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QUICK-DRYING STAMP-PAD INKS

By C. E. Waters

ABSTRACT

Inks for use with rubber stamps are generally made by dissolving dyes in a mixture of glycerol and water. They will not dry on the pad, because glycerol is practically nonvolatile at ordinary temperatures. When an impression is made on paper, the ink "dries" by being absorbed. If the paper is absorbent, the ink may penetrate rapidly enough, but on well-sized paper it may take many seconds, or even a few minutes, for the ink to be absorbed. If many papers must be stamped in quick succession, the danger is incurred of blurring the impressions. Alcohol is one of a number of volatile organic liquids that can be added to ink made with glycerol and water, to make it sink rapidly into paper. Alcohol has the drawback of being much more volatile than water, and if ink containing it is put on a stamp-pad, much of the alcohol may be expected to evaporate soon, and the ink will no longer be quick-drying.

It has been found that Butyl Carbitol, the monobutyl ether of diethylene glycol, is not only as efficient as alcohol for making glycerol-water ink sink rapidly into paper, but it is so slowly volatile that a pad can be exposed to the air for weeks, yet the ink will still be absorbed quickly.

Most of the inks intended for use with rubber stamps are solutions of dyes in a solvent that will not dry on the pad on which the stamp is inked. The solvent is generally a mixture of glycerol and water, because glycerol, in addition to being practically nonvolatile at ordinary temperatures, is hygroscopic and never becomes completely dehydrated under atmospheric conditions.

Ink made with glycerol and water changes in fluidity according to the relative humidity of the atmosphere. It is a common complaint that it becomes watery in summer, when the air is apt to be highly humid. It does not seem to occur to many users of rubber stamps that the simple expedient of closing the lid of the box which holds the pad would be some protection against the absorption of an excessive amount of water. In cold weather, in heated buildings, the relative humidity of the air is low, and then the ink loses a large part of its water.

It thus happens that impressions made with the ink on paper dry slowly at all seasons: in summer, because the stamp takes from the pad such a large quantity of the watery ink that it takes a long time to sink into paper, for there is little or no evaporation of water from it; in winter, because the relatively concentrated and viscous ink does not readily sink into paper. If many papers must be stamped in quick succession and the ink dries slowly, the impressions may be made unsightly, or even illegible, by smearing. This state of affairs has created a demand for quick-drying inks.

There are various formulas for stamping inks made with oils, instead of with glycerol and water. They dry rapidly by being absorbed by the paper, but they can be used safely only with metal stamps, on account of the harmful effect of oils upon rubber. There are also formulas which require the use of alcohol or of ethyl acetate in a mixture of glycerol and water. Alcohol and ethyl acetate are much more volatile than water, but their rapid evaporation plays only a minor part in the drying of impressions made on paper. If a drop of water is put on a piece of good writing paper, it sinks in slowly. If a drop of alcohol, of ethyl acetate, or of several other organic liquids that might be used in ink, is put on the paper, it is absorbed almost instantly, spreads, and shows as a wet spot on the opposite side of the paper. If successive small portions of one of these liquids, for instance alcohol, are added to a mixture of glycerol and water, which contains dissolved dye, a point will be reached at which absorption by paper is rapid. If impressions are made on paper, there will be a narrow range within which the only marked effect of adding more alcohol is to increase the rate of drying by absorption. Beyond this range, with more and more alcohol, the impressions lose their sharpness, and may become blurred to illegibility. The amount of alcohol that must be used to noticeably increase the rate of drying, or that can be added without causing blurred impressions, depends greatly upon the paper. It was observed repeatedly when testing the stamp-pad inks described in this paper, as well as the recording inks discussed in an earlier paper,[1] that there was somewhat more feathering on the bond paper used by this and other Government Bureaus for letters than there was on ordinary scratch-pad paper.

Ottley [2] patented a mixture of organic liquids to be added to commercial inks to make them dry quickly. Some of the liquids have boiling points below, and some above, that of water. Although the patent says that all the liquids are "rapidly and completely volatile," more stress is laid upon the fact that the mixture "is therefore seen to be a penetrant, i. e., an agent promoting penetration."

In a later patent, Miner and Sayler [3] tell how to make writing ink sink into paper rapidly, by adding caustic soda to it. To prevent feathering on paper, small amounts of starch, of wilkinite, which is a variety of bentonite, and of ethyl xanthate are added.

So far has has been discovered, no stamp-pad ink made quick-drying by the addition of a "penetrant" that has a rather high boiling point has heretofore been described.

When spread on a stamp-pad, ink containing alcohol, ethyl acetate, or other similar liquid may be expected to become less and less quick-drying because of the evaporation of the volatile solvent. In the attempt to find a liquid that has the desirable penetrative properties of alcohol and is less volatile, two ethers of diethylene gylcol were tested. These were the monoethyl ether, commonly known as "Carbitol", and the monobutyl ether, "Butyl Carbitol." Carbitol boils at about 202° C, and Butyl Carbitol at 231° C, both at 760-mm pressure. These temperatures are in strong contrast with 78° C, the approximate boiling point of 95-percent ethyl alcohol, but they are lower than the

[1] C. E. Waters. *Inks for recording instruments*, J. Research NBS **17**, 651–5 (1936) RP935.
[2] George B. Ottley. U. S. Patent 1,897,071, issued Feb. 14, 1933, for "quick-drying ink."
[3] Carl S. Miner and Galen H. Sayler. U. S. Patent 1,932,248, issued Oct. 24, 1933, for "permanent quick drying writing fluid."

boiling point of glycerol, 290° C. It was already known that neither of the ethers could be used without glycerol, because of excessive blurring, but it seemed desirable to find out how they would behave when mixed with glycerol and water, and exposed freely to the air. Accordingly, the following liquids were tested:

1. A mixture of equal volumes of glycerol and water.
2. The same as 1, with one-third its volume of Carbitol.
3. The same as 1, with one-third its volume of Butyl Carbitol.
4. Carbitol.
5. Butyl Carbitol.

Two-gram portions of these liquids were put in glass crystallizing dishes of about 48 mm inside diameter. In a dish of this size, if the bottom were perfectly flat and there were no meniscus, 2 g of water would make a layer 1.1 mm deep. The five liquids would make layers of depths slightly different from 1.1 mm. A 2-g sample of any of the liquids is enough to show definite changes in weight, and in a layer about 1 mm deep it responds more quickly to variations in atmospheric humidity than if it is in a deeper layer.

The first series of tests was started August 9, and was discontinued September 29, a period of 51 days. There was a steady loss in weight of all the liquids, except when the relative humidity was very high. The mixture of glycerol and water lost 772 of the 930 mg of water it contained at the start. Butyl Carbitol is hygroscopic, but it is also volatile, and the 2 g lost 224 mg. Because of its volatility, the mixture of glycerol and water to which it was added lost a total of 833 mg. The Carbitol lost 773 mg, and its mixture with glycerol and water, 914 mg.

A second series of tests was made in the same way as before, with the following liquids:

1. A mixture of equal volumes of glycerol and water.
2. The same as 1, with one-fourth its volume of Butyl Carbitol.
3. The same as 1, with one-fourth its volume of 95-percent ethyl alcohol.
4. Ink made by dissolving the dye fuchsine in the same mixture as 2.
5. A commercial ink made with glycerol, and containing ethyl acetate.

This series of tests was continued for 14 days, during most of which time the indoor air was very dry, so all the liquids lost most of the water they contained at the start. The mixture to which ethyl alcohol had been added and the commercial ink lost their volatile solvents, which would have occurred even with high relative humidity.

During the 2 weeks, the glycerol and water lost 882 mg, or about 95 percent of the water the mixture contained originally. The residue would almost have met the requirement of the United States Pharmacopoeia, that glycerol shall contain about 96 percent of the anhydrous substance. Liquids 2 and 4, of which Butyl Carbitol comprised one-fifth the volume, lost 812 and 809 mg, respectively. The alcohol mixture lost 1,055 mg. The viscosity of the commercial ink had already led to the suspicion that it contained more glycerol than 4, the laboratory ink, and its loss of 840 mg may be explained on this basis. The combined weights of water and ethyl acetate in the commercial ink might have been less than the combined weights of water and Butyl Carbitol in the laboratory ink, yet the commercial ink could

have shown the greater loss, on account of the low volatility of Butyl Carbitol.

In order to find out how the laboratory ink and the commercial ink behaved on pads, the same volume of each was applied to pieces of blotting paper, 44 by 50 mm. Impressions were made with a rubber dating stamp nearly every day for 19 days, on Government letter paper (25 percent rag bond) and on scratch-pad paper. With few exceptions, the impressions made with the laboratory ink were not smeared when rubbed immediately with the tips of the fingers. By the same test the commercial ink was sometimes not dry half a minute or more after the impressions were made.

The composition of the laboratory ink was decided upon after a series of tests had been made with inks prepared by adding increasing amounts of Butyl Carbitol to a solution of dye in a mixture of equal volumes of glycerol and water. Small pads of felt were inked, and impressions were made from them for a month. When 1 volume of Butyl Carbitol was added to 5 volumes of the dye solution, the impressions made with the ink dried rapidly, and when the proportion of dye solution was reduced to 3 volumes, there was no excessive feathering of the impressions. The laboratory ink, with 1 volume of Butyl Carbitol and 4 volumes of dye solution, is midway between these two. It has been given a practical trial in different offices in the Bureau, including the Mail and Files Room, where thousands of letters are stamped every month. The first pad was put in that room September 22, was reinked some time in November, and again early in January. During most of that time the lid of the box which holds the pad was not closed.

The ink is conveniently made by dissolving dye in the mixture of equal volumes of glycerol and water, filtering the solution if necessary, and adding to it one-fourth its volume of Butyl Carbitol. Before the final mixing, there is apt to be some evidence of precipitation of dye at the boundary between the glycerol-water and the Butyl Carbitol. For this reason it seems advisable in general to make the ink in the way outlined, instead of dissolving the dye in the mixture of the three liquids.

To make 1 liter of ink, there will be required 400 ml each of glycerol and water, and 200 ml of Butyl Carbitol. When the first two are mixed, the total volume is a little less than 800 ml, and there is no doubt a further contraction when the third liquid is added. The total contraction is probably overcompensated by the volume of the dye. The weight of dye to be used depends largely upon its color strength. Some dyes that have made inks of satisfactory depth of color when used in the amounts stated, per liter, are listed here. Their Colour Index numbers are given for better identification.

Dye name	Colour Index No.	Grams per liter
Fuchsine (magenta)	677	16
Light green *SF*	670	32
Methyl cotton blue	706	24
Crystal violet	681	16
Nigrosine	865	48

For those who might wish to make the ink in quantity, say by the gallon, it is pointed out that 8 g in 1 liter is equivalent to 1.0688 avdp oz/gal. All the weights of dye in the table are whole multiples of 8, so the amount of each dye required for 1 gal of ink can be found with little trouble. The concentrated forms of the dyes should be used. It is a common practice to mix colorless diluents with dyes before they are sold, so each new lot of dye bought should be tested to find out whether it has satisfactory color strength. If not, more of it must be used in a given volume of solvent.

A newly inked pad will sometimes dry out so much in the first day or two that it must be given more ink, but after this there is usually no trouble experienced with it. For use indoors in winter, when the relative humidity of the air is low, it might be advantageous to make the ink with a mixture of 2 volumes of glycerol and 1 of water. In this case the proportion of Butyl Carbitol should be increased to one-third the volume of the solution of dye, so that the finished ink will still contain 1 volume of Butyl Carbitol and 2 volumes of glycerol. Ink so made might be too hygroscopic for use in summer.

Because the ink dries almost entirely by being absorbed, the rubber stamp should not be inked too heavily, especially if the characters are large, with heavy lines, and if the stamping is done on thin paper. As already remarked, the ink dries somewhat slowly on some kinds of paper. It dries rapidly on most of the letters received by this Bureau, and this led to an unexpected result. When using the old, slow-drying ink, it was possible to stamp three or four letters with one inking of the rubber stamp. The new ink is taken up so rapidly by paper that the stamp must be inked more frequently. The chief fault so far seen is that heavily inked impressions are apt to show on the reverse of the sheet.

WASHINGTON, February 8, 1938.