U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP935

Part of Journal of Research of the National Bureau of Standards, Volume 17, November 1936

INKS FOR RECORDING INSTRUMENTS

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ABSTRACT

Inks for recording instruments are made by dissolving dyes in a mixture of glycerin and water. They dry chiefly by being absorbed by the paper, and for that reason lines drawn with them have a tendency to "feather", or have irregular edges. The paper and the nature of the dye determine whether or not there will be feathering. A series of 38 inks was made by dissolving each of 19 acid, or basic dyes in 2 mixtures (1:1 and 1:3) of glycerin and water. Another series of inks was made by dissolving each of 16 direct dyes in the 2 mixtures of glycerin and water; and a third series by dissolving the same 16 dyes in similarly diluted ethylene glycol. All the inks were tested by drawing lines on five kinds of paper, three of which were charts provided with recording instruments.

In the 190 tests of the 38 inks of the first series, on the 5 papers, only 10 lines were rated as nonfeathering, with 108 slightly, and 72 decidedly, feathering. The proportion of water made little difference in the results.

The inks of the second and third series, made with direct dyes, were in general greatly superior to those of the first series. The 16 direct dyes, each in 4 solvents, made 64 inks, with which 320 lines were drawn on the 5 papers. Of these lines, 227 were rated as nonfeathering, 48 as slightly feathering, and 45 as decidedly feathering. Further analysis of the results shows that glycerin is better than ethylene glycol at the same dilution, and that the inks with the larger proportion of water made sharper lines than those with less water.

There are numerous kinds of instruments for making continuous records of temperature, barometric and steam pressures, electric voltage, etc. The record consists of a line, or of a series of dots, on a circular card or on a long roll of paper. The instrument may have to run a long time without attention, so there must be an ample supply of ink of a kind that will not dry on the pen if it is indoors, nor freeze at outdoor temperatures in winter. For many years the United States Weather Bureau has used recording ink made by dissolving a dye in a mixture of equal volumes of glycerol and water. This mixture is a good "antifreeze", yet there are parts of the United States where it would be solid in winter. To overcome this difficulty, enough ethyl alcohol to keep the ink fluid at any winter temperature is added to the ink.

For use with instruments located indoors, a mixture of 1 volume of glycerol and 3 volumes of water has been found to make a satisfactory recording ink.

The properties of glycerol that make it so valuable in recording inks are disadvantages as soon as the ink is put upon paper. Because the ink must dry almost entirely by being absorbed, the marks are apt to be "feathered", or have uneven edges. The ink spreads in all directions from the actual marks made by the pen and does not simply sink into the paper.

Whether or not feathering occurs depends to a great extent upon the properties of the paper or card upon which the record is made,

but the results of tests to be described in this paper indicate that the nature of the dye is not to be overlooked. That this was the case had been suspected, and in order to get definite information on the subject, a number of experiments were made with inks prepared by dissolving selected dyes in glycerol and water of two dilutions. One set of inks was made with a mixture of equal volumes of glycerol and water, and another set with a mixture of 1 volume of glycerol and 3 of water. A series of 19 dyes, 17 of them acid and 7 basic, were chosen for the first series of experiments. Enough of each dye to give a satisfactory depth of color was dissolved. With the 36 inks made from these dyes, lines were drawn on 9 kinds of paper, including the thin cards provided by the manufacturers of some recording instruments. The lines were drawn with an ordinary gold writing pen, and after they had dried spontaneously, were inspected and rated. According to their appearance they were marked "*N*" (no feathering, "*SF*" (slight feathering), and "*F*" (decided feathering). Naturally there were no hard and fast boundaries between the three groups. Probably the majority of the "*SF*" lines would have passed muster as very satisfactory for nearly all uses.

Later, 2 series of tests were made with 16 other dyes, on 5 kinds of paper that were duplicate sheets of 5 of the kinds used in the first series of tests. A less confusing comparison can be made between the 2 sets of dyes if only the results obtained with these 5 kinds of paper are considered.

Table 1 summarizes the results on each of the 5 papers on which lines were drawn with 38 inks made with acid and basic dyes. Paper no. 3 was scratch-pad paper used at the National Bureau of Standards. This paper is usually satisfactory for writing with blue-black iron gallotannate ink, but at times red writing ink, made by dissolving a dye in water, shows a tendency to feather on it. Number 5 was a bond paper, used as a "heavy second" sheet for writing official letters at the Bureau. Numbers 7, 8, and 10 were circular charts, of different thicknesses, for use with 3 kinds of recording instruments.

TABLE 1.—*Tests with acid and basic dyes*

[Dissolved in the two mixtures of glycerol and water]

Paper number	3	5	7	8	10
Total *N*	6	0	0	0	4
Total *SF*	29	11	10	30	28
Total *F*	3	27	28	8	6

It is evident that 2 of the papers were distinctly inferior to the other 3, and that the 19 dyes did not make conspicuously good recording inks, unless the lines rated as "*SF*" would be acceptable. Only 10 of the total 190 lines were rated as "*N*".

An analysis of the results of the 190 tests made it clear that the nature of the dye had less to do with the feathering than the paper on which the lines were drawn. It seems unnecessary to give the detailed results, in view of what is to follow.

Direct dyes are those that are readily taken up by vegetable fibers and are firmly held, without the use of a mordant, to produce insoluble compounds with the dyes in and on the fibers. It seemed possible

[1] Acknowledgment is made of the courtesy of A. K. Gyzander, of the National Aniline & Chemical Co., New York, N. Y., for supplying without charge a 2-ounce sample of each of the dyes.

that inks made with direct dyes might show less feathering than those just discussed, because the fibers of the paper might adsorb the dyes at the marks made by the pen, or so close to the marks that their outlines would remain sharp. A few preliminary tests with direct dyes that happened to be at hand were sufficiently encouraging to make it desirable to carefully test a series of direct dyes obtained from a single manufacturer. Accordingly, 17 direct dyes were so obtained,[1] and were made into 34 inks by dissolving them in the 2 mixtures of glycerol and water, at the rate of 10 g of dye in a liter. This is the concentration of the recording inks used by the Weather Bureau.

One of the dyes, toluylene orange *R*, did not dissolve completely, and the turbid solution showed practically no sign of clearing by settling when left undisturbed for several days. Another dye, diamine green *B*, set to a sort of soft jelly on standing overnight. This became fluid when shaken, and there was no difficulty about drawing the lines with it. In all the tests with direct dyes, the lines were made with a ruling pen. There was one yellow dye, chloramine yellow, which is not included in the discussion of the inks made with direct dyes. Because of its pale color, and its brightness, there was little contrast between the lines and the white paper, so it was impossible to decide how the lines should be rated. Of the remaining 16 dyes, 2 were labeled differently by the manufactuer, though they had the same number in the Colour Index. They were considered as two distinct dyes, however. There were 32 inks in this set. Table 2 shows how much better results the direct dyes gave than were obtained with the acid and basic dyes.

TABLE 2.—*Tests with direct dyes*

[Dissolved in two mixtures of glycerol and water]

Paper number	3	5	7	8	10
Total *N*	26	21	27	25	32
Total *SF*	4	11	2	5	0
Total *F*	2	0	3	2	0

Of the 160 lines, 131 were rated as nonfeathering. If there had been the same proportion in the first series, 155 of the 190 lines would have been nonfeathering, instead of only 10.

Ethylene glycol is a liquid that is like glycerol in being hygroscopic and practically nonvolatile at ordinary temperatures, but differs from it in being somewhat more fluid. It was thought that it might make inks as good as those prepared with glycerol, so the 16 direct dyes were used for a series of 32 inks, half of which were made with a mixture of equal volumes of ethylene glycol and water, and the other half with 3 volumes of water to 1 of the glycol. They were tested on the same five papers as the other inks. The results of the 160 tests are in table 3.

TABLE 3.—*Tests with direct dyes*

[Dissolved in two mixtures of ethylene glycol and water]

Paper number	3	5	7	8	10
Total *N*	11	16	27	20	32
Total *SF*	8	4	2	7	0
Total *F*	13	12	3	5	0

A comparison of table 1 with tables 2 and 3 shows that the direct dyes are far superior to the acid and basic dyes that were tested. The direct dyes were selected for their range of colors, and not because of any definite knowledge that these particular ones would prove to be so superior. Indeed, the preliminary tests with direct dyes, referred to above, were made with nine dyes, only three of which were the same as those used in the more careful tests. It would strengthen the case for the direct dyes if the results of the preliminary tests were given, but this does not seem necessary.

Tables 2 and 3 show that mixtures of glycerol and water are better than mixtures of ethylene glycol and water as solvents for making recording inks. Table 4 presents the results in a different way, and shows that the inks with the larger proportion of water are much better than the others, so far as the direct dyes are concerned. There was no such clear-cut distinction in the case of the inks made with acid and basic dyes, so it is not worth while to give the detailed results of the tests made with them.

TABLE 4.—*Tests with direct dyes*

[Showing the effect of increasing the proportion of water]

Group	Glycerol-water		Glycol-water	
	1:1	1:3	1:1	1:3
Total *N*	52	79	27	69
Total *SF*	21	1	15	11
Total *F*	7	0	38	0

It should be said that the 2 sets of inks made with the 19 acid and basic dyes were prepared and tested 3 days apart, under somewhat different weather conditions on the 2 days. The 4 sets of inks containing the 16 direct dyes were prepared on different days, but the 160 lines were all drawn within about 3 hours, on a morning when there was no noticeable change in the weather. The temperature of the laboratory was 28° C (82° F), and the relative humidity about 65 percent.

TABLE 5.—*Direct dyes used in the tests*

Name of dye	Colour Index number	Name of dye	Colour Index number
Benzo fast scarlet	326	Benzo sky blue	520
Congo red	370	Diamine violet *N*	394
Toluylene orange *R*	446	Oxamine blue *4R* (Erie violet *2B*)	471
Toluylene orange *G*	478	Bismarck brown *R*	332
Pyrazol orange	653	Benzamine brown *3GO*	596
Chloramine yellow	814	Columbia black *FF* extra	539
Chloramine green *B*	589	Direct deep black *RW* (Erie black *RXOO*)	582
Diamine green *B*	593	Direct deep black *RW* (Erie black *RW*)	582
Diamine sky blue *FF*	518		

For the information of those who may be interested, the names of the direct dyes are given in table 5. The yellow dye is included because it might be needed to modify the hue of an ink of another color. The corresponding numbers of the dyes in the Colour Index are given for the better identification of the dye types. The names

of the dyes are not those on the manufacturer's labels, because it seemed better to use the preferred names in the Year Book of the American Association of Textile Chemists and Colorists, but in three cases the manufacturer's names are added because there might otherwise be confusion.

A drawback to the use of a few of these dyes is the comparative dullness of their hues, in spite of the fact that they were selected because they were known to be brighter than the average direct dyes. The lines drawn with congo red were dark brownish red, and the solutions could have been less concentrated, to advantage. Chloramine green *B* and diamine green *B* made dull lines. If a brighter direct green dye cannot be had, a mixture of chloramine yellow and a blue dye might be tried. The three black inks should have contained more dye. This suggested the thought that if the solutions are made stronger so as to get a greater depth of color, the dye may not all be absorbed by the paper, and this may cause feathering, though the solution containing 10 g in a liter was satisfactory. To test this idea, eight inks were made with two concentrations of four of the dyes in the mixture of equal volumes of glycerol and water. Congo red and diamine sky blue *FF* showed feathering at a concentration of 10 g in a liter, so each of them was dissolved at concentrations of 5 and 7.5 g in a liter. Of the black dyes, Erie black *RXOO* was dissolved at the rate of 12.5 and 15 g, and Erie black *RW* at 11 and 12 g in a liter. These eight inks and the four originally tested were tried on the scratch-pad and bond papers. Changing the concentrations of the dyes had no definite effect upon the feathering of the inks.

It is believed that the results here given are sufficient to show that for making recording inks with a minimum of feathering, only the direct dyes should be used; that a mixture of 1 volume of glycerol, or of glycol, and 3 volumes of water is a much better solvent than a mixture of equal volumes of the two liquids; and that ethylene glycol is not as good as glycerol at either dilution.

The inks were prepared on July 9. On October 2 they were inspected, and it was found that some of the corks of the tubes in which the inks had been kept were moldy. When shaking the tubes to dissolve the dyes, all the corks had been wet with the inks. Of the inks made with equal volumes of glycerol and water, six contained dyes that permitted the growth of mold. Three, and possibly four, species of mold were growing and fruiting on the corks. With the mixture of 1 volume of glycerol and 3 volumes of water, there were 13 moldy corks, and in addition mold was growing on the surface of 3 of the inks. No mold could be detected on the corks that had been in contact with the inks made with ethylene glycol at either dilution.

WASHINGTON, August 17, 1936.