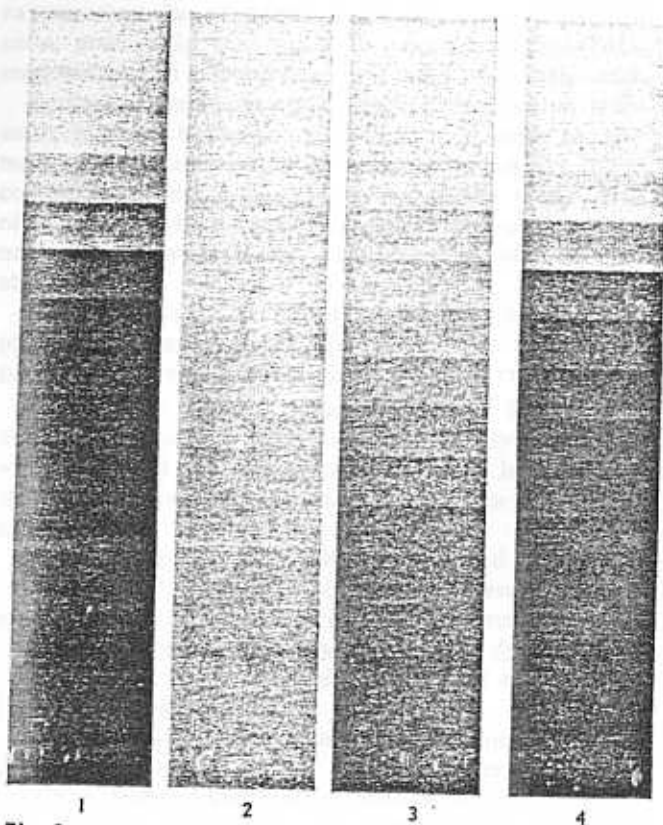

Fig. 4 Print wedges showing the effect of the action of imbibition dyes and buffer on the pH of solutions. Print made of cyan dyes transferred to mordanted base . . . No. 1—Buffered dye solution; 50 cc of 5% acid per liter . . . No. 2—Buffered dye solution; 20 cc of 5% acid per liter . . . No. 3—Buffered dye solution; no acid . . . No. 4—Dye without buffer; 1 cc or 5% acid per liter

Equilibrium. Another factor closely related to transfer time is the time taken for the undyed matrix to absorb all the dye it will absorb and thereby come to equilibrium with the dye bath. This time should be definite, and again, as short as possible. If the equilibrium time is excessive and prints are being made in succession, the possibility of incomplete dyeing may bring about degraded print shadows due to insufficient dye absorption in the thickest portions of the relief gelatin—the shadows of the picture.

Miscellaneous Factors. Besides the above requirements, it is desirable that the dyes do not stain permanently either the gelatin or the support of the relief. The dyes should not change hue appreciably upon drying. Most usable dyes do change slightly when dryed. The more the dyes change color

or stain the matrices, the more difficult it will be to judge the final appearance of the print, before it is completed. The national availability of the dyes chosen is of some consequence, as many dyes come from Europe. The more highly standardized the manufacture of the dye, the more consistent the product for color printing.

Preparation of Support

The dye images in the matrices can be transferred to any soft, damp, gelatin surface. Unless the gelatin is properly prepared, however, the picture will tend to be dull and diffuse. The preparation of the final image support consists of depositing in the gelatin layer a substance having an affinity for dyes of the type used. The hydrous oxides of heavy metals— iron, tin, chromium, copper and aluminum—are good basic mordants for acid dyes.[4,5] These mordants must be colorless and of such a nature that they can be deposited in the layer of gelatin. One of the most common mordants is aluminum hydroxide. This substance is put into the gelatin by bathing in a bath of aluminum sulfate and sodium carbonate. Other aluminum compounds act as mordants—even the small quantity of alum remaining after fixing out photographic papers is sufficient to act as a mordant. The dye is absorbed to the mordant and so the image is not allowed to spread. A further practical improvement is to keep the transfer surface at the proper pH value. If the gelatin is strongly alkaline, the dyes will tend to bleed, even though they transfer rapidly. If the paper is too acid, the dye transfer times becomes excessive.

Necessity for Buffering

In the customary relief imbibition processes, the absorption of the acid dyes to the matrix is controlled by the amount of acetic acid in the dye bath. However, if one prepares a dye solution containing from 0.5 to 1.0 gram of an acid dye, depending on saturation, in a liter of water and adds a few drops of glacial acetic acid, the dye will become strongly absorbed to the thick gelatin portions of an immersed step wedge matrix, or the dye may even precipitate out of solution. Not all of the acid dyes react in the same way to the same amount of acid. Azo Rubine, for example, requires considerably more acid to precipitate it than does Anthraquinone Blue, which is precipitated with just a few drops. The amount of acid which causes precipitation varies according to saturation of the dye solution. It also varies somewhat between samples of the same dye from different manufacturers. This shows that there is too great an increase in the acidity or hydrogen-ion concentration of the solution and indicates that the water-dye solution does not have the necessary reserve power to prevent a rapid change in its H^+/OH^- ratio.

In order that the absorption of dye may be controlled, over a wide range it is desirable to be able to add a considerable amount of acid to obtain proper density without destroying balance or causing precipitation of the dye. These difficulties may be overcome, provided a solution can be found whose ions do not

cause precipitation of the dye, but which has the proper acidity or pH, and the power to protect itself from changes in hydrogen-ion concentration. Solutions having the property to resist changes in hydrogen-ion concentration are called buffers.

Buffers are mixtures containing, usually, a weak acid and its salt, or a weak base and its salt. An example of the former is acetic acid and sodium acetate.*

Buffer Problems

Buffer solutions which are useful over greater pH ranges may be prepared from polybasic acids and salts, preferably acid salts, i.e., disodium phosphate, monopotassium phosphate, citric acid and boric acid.

Certain types of dyes marketed for imbibition processes may be buffered by adding such salts as ammonium acetate or potassium citrate to the dye baths containing acetic acid. However, of the many dyes of this class which have come under our observation, none fills very well the requirements of hue and stability.

Having found a balanced set of acid dyes of the previously stated requirements, the second major problem becomes that of finding the correct buffer.

Salting Out Effect. In attempting to find a suitable buffer for the dyes selected, $\frac{1}{2}$% dye solutions were prepared by dissolving the dye in hot distilled water, and adding equal quantities of the test buffer to it.

These solutions were allowed to stand 120 hours to observe if precipitation had occurred. All attempts to use a single salt in various percentage concentrations were unsuccessful for the dyes chosen. One or all of the dyes often precipitated out in from 15 min. to one hour.

Since the borate and the phosphate ions were the least objectionable of the single ions tried, and to obtain a buffer combination with a wide pH range, mono-sodium phosphate and borax were chosen as buffer components. For practical purposes, 5% $NaH_2PO_4.H_2O$ (pH of 4.4) were combined with 2% $NaH_2B_4O_7.10H_2O$ (pH of 9.3) solutions to give a series of buffer mixtures. Mixtures of these solutions with pH values ranging from 4.4 to 9.3 did not cause precipitation of the dyes in 21 days. Proportions of the two reagents which produced the various pH values are shown on the pH curve in Fig. 3.

Balance of Dye Contrasts. Having found a buffer combination that does not precipitate the dyes, the next step becomes that of finding a condition of balance of the three dye solutions at all contrast. The factors controlling the contrast of the individual dye baths are: (1) the concentration of the dye. (2) the pH of the buffer, and (3) the components of the buffer. In practice, it is unusual to find a condition where the three dyes balance with a buffer of the same pH.

After numerous dyeing tests with relief step wedges of equal densities, it was found that by using monosodium phosphate-Borax buffer solutions, with a pH of 6.4* for the magenta, a pH of 5.5 for the yellow and a pH of 7.0 for the cyan dyes, satis-

Dye and Buffer Ion Combinations. Since the monosodium phosphate-borax proved satisfactory, other buffer combinations were tried to determine whether the pH of the buffer was the only factor affecting the absorption of the dyes or if the ions of other buffer combinations might also have an effect.

Consequently, several buffer combinations with similar pH values were prepared among which were, monopotassium phosphate and disodium phosphate, boric acid and borax, citric acid and disodium phosphate, monopotassium phosphate and borax, monopotassium citrate and borax, and boric acid and disodium phosphate.

All combinations containing ions of monopotassium phosphate, citric acid, and monopotassium citrate caused precipitation of the dyes in short periods, even though used at the same pH as previously found successful. The use of buffers with slight deviations of pH from the above did not remedy the situation. The boric acid-borax combination was better, but not so satisfactory as the buffer already chosen.

Preparation of Dye

The choice of dyestuffs has been shown to depend on many factors. The experimenter must choose from the commercially available dyes those which fill as many criteria as possible. The dyes are manufactured chiefly for dyeing fabrics and the maker carefully tests various batches of dye to see that they give the exact shade under normal usage. Photographic color printing, however, is not normal usage and variations in dye batches are occasionally found. The variations are very slight and are not sufficient to cause concern. Three identical gelatin relief wedges are very handy in that they can be dyed in the appropriate dyes and examined against a standard for color, or among themselves for color balance.

The three dyes chosen for color printing are as nearly of the correct hue as possible. Their density-wave length curves are shown in Fig. 2. The cyan dye is Acid Anthraquinone Blue AB and its color-density curve is shown by curve 7. The magenta dye is Anthraquinone Rubin R Conc. and its color-density curve is shown by curve 5. The yellow dye is F.D. & C. Yellow No. 5 and its color density curve is shown as No. 1 in Fig. 2. There are a few others of the correct hue that are fast to light and many that are not light fast.

Other stable dyes of the correct hue that can be substituted for the three chosen dyes are:

Cyan: Alizarine Astrol B—General Dyestuff Corp.

Magenta: Alizarine Rubinol R—General Dyestuff Corp. Erio Anthracine Rubine B—Geigy Dyestuff Corp.

Yellow: Tartrazines—Almost all dye manufacturers. Of these extra dyes, the Alizarine Astrol B is of the same type as Acid Anthraquinone Blue AB.

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* The pH of the buffers were determined color-metrically by adding either four drops of 0.02% methyl red (pH range, 4.4—6.0) or bromthymol blue (pH range, 6.0—7.0) to 10 ml. (10 cc.) of the buffer mixture in a test tube. The colors produced were compared as to hue and intensity with the McIlvaine citric acid-disodium phosphate solutions, taken as standards.[10][11]

The magneta dye, Alizarine Rubinol R, is the same as the chosen color except that it is somewhat more concentrated. Erio Anthracine Rubine B is an excellent magenta and would be the first choice if not cut off at present due to the foreign situation. The transfer time with this last dye is approximately half that of the other magentas. All the large manufacturers supply tartrazine and any of these dyes may be used in place of the suggested yellow. The F.D. & C. No. 5 Tartrazine is suggested because of its purification and constancy, even though somewhat more expensive. This dye is a pure food color.

In use, these dyes are bought directly from the manufacturer and prepared by the user. Most dyes are produced by several firms under different trade names. The similar products can be identified by the use of dye catalogs[6][7][8] which number the dyes by types. Quantities of about one pound are about the smallest amount worth obtaining, as the dyes are quite reasonable when bought in this manner. The commercial names and manufacturers of the three dyes selected are:

Cyan—Dupont Acid Anthraquinone Blue AB— Dupont Organic Chemicals Division, 40 Worth Street, New York City.

Magenta—Dupont Anthraquinone Rubine R Conc. Dupont Organic Chemicals Division, 40 Worth Street, New York City.

Yellow—F. D. & C. Yellow No. 5 (Tartrazine) National Aniline and Chemical Corp., 40 Rector Street, New York City.

The dye solutions are made up for use by dissolving the dye in hot distilled water and then adding the prepared buffer solution. The quantities used in making up one liter of each dye solution are:

Cyan dye	1.3	grams
Monosodium phosphate ($NaH_2PO_4.H_2O$)	7.5	grams
Borax ($Na_2B_4O_7.10H_2O$)	7.0	grams
Magenta dye	3.0	grams
Monosodium phosphate	12.5	grams
Borax	5.0	grams
Yellow dye	2.0	grams
Monosodium phosphate	20.0	grams
Borax	2.2	grams

If desired, the above weights of dye can be dissolved in one-half liter of water and the proper buffer solution added in equal volume. The pH of the various buffer solutions are: 7.0 for the cyan, 6.4 for the magenta, and 5.5 for the yellow. The addition of about 10 cc of formaldehyde per liter of buffered dye solution is advisable to prevent the formation of mold in stored solutions. The dye solutions should be carefully filtered after cooling.

The dye baths as compounded above give a low density or contrast. If less contrast is wanted, the dye baths may be diluted with equal parts of water. When greater contrast is desired, equal quantities of 5% acetic acid are added to the dye solutions. The color contrasts will remain balanced with equal additions to each dye, but if the negatives differ in density range, the acid additions may be made unequal to counteract the lack of balance in the separation records. After the matrices are fully dyed (equilibrium has been attained), they are rinsed in 1% acetic acid to remove the surplus surface dye before being transferred to the prepared gelatin surface. The order of transfer is immaterial, but the shortest total transfer time is obtained by transferring the yellow last, either the magenta or cyan being put down first. The transfer times of magenta-cyan-yellow are roughly in the ratio 5-4-1 for these dyes.

If the dye baths have been raised to a high acid content and a lower contrast is desired, the acid may be readily neutralized by the addition of an alkaline solution, such as sodium or ammonium hydroxide. With the suggested dyes, the sodium hydroxide is preferable. For convenience, a solution is prepared so that 1 cc of sodium hydroxide solution will neutralize 1 cc of the 5% acetic acid—a strength of 33 grams (C.P. pellets) sodium hydroxide per liter of water. For example, if a dye bath containing 30 cc of 5% acetic acid is desired and the only available bath contains 55 cc of acid, the addition of 25 cc of the sodium hydroxide solution will give the desired contrast.[11]

Standard buffered dye baths will keep indefinitely if stored without acid. If too much acid is present, the dye will tend to precipitate. This is especially true with the magenta. The sodium hydroxide neutralizing solution can be used to prevent such dye losses. After use at a high acid content, the dye solution, before being stored, is raised to a higher pH by the addition of the sodium hydroxide solution. Dyes treated in this manner will not give any trouble.

References

[1] Bogue—"Colloidal Behavior," Volume I.
[2] Linder & Picton—*Wied. Annal.*, III, 35, 582.
[3] "Encyclopaedia Britannica," 14 ed., 7, 796.
[4] Bancroft & Ackerman—*Journal of Physical Chemistry*, 35, 2568.
[5] W. B. Weiser—"Inorganic Colloid Chemistry"—Vol. II.
[6] Schultz—"Farbstofftabellen."
[7] Rowe—"Color Index."
[8] Shreve—"Dyes Classified as Intermediates."
[9] Chapin—"Second Year College Chemistry."
[10] Kolthoff & Rosenblum—"Acid Base Indicators."
[11] MacIlvaine—*J. Biol. Chem.* 49, 183, (1921).
[12] Henderson—*Photo Technique*, January 1946.

PIONEER PHOTOGRAPHER

At the age of 97, William H. Jackson, a father of photography, is shown trying his hand in the darkroom of the Department of the Interior. He was official photographer for building of first transcontinental railroad.