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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

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Annual report September 30, 1985

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Executive summary

This report covers the period October 1, 1984 to September 30, 1985. During this period, a report discussing principles important in formulating intaglio inks and giving several recommendations was provided to BEP. Other reports on evaporation from intaglio inks, on a short thermogravimetric study of correctness of weighing out the ingredients in the inks, and on a thermomechanical study of gummed paper were also provided to BEP. Reviews of these reports are included here.

In the report which discussed the formulation of intaglio inks, alkyds were recommended as the most practical new resin system to polymerize in air. The alkyd should have a well-chosen molecular weight distribution and be dispersible in a water-containing solvent system. UV irradiation of the newly printed currency paper can probably be used to skin the ink rapidly and prevent blocking, especially if a photoinitiator system is added to the formulation. This may allow printing of both sides of the currency paper in one pass. Replacement of the various pigments and fillers currently in use by dyes attached to the backbone of an organic polymer, either in water-soluble form or in the form of a glass should be investigated.

We have developed several methods to characterize intaglio inks and have used these methods to examine whether change take place in inks during mixing and milling. Two intaglio inks were sampled during mixing and milling at BEP and characterized in terms of cure times, ash residues, ultraviolet absorbance spectra measurements, and gel permeation chromatographic measurements. The results show that even when mixing to homogeneity on the scale of fractions of milligrams has been accomplished, the state of dispersion of the solid components of the ink in the liquid components of the ink may be critical on a scale much finer than this.

Cure times, ultraviolet absorbance measurements, and gel permeation chromatography measurements have been used to follow ink cure. Refinement and application of the techniques developed in these studies are expected to lead to data which will help greatly in understanding the variables which influence the air-cure of intaglio inks. Application of these techniques and the development of new techniques as the needs arise will help in the design of improved inks.

A rapid method of analysis using thermogravimetry to determine solid residues left after an ink has been ashed has been developed. Analysis time is 15 minutes. The reproducibility of one determination is roughly 0.3%. The method showed that specimens from one ink sample had on the average 0.3% more liquid than specimens from the other (this average value was obtained from about 25 separate determinations and hence has an uncertainty of about 0.06%). UV spectroscopy showed that the second ink sample contained more tung oil. Cure time studies showed that it cured more quickly.

Several interesting results arise from the study of cure time variation with extent of mixing and milling. First, both the variations in properties within a batch and between the two batches were less than our earlier work on these inks had led us to expect. These two ink samples clearly do not show the width of variation that exists in intaglio inks. When we examine more inks in the future we may find other differences. Even so,our results are very informative. Four points are worth noting:

1) The inks were fairly homogeneous on a scale of about 0.1 milligrams yet showed significant differences in curing behavior.

2) The time of cure increased with increased grinding.

3) The addition of the small scale mix, which contains the driers, had little or no effect on the cure time for the second ink until the ink had been milled.

4) The intensity of the blue color in the liquid-extracted portion of the ink changed with extent of cure.

Dispersion of the solids in the ink seems to be critical. An explanation for the variation of cure time with extent of mixing is that the solids remain aggregated, or at least poorly dispersed, and therefore absorb more liquid inside the aggregate by capillary action than they would if the aggregates were well dispersed and the liquid were merely absorbed on the separated particles. The ink then acts as though it were more highly filled than it really is. With a highly filled ink such as BK62 mod 3, this may make the ink unstable. The phenomenon is well known in the manufacture of paints.

Carbon black acts as an antioxidant in most of its forms. Dispersion of carbon black may be an important factor in slowing the cure rate of the ink. Thought should be given to omitting the furnace black from the ink formulation and using a volatile antioxidant instead. This will give good storage properties and perhaps better control of cure since furnace black is known to aggregate easily and to be difficult to disperse. A volatile antioxidant would evaporate from the ink on the press and allow the setting reaction to proceed from that point on.

The technique of gel permeation chromatography was developed to provide distributions and averages of these distributions in terms of log hydrodynamic volume. This is a new way of classifying molecular size for systems which are mixtures of materials. The average log hydrodynamic volume of the soluble part of the vehicle is a useful index with which to follow the cure of the ink.

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1: Introduction

Our work during the report period has covered three main areas. First, the fundamental chemical and physical principles involved in the formulation of a water-dispersible intaglio ink usable on the printing presses at BEP were developed. Based on the review, 19 recommendations for further study were presented. Second, efforts were made in close cooperation with BEP to develop measurement techniques and to supply data to BEP to aid in diagnosing the sources of problems with inks currently in use. Third, two BEP intaglio inks were studied in considerable detail. These BK62 black intaglio inks were followed through the processes of mixing and milling. Cure studies on these inks were also carried out.

2: Review of intaglio ink formulation and cure

2.1: Formulation of intaglio printing inks

The report "Intaglio Ink Considerations" by B. Dickens has been accepted as NBSIR 85-3216. The areas covered are:

Film-forming resins
Intaglio printing ink vehicles
Initiation systems for intaglio printing inks
Filler considerations
Pigment considerations
Mechanism of cure for drying oils and alkyds
Resin considerations
Solvent/dispersing phase considerations
Drying agent considerations, and
Recommendations

This report provides information on ways in which improved intaglio printing inks can be developed. Particular emphasis has been placed on the part of the ink which sets, i.e., the so-called vehicle or resin, on the ways in which setting of an ink can be induced, on ways in which the formulation of the ink may be expected to influence the setting reaction, and on the constraints imposed by the BEP printing presses. The goals were to help in the selection of a new ink vehicle which will perform satisfactorily on the presses at BEP, and to provide insight into other aspects of ink formulation and cure to reduce the spoilage in production runs.

Alkyds were recommended as the most practical resin system to polymerize in air. The alkyd should have a well-chosen molecular weight distribution and be dispersible in a water-containing solvent system. The solubility of oxygen in the ink formulations and solvent mixtures should be determined and the compositions adjusted to provide a level of oxygen which gives optimum cure. UV irradiation of the ink immediately after it has been placed on the currency paper can probably be used to skin the ink rapidly and prevent blocking. This may allow printing of both sides of the currency paper in one pass. Replacement of the various pigments and fillers currently in use by dyes attached to the backbone of an organic polymer, either in water-soluble form or in the form of a glass should be investigated. Thixotropy of the dispersed ink should be adjusted by using sodium carboxy methyl cellulose instead of the silica currently in use. Reasons for the selection of alkyds and a brief discussion of the possibilities for initiation of cure in the ink are given below.

2.2: Film-forming resins

The earliest polymeric system used in films and coatings was based on naturally available and slightly processed oils from various seeds, fruits, and nuts. Some of these oils "dry", that is, polymerize and become non-tacky, and some do not. Drying oils are usually heat-treated prior to application to increase their degree of polymerization. This increases the viscosity and decreases the drying time. The rate at which they dry depends on the number of active groups per molecule and on the rate of attack on these groups. The physical and chemical changes accompanying the drying of drying oils have been studied extensively. The reaction responsible for the drying process is a free radical reaction. In the normal mode of use, the free radicals are produced by the attack of the drying agents (certain metal salts) on hydroperoxide groups, which are only formed in the presence of oxygen. Drying oils are one of the few systems which polymerize satisfactorily in the presence of air.

An alkyd is basically a long chain molecule with several kinds of pendant groups. Some of these groups are derived from drying oil molecules. In this sense, alkyds are modified drying oils and dry by the same mechanism. The length of the alkyd molecule is a matter of choice. Long chains require fewer bonds to polymerize than short chains do. Also, chemical groups are incorporated into the alkyd molecule to confer such useful properties as dispersibility in water and resistance to weathering. Alkyds are extensively used in paints, for which there is an enormous market. Alkyd paint films do not survive severe weathering conditions, although they are appreciably more resistant than films based on simple drying oils. Acrylic and other vinyl components have been incorporated into alkyds to give better environmental resistance and to give a faster dry by producing a material with a glass transition temperature near room temperature so that the material quickly becomes a glass rather than a sticky rubber. The various monomers may be chemically combined together to give an extended molecule or the alkyd can be physically mixed with an acrylic or similar polymer which is deposited unchanged on evaporation of the solvent.

2.3: Effect of oxygen

Oxygen is needed in the drying of drying oils to produce hydroperoxide groups. In the drying oil polymerization mechanism, the hydroperoxide groups formed during the oxidation are decomposed by the driers to give more free radicals which continue the drying. This means that the drying reaction is autocatalytic and that the rate of drying increases with time, at least in the early stages. The usual situation in free radical polymerization is that the free radicals are initially generated from an added initiator, so that both the concentration of initiator and the rate of polymerization decrease with time. In general, oxygen inhibits free radical polymerizations because oxygen, when available, adds very quickly to the hydrocarbon free radicals on the polymerizing molecules (20,000 times more rapidly than the monomer does for methyl methacrylate) to give peroxyl radicals which are not as reactive as the original hydrocarbon radicals. Polymerization of drying oils using the relatively unreactive peroxyl radicals is possible only because drying oils contain very easily abstracted hydrogen atoms in the -CH2- groups next to the double bonds.

Where very easily abstracted hydrogen atoms are not available, which is the case for most materials, the peroxyl radicals attack the monomer molecules only very slowly. Peroxyl radicals on polymethyl methacrylate add to methyl methacrylate monomer at 1/60 the rate of the parent hydrocarbon radicals. In most polymerizations, transformation of the original reactive hydrocarbon radicals into peroxyl radicals causes the polymerization reaction to slow down or stop. Most classes of free radical polymerization are significantly inhibited by oxygen, so oxygen must therefore be excluded as much as possible from the polymerization reaction. For these materials to be good candidates for use in intaglio inks, the rates of initiation would have to be high enough to consume all the oxygen already dissolved in the film and to carry the polymerization reaction to completion before much more oxygen could diffuse into the film and interfere. Initiation mechanisms will now be discussed briefly.

2.4: Initiation systems for intaglio inks

Electromagnetic radiation in the form of microwaves (billions of hertz) or radiofrequencies (millions of hertz) acts on polar and dipolar molecules to tumble them rapidly. This is a method of selectively heating a component in the reaction mixture. Microwaves have been used to selectively decompose peroxyesters in prepolymer mixtures to effect polymerization and to polymerize acrylates by irradiating the monomers. One of the problems in the use of microwave and radiofrequencies in intaglio printing on paper is not to heat the water in the paper to unacceptable limits. Exploratory work will be necessary to find whether a suitable frequency domain exists to accomplish this. It is also uncertain whether thin films can be heated sufficiently by these frequencies to generate free radicals at the appropriate rate.

In the case of films which are somewhat transparent in the ultra-violet (UV) part of the electromagnetic spectrum, UV radiation can be used to break apart the more sensitive chemical groups and form free radicals, especially in thin films. Printing inks are necessarily colored and are highly filled with mineral phases. Since they absorb and scatter visible and UV radiation very strongly, neither UV initiation nor visible light initiation is an attractive option for the main method for initiating polymerization in these inks.

Cure of the top 10 microns on the surface of ink already in place on the currency paper using UV radiation could reduce or prevent sticking together of adjacent sheets of currency paper ("blocking" in the printing sense), which is a significant problem. Cure of the surface using UV or visible light could be effected by including a suitable photo-initiator system in the ink formulation. This is probably the most promising route to reducing spoilage from blocking.

The most promising approach for the general in-depth polymerization of intaglio inks at the present time is to take advantage of the fact that free radicals can be produced over a long period of time in an auto-catalytic fashion without the use of high energy radiation by using drying oil technology. The first necessity in designing the ink system is to overcome the limitations of conventional chemical systems in performing adequately in both storage and on the press. Using as the initiating species a group which is produced in the polymerization reaction means that the system will be auto-catalytic. It is this property which has made drying oils a viable system for film formation and in particular for intaglio inks. In the drying of drying oils, the hydroperoxides produced by the action of oxygen on hydrocarbon free radicals are decomposed by the driers into one free radical and one ion per hydroperoxide group. The hydroperoxide groups are formed in a repetitive "propagation" step of the oxidation reaction. Hence, one free radical produces several hydroperoxide groups. Because these hydroperoxide groups later produce free radicals under the influence of the driers, the rate of polymerization accelerates with time. The newly applied ink can probably then be skinned using a medium pressure mercury lamp, which requires much less shielding than electron beams, or by visible light, although in this case the ink would be slightly light-sensitive.

2.5: Stabilization of the inks

The second necessity in designing the ink system is to control the early effect of this free radical oxidation reaction, and hence stabilize the ink during pre-use storage. This may be done by including in the formulation a small quantity of antioxidant, which combines with free radicals containing oxygen, and which will soon be used up at the temperature of the printing press but which will last for days at room temperature. If an antioxidant which is volatile at the printing temperature is used, then its concentration will be depleted by evaporation as well as reaction. Methyl ethyl ketone oxime and butanal oxime are feasible candidates. Considerations presented later in this report suggest that the carbon black in current BEP ink formulations may be acting as an antioxidant which is not only nonvolatile but also is difficult to disperse.

2.6: Effect of the initial molecular size distribution

Drying oils are not water-soluble because they do not contain groups which are sufficiently polar. Also, drying oils are known to continue oxidizing after they have become non-tacky, and this further oxidation eventually causes deterioration in the film. Therefore, the number of oxidizable groups should be just sufficient to give an acceptable rate of drying and acceptable mechanical properties of the cured film. Alkyds can be made with polar groups, air-drying cure behavior, and form more durable films than drying oils do. Therefore an alkyd is the material of choice as an intaglio ink vehicle. Because alkyds are used in the paint industry, there seems no danger of shortages in supply.

Fewer bonds are needed to "cure" molecules which are already large. A film made from large molecules will dry more rapidly than a film made from small molecules. If the larger molecules contain more reactive groups than the smaller molecules, then drying is even faster. Well-controlled changes can be made in the functionality (number of potential polymerizable links per molecule) drying oil type of alkyd, and the fatty acid components can be adjusted to influence the rate of drying and the likelihood of further oxidative degradation. Thus, molecules which are larger than either drying oils or modified drying oils can be prepared with consistent properties. Hence, an alkyd which will dry more quickly than a drying oil can easily be made.

Polymers made by free radical processes or simple addition processes contain molecules with a range of molecular weights. The population of polymer molecules is known as the molecular weight distribution of the polymer. The molecular weight distribution has a very significant effect on the rate of formation and final properties of a film. Thus, a mixture of alkyds of the same chemical composition but with well-chosen molecular weight distributions should be used. The influence of molecular weight distribution on the resin used should be studied.

2.7: Recommendations

1. The ink vehicle should be an alkyd because only molecules with allylic hydrogens will polymerize successfully in air. A water-dispersible alkyd should be strongly considered. Water-dispersible alkyds are available from at least 10 US companies.

2. A second candidate would be a water-dispersible alkyd resin containing methacrylate groups, as described by Larson and Emmons. The polymerization of the methacrylate part will be poisoned by air, so a formulation based on this kind of resin could remain tacky. This depends on how much oxygen is available in the interior of the resin during setting. The oxygen content of the resin depends on the solubility of oxygen in the resin/water/organic solvent mixture and on the rate of the setting reaction, because the drying oil part of the molecule consumes oxygen as it sets. On the other hand, the drying oil part will not set without some oxygen being available, because oxygen is needed to produce more hydroperoxide groups which will then be decomposed by the drying agents to give the free radicals which drive the setting process. It is probably safer, more reasonable, and requires less fine-tuning (and hence is less prone to variation) to rely exclusively on the drying oil mechanism and to select a drying oil type of alkyd.

3. From the points of view of reducing environment pollution, costs, and maintenance problems, the resins should be dispersible in water using the amine or ammonium salt as necessary. There are conflicting reports as to whether these amines retard setting. Ammonia is more volatile, and would retard the setting reaction less than the less volatile amines. However, films based on ammonium salts are known to discolor more rapidly than films based on higher amines. Fortunately, BEP's currency inks are dark in color, so this is probably not important in BEP's application. If water is to be used as a cosolvent for the ink, efforts should be made to decrease the press temperature during printing. This will decrease the rate of evaporation of water, which will make the behavior of the ink on the roller more stable. The humidity in the printing room should also be controlled.

4. Microwave and radiofrequency radiation could play an important part in evaporating the water from an ink dispersed in water. This would simultaneously heat the ink, dry it and therefore make it more able to dissolve oxygen, and help it set. Dielectric measurements on the ink formulations and currency paper should be made to provide estimates of the efficacy of the process. Test cures should be carried out.

5. The effect of water as solvent on the cure rate must be established. From the point of view of retarding the evaporation of water, decreasing the temperature will keep more water in the ink. This will also decrease the amount of oxygen able to dissolve in the ink because oxygen is less soluble in water than in most organic materials. From the point of view of oxygen solubility, decreasing the temperature will also decrease the amount of dissolved oxygen, since oxygen solubility in organic materials generally increases with increasing temperature.

6. Investigations should be carried out to determine whether the solution thixotropy can be adjusted using sodium carboxy methyl cellulose instead of silica. The intended function of silica is to act as a thickening agent. Our very recent work suggests that a second function of silica may be to act as a desiccant which dehydrates the ink by combining with any water present. The final effect of this is not yet known, although some considerations were given in paragraph 5. A recent paper (K. O'Hara and W. P. Gordon, "Thixotropy in industrial coatings", XIth International Conference in Organic Coatings Science and Technology, Athens, Greece, July 8-12, 1985) discusses the use of resins which themselves are thixotropic.

7. If water is to be considered as a possible solvent or component of the solvent system, the ink vehicle will have to contain acid or other polar groups to make it soluble. Since the calcium carbonate would react with these groups to form a scum, a replacement should be sought. An organic extender such as polystyrene, sulfonated polystyrene, acrylate, or polyester should be considered, provided it can be safely and successfully mixed into the resin and the effect of the difference in refractive index of the polymeric material from that of calcium carbonate can be tolerated. A recent paper (S. Konishi, T. Nakaya, and T. Ueda, "Rheological properties and application performances of the new water-borne paint", XIth International Conference in Organic Coatings Science and Technology, Athens, Greece, July 8-12, 1985) documents the superior performance of a paint containing small spherical polyester particles as a filler.

8. A water-soluble acrylic or equivalent resin should be added to the ink. This will impart a reasonably high glass transition temperature to the film in the early stages of drying to produce a tougher and more tack-free film.

9. The replacement of pigments by stable (and soluble) dyes should be investigated. This will reduce the necessity to mill the ink, and will make the cure more reproducible because the ingredients will be more easily dispersed.

10. The use of organic glasses containing the appropriate dyes grafted onto the polymer backbone should be explored. An extension of this scheme would be to consider currency note validation or even recognition schemes using automated equipment by including a fluorescent species on the polymer backbone. Unfortunately, practically all salts fluoresce strongly by emission from defects in the crystals and crystallites, and this would complicate the situation. A powerful fluorescer such as anthracene might be able to overpower most other fluorescers, but the apparent denomination of a bill (as read by a fluorimeter) could conceivably be changed by soaking it in an appropriate solution.

11. Ink layers thicker than 2 mils (50 microns) cure slowly in the interior. UV initiation of cure would probably not be useful in assisting curing beyond depths of about 10 microns in black inks. The engravings should be designed so that they are as shallow as feasible, with 50 microns as the maximum depth.

12. A volatile oxime anti-oxidant such as methyl ethyl ketone oxime or butanal oxime should be added to the ink. This will retard the setting reaction until the ink is heated on the press. Since carbon black acts as a nonvolatile antioxidant and is difficult to disperse, its use in BEP inks should be minimized.

13. The effect of molecular weight distribution of the resin in the uncured ink on the cure rate should be investigated. The molecular weight distribution can be adjusted by mixing two or more resins with different molecular weight distributions. It was shown in one investigation that adding 20% of a higher molecular weight material greatly decreases the drying time, in agreement with crosslinking theory. There is presumably a limit to the amount of high molecular weight material which can be

added. The viscosity will be increased. Also, as the molecular weight is increased, fewer bonds will be needed to set the ink and the ink may become unstable.

14. Oxygen is necessary for the cure of alkyds. Conversely, the ink is stable in the absence of oxygen. Oxygen is more soluble in organic solvents as the temperature is increased and is less soluble in water than in many organic solvents. The solubility and diffusion rate of oxygen in the various solvent/dispersing agent formulations should be determined, and the effect of oxygen solubility on ink stability and cure should be established.

15. The UV absorbance spectra of the curing resin and the mixed inks should be measured and used to determine the optimum wavelength at which to irradiate the newly printed ink in order to "skin" it using a photoinitiator. The procedure may allow immediate printing on the other side.

16. The effect on the cure rate of skinning of the ink by irradiating to activate an added photo-initiator should be determined. Oxygen diffusion will probably be slowed down by a hard skin on the ink, and will presumably be slower in materials with components such as acrylics added to raise the glass transition temperature.

17. If water is to be used as a cosolvent, amines must be added to disperse the resin. The action of such amines on the cure must be clarified. There are conflicting reports on whether they accelerate the reaction or inhibit it. They seem to inactivate the cobalt drier.

18. The influence on the cure rate of viscosity-reducing agents added to the water dispersion of the ink should be clarified.

19. There is need for a better understanding of the action of the driers, in particular whether they "fix" oxygen as well as decompose hydroperoxide groups, whether they influence the reactivity of the carbon-carbon double bonds by producing trans configurations from cis configurations in the alkyd side chain, whether they are "consumed" by coordination to oxygenated groups, and whether they are poisoned by amines.

3: Report on test for solvent evaporation from green ink

A report "Thermogravimetric Study of Low Temperature Weight Loss from Three Intaglio Printing Inks", by J. C. Phillips and B. Dickens was provided to BEP. Thermogravimetry consists of monitoring the weight of a specimen continuously while it is being heated. Dr. E. Graminski of BEP provided for weight-loss measurements the three intaglio printing inks: BEP black ink BK ASB 85-074; SICPA black ink ASB 85-073; and SICPA green ink ASB 85-072.

The inks were heated at 2 degrees Celsius per minute in nitrogen and their weights monitored continuously using the thermogravimetric apparatus. This is the heating rate used in the flashpoint test for highly viscous liquids. The results are shown in graphical form in Figure 1.

The BEP black ink lost less weight than the two SICPA inks. The BEP black ink lost 0.9% of its initial weight by the time the temperature reached 50C. At the same temperature, the two SICPA inks had each lost 1.3% of their initial weights. This difference in weight loss behavior took place over the range 30 to 60C, at which temperature the two black inks began to follow very similar weight-loss trends with increasing temperature. At 85C, the green ink began to lose weight much more rapidly than the two black inks. The runs were ended at 130C because the original request was to characterize their behavior from room temperature to a temperature sufficiently above the temperature of interest, 50C (roughly 120F). By the time the specimens had reached 130C, the total weight losses were 10.4% for the BEP black ink, 11.1% for the SICPA black ink, and 14.8% for the SICPA green ink.

4: Report on test for inhomogeneity of mixing

4.1: Introduction

A report on a prototype study employing thermogravimetry was supplied to BEP by J. C. Phillips and B. Dickens. Intaglio printing inks currently in use at BEP give small but significant amounts of spoilage. During one of our early visits to BEP, it was pointed out to us that a possible source of variability leading to abnormal behavior of BEP inks is that the ingredients have not been correctly weighed out. Since thermogravimetry is a rapid method of analysis in favorable cases, we decided to apply the method in an exploratory study to several BEP intaglio printing inks for which spoilage records were available. Such inks were already on hand at NBS.

4.2: Experimental

Both black and green inks were used. Between 40 and 70 mg of ink were weighed into the thermogravimetry cup. Runs were made in nitrogen or in mixtures of oxygen and nitrogen. A heating rate of 4C/min was used. The specimen weight was recorded continuously. In the case of the black inks, the color of the residue was noted.

4.3: Results

Figure 2 shows duplicate runs of weight loss from specimens of black ink BK62 mod 3 heated in nitrogen. The differences in the final residues are about 1%. This is an indication of the reproducibility of the process.

Figure 3 shows weight-loss data for several black inks for which spoilage data are also given. The ink with the highest spoilage rate gave the smallest residue. There is some correlation between these quantities for the four inks.

Figure 4 shows the effect of increasing the oxygen content of the atmosphere surrounding the black ink specimen during the thermogravimetric experiments. Two effects are obvious. The first is that, for weight-loss in oxygen, the non-volatile residue is a greater fraction of the initial weight of the specimen. The second effect is that weight-loss occurs at lower temperatures in oxygen-containing atmospheres.

Figure 5 shows weight-loss data for green inks, which are simpler than black inks to examine by thermogravimetry because they do not contain carbon black. Again, the lowest residue and hence the lowest filler content is associated with the worst ink.

4.4: Discussion

The weight-loss curves in Figures 2 to 5 show several stages, which are associated with the components in the inks. Thus, thermogravimetry is a possible method of rapid analysis to aid in quality control of amounts of ingredients in newly mixed inks. The runs in this short study were all made at heating rates of 4 degrees Celsius per minute. Using slower heating rates and smaller sample will probably increase the separation of the weight loss stages for each of the components. Such refinements were beyond the range intended for the study.

A residue of about 55% was found for degradation in nitrogen, and 67% for degradation in oxygen. The value of 67% for degradation in oxygen is numerically consistent with the various iron pigments being oxidized to their highest valence states in oxygen, the water of hydration in yellow iron oxide being lost, the furnace black being oxidized to carbon dioxide, and the calcium carbonate being decomposed to calcium oxide, with the barium sulfate remaining unchanged. The value of 55% for degradation in nitrogen is consistent with the furnace black reducing the other materials, so that the iron oxides go to their lowest valence state, the other iron pigments are decomposed to either oxides or carbides, the calcium carbonate is decomposed to calcium oxide, and the barium sulfate is reduced to barium oxide.

Differences in solid residues from specimens taken from different parts of a newly mixed batch of ink can test uniformity of mixing to a level of mixing of about 1% based on specimens weights of several milligrams. A filler particle of 5 microns radius weighs about 0.1 nanograms. The thermogravimetric ashing procedure obviously only checks the grosser features of the mixing of the ink.

The inks which had higher failure rates had lower residues in our study, but it is not to be expected that all failures would correlate in the same way. An aspect of ink formulation that may be relevant is that more drier (an accelerating agent for the ink cure process) must be added to the ink formulation when fillers are used than is needed in the absence of fillers. The explanation for the additional amount of drier is that the major part of the drier is absorbed on the fillers. Thus, a lower residue in the thermogravimetric experiments corresponds to an ink which contains less filler and hence effectively contains more free drier. Such an ink will cure more quickly than expected. Faster cure would also be expected in those cases where the extra liquid is tung oil or small scale mix. In an earlier study conducted for BEP, Hunston in the Polymers Division at NBS showed that spoilage rates could be correlated with speed of cure, the worst inks being those which cured the fastest.

The weight-loss data in the presence of nitrogen are expected to correspond to simple evaporation of the components, with perhaps some reaction between such components of the residue as carbon black and the pigments as the temperature approaches the upper limit used. Runs in nitrogen and oxygen show differences which are associated with the oxidation of the organic components to small volatile molecules and addition of oxygen to the non-volatile ink components. Analysis of these stages and differences in weight loss would aid in differentiating between the various non-volatile components but are too time consuming to be useful to BEP.

Similarly, the thermogravimetric stages of weight loss could be associated with specific ingredients by conducting experiments where ink samples were prepared by mixing a little of each of the various ingredients in turn into otherwise normal pre-mixed inks. The details of the thermogravimetric curves depend on the sample size and heating rate. An investigation of the effects of these variables on the intermediate stages of weight loss was too extensive for this kind of initial study.

The reactions taking place in the thermogravimetric experiments in the presence of oxygen are complex. No effort has been made here to characterize these reactions because they take place at temperatures which are very high compared with the temperatures of ink cure and are therefore of limited interest.

The results obtained suggest that useful information on weighing of ingredients, and possibly on spoilage, especially where the residue is seen to be abnormal, can be obtained fairly rapidly (3 hours) using thermogravimetry as a method of relatively rapid analysis. (Note: Later in this report, we give thermogravimetric determinations of ink residues which were carried out at 200C per minute. A total time of only 15 minutes was required for heating up and cooling down.)

5: Report on test of thermomechanical stability of gummed papers

Several samples of gummed paper were received from Mrs. B. Vaudreuil of BEP for study of the thermal mechanical properties of the attached gum. The samples, with their BEP codes, were:

LP-52-33 (PVA-dextran gum combination), which gave a build-up of gum on the impression roller of the printing press when used in the temperature range 50C to 70C.

LP-52-29 (gum as above), which did not give a build-up of gum on the impression roller.

LP-30-PC (dextran gum) no gum build-up.

LP-30-EF (dextran gum) caused gum build-up.

LP-53-SMCL (dextran gum) no gum build-up.

Thermomechanical measurements were made with a Perkin-Elmer thermal analysis module. The specimens were heated from 25C to 100C at 4C per minute while their thicknesses were monitored continuously using a weighted probe pressing on the gummed side. Both round ended and flat ended probes were tried, with various weights on the probe. The results indicate that these differences did not affect the experimental data.

There was some initial problem with specimen preparation. Specimens cut out of the supplied sheets using a cork borer gave unreliable measurements of the initial thicknesses of the specimens and of the change of thickness with temperature because the twisting action of the cork borer buckled the specimens. Specimens cut out of the supplied paper sheets with scissors gave good measures of the initial specimen thicknesses. The specimens were about 120 microns thick (0.12 mm) and the thickness decreased about 5 microns during the measurements. The spread of the measurements was about 1 micron. In spite of this fairly good precision, we could not differentiate between the gummed papers on the basis of our measurements (Figures 6, 7, and 8).

Gel permeation measurements of the molecular weight distribution of these gums proved not to be feasible. The gum on specimens LP-29 and LP-33 did not dissolve in the solvent (tetrahydrofuran) for which the GPC columns are calibrated. The remaining specimens produced cloudy suspensions which, if used unfiltered, would block the filters and columns, and, if filtered, would no longer be representative of the original specimens. It appeared that water or an aqueous-compatible solvent would be needed to examine the molecular weight distribution of the gum materials. Changing solvents requires a major effort to recalibrate, even when the appropriate molecular weight standards are available. We did not have the calibration standards and chromatographic columns needed to use water as the solvent.

6: Further tests for mixing homogeneity

6.1: Experimental Techniques

6.1.1: Introduction

Intaglio inks are stiff pastes containing about ten ingredients which must be weighed out, mixed, and then milled to disperse the various solid aggregates of particles in the liquid phase. We proposed to answer the questions:

1) how well can the weighing/mixing processes be checked in a quick test?

2) does the ink cure significantly during the mixing and milling processes?

3) does the cure behavior of the ink change during mixing and milling?

In response to the first question, we refined our thermogravimetric technique of determining ink residues to develop a rapid method of analysis by ashing small specimens of ink. The analysis time is 15 minutes per specimen and the method now has a precision of about 0.3% for a single determination.

In response to the second question, we devised a method to follow changes in molecular size of the soluble part of the ink using gel permeation chromatography.

In response to the third question, we used the time required by the curing ink to attain a pre-determined viscosity as a rapid estimate of cure time. The cure time was then used to follow any changes in cure behavior with mixing and milling.

For three specimens of mixed and milled ink, we also followed the cure of the ink in more detail using "molecular" parameters such as the ultraviolet absorbance of the triple bond moiety in the tung oil and the hydrodynamic volume of that part of the curing ink which was soluble in tetrahydrofuran.

6.1.2: Experimental details

Two successive batches of black intaglio inks (BEP BK62 mod3) were sampled during mixing and milling, as indicated in the left hand column of Table 1. Specimens were taken from various parts of the mixing vessel before and after the small scale mix was added. The specimens were taken from the top and from the middle of the mixing vessel, and from locations near the side of the vessel where the ink appeared to be in a thick layer and in a thin layer. Specimens were also taken of the ink being pumped onto the three roller grinding mill, and before and after each of the two grinds in the milling process. The specimens taken after each grind were from three positions (designated left, middle and right in Table 1) on the apron over which the milled ink falls into the storage drum, and after the ink had sat in air for several minutes on the apron. Left, middle and right refer to directions seen when looking at the roller mill over the apron. After the ink had been pumped to the second grind, a sample was taken from the bottom of the mixing vessel. The temperature of the ink was measured at each of these stages. The inks attained temperatures of roughly 50C during mixing, and roughly 60C during milling. The identification of the various specimens is given in Table 1. The specimens were characterized in three ways: ash content (determined in air); average size of soluble molecules; and cure time.

6.1.3: Rapid ashing using thermogravimetry

In the ashing experiments, a Perkin-Elmer system 7 thermogravimetric analyzer was used to provide quick and precise estimates of the uniformity of mixing from the residue left after combustion of the inks. (Manufacturers' names and products are mentioned where necessary in this report to define the procedures and materials.) Ink specimens of 10 to 20mg were heated in air from room temperature to 800C at 200C/min and held at the higher temperature for about 3 minutes. Weight loss was essentially complete after the first 3.5 minutes of the total time of seven minutes, but the additional time provided a plateau from which the weight of the residue could easily be estimated. Reddish residues which were roughly 70% of the initial weights of the specimens were obtained. The iron oxide in the ink was presumably being oxidized to the trivalent state from the divalent state. In the cases of the larger specimens, the residue gained weight slightly during the last 3.5 minutes because sufficient oxygen had not been available for all the oxidation to take place during the time the specimen was being heated to 800C. The weight percentages of residue (or ash) found for the specimens are given in Table 1.

In most runs, sample sizes of about 15mg were used because we wanted to minimize effects from oxidation of the specimen as it was being placed in the sample holder and weighed. Later, we ran several specimens at much smaller sample size, and showed that appreciably better resolution is obtained at specimen sizes of 2 to 4mg (Figure 9).

6.1.4: Molecular sizes from gel permeation chromatography

For the estimation of molecular size using gel permeation chromatography, about 40mg of ink were dissolved in 10ml of tetrahydrofuran and the solutions were centrifuged for 2 hours at about 3500rpm. Trials showed that these long centrifuge times produced solutions freer of particulate matter (which would have eventually blocked the filters and perhaps the columns in the GPC) but that there was no loss of soluble material compared with solutions which had been centrifuged for 1/2h or 1h or had been filtered twice. Specimens which had been milled extensively gave blue-black solutions. The other solutions were clear. The chromatograms were measured using the refractive index detector on a Waters 150C chromatograph equipped with 10,000, 1000, and two 100 angstrom micro-styragel columns. The columns were calibrated in terms of hydrodynamic volume using narrow molecular weight standard samples of polystyrene. The measurements were taken and the results processed using computer programs written by Barnes, Dickens and McCrackin (1985). Some aspects of these computer programs were specially written for this work. In particular, the chromatograms can be transformed into terms of hydrodynamic volume. This is a quantitative way to use the GPC technique to characterize materials for which the Mark-Houwink parameters, which relate hydrodynamic volume to molecular weight, are unknown, as in the case of bodied tung oil and the other ink ingredients, or inapplicable, as in the case of mixtures of materials such as an ink. Averages calculated from the distribution of hydrodynamic volumes in the mixed and milled ink specimens are given in Table 1.

6.1.5: Cure times

"Cure" times for exposure of ink on a rubber mill at 70C in air were determined, and are given in Table 1. The cure was followed using a squeeze flow technique in which specimens of ink were taken from the roller of the rubber mill every 2 minutes and placed between two parallel plates to give a layer of ink at least 1/8 of an inch thick. A load was immediately applied to the top plate and the thickness of the ink layer was measured after the squeezing flow of the ink out from between the plates had ceased (about 30 seconds). In the early stages of cure of the ink, the final thickness of ink layer obtained was quite small. As the ink became more cured, the final thickness of the ink layer increased considerably. The cure time is defined as the time required for the minimum thickness to exceed 30 thousands of an inch. This occurs within 2 minutes of the point at which the viscosity becomes so high that it can no longer be measured with standard equipment, and the material is near the gel point.

6.2: Results of study of mixing and milling

6.2.1: Introduction

In the manufacture of an intaglio ink at BEP, some ten ingredients are weighed out and mixed. The basic problem with relating analyses of homogeneity of mixing to ink performance is that the desired rapid methods of analysis rarely measure individual components.

6.2.2: Thermogravimetric measurements

The thermogravimetrically determined ash contents show that the inks were satisfactorily mixed, even on a scale of milligrams. This means that a specimen of 10 milligrams is indistinguishable from another specimen of 10 milligrams taken from either a completely different part of the mixing process or, in the case of the two inks studied here, from a specimen of the other ink. No special care was taken when the ingredients were weighed and mixed at BEP. The first ink was mixed 10 minutes before and 10 minutes after the adding of the small scale mix. The second ink was mixed 26 minutes before the small scale mix was added and 5 minutes after. The averages of the residues from the two inks indicate (Table 1) that the second ink had 0.3% more liquid than the first.

6.2.3: Determination of hydrodynamic volume averages

The size of the molecules in the liquid has been estimated from their hydrodynamic volume. Since the ink contains a mixture of liquids, including bodied tung oil and varnish, which themselves contain molecules with a range of sizes, a distribution of hydrodynamic volumes is obtained. The distribution has been averaged in various ways to search for a numerically stable quantity to characterize this aspect of ink cure. The averages of the logarithm of the hydrodynamic volume are the most stable, as expected. The hydrodynamic volume averages obtained for the various specimens from the different stages of mixing and milling are all very similar. When these values are compared with those given for curing ink in the next section of the report, it will be obvious that the ink does not cure measurably during the mixing and milling processes.

6.2.4: UV absorbance measurements

In work reported later in this report, the process of cure was monitored using UV absorbance to follow the remaining abundance of the tung oil triple bond sequence. The preliminary measurements we made to check the feasibility of this approach were also useful to show (Figure 10) that the specimen of the second ink had slightly more tung oil (more UV absorbance at 271nm) than the two specimens of the first ink. This is consistent with the specimen of the second ink curing in 4 minutes less time than the two specimens from the first ink. The thermogravimetric measurements had shown that the second ink contained slightly more liquid.

6.2.5: Differences in cure times

The most striking result from these studies of mixing and milling is that the cure times for the specimens of the second ink taken during the mixing process are much lower than those for the first ink, although the cure times become comparable for the two inks for those specimens which have been milled. Intermediate cure times were found for the specimens of the second ink which had stood at 50C or so for the 3.25 hours which elapsed between mixing and milling. The first ink stood for 4.2 hours at about 50C before being milled. Both inks were within specification at BEP when the milling had been completed. The first ink contains slightly more (0.3%) solid than the second ink. Only the second ink was sampled extensively before the small scale mix was added. The initial viscosity of this ink was higher before the small scale mix was added, as expected because at that point there was less liquid in the mix. The specimen of the first ink taken before the small scale mix was added was unusually small and therefore was unusually accessible to the air. This specimen cured rapidly in the container and could not be used in the cure time measurements. The other specimens were much larger than this specimen. These larger specimens may be kept uncured for months, especially if kept in a freezer.

The actual cure times for the specimens of the second ink are (Table 1): 20 to 21 minutes before the small scale mix was added; 20 to 22 minutes after the small scale mix was added; about 26 minutes after the ink had stood 3.25 hours at 45 to 50C and then had been mixed further by being forced through the delivery pipe to the roller mill; and about 30 minutes after milling. The cure times are similar for the specimens of the second ink taken before and after the small scale mix was added and mixed into the ink for five minutes. The thermogravimetrically determined residues of the mixed ink specimens are very similar to those of the milled ink specimens, so the ink is obviously well mixed. The variables which remain for consideration are the dispersion of the ingredients in the ink and the absorption of the liquid components by the solid fillers.

6.2.6: Dispersion of solids in the inks

Formulations of BEP inks are given in terms of weight and weight percent in Table 2. The small scale mix contains the drying agent which is supposed to increase the rate at which the ink cures. It also contains some surfactant/viscosity thickener and is about 50% solvent. The net result of adding the small scale mix is to decrease the viscosity of the ink. The thermogravimetrically determined residues show that even after only 5 minutes of mixing after the small-scale mix had been added, the specimens of ink appear to be well mixed on the scale of milligrams. (Since even a coarse filler particle of 10 microns in diameter weighs only about 0.1 nanograms, the thermogravimetric method can give no idea of the amount of dispersion of small aggregates of materials.)

Although it may turn out that poor dispersion of the solids is not the real reason why the second ink cured more quickly, it is otherwise difficult to explain why 5 minutes of mixing to a level of homogeneity better than 0.5% according to the thermogravimetric results and several hours of standing were not sufficient to change the cure behavior of the ink. We presume that the 25 minutes of mixing before the small scale mix was added were not sufficient to disperse the solids, either because the viscosity of the ink was too high or because the solids were not dispersed until they had absorbed the surfactant and/or solvent in the small scale mix.

Thus, the dispersion of the solid ingredients in the ink seems to be critical. 10 minutes of mixing seems to be enough to disperse the ingredients sufficiently well in the ink. 5 minutes seems to be too little time. Delivery to the roller mill and the milling process itself will increase the dispersion considerably. It may be worthwhile to install timers on the mixing machines if they are not already in place, and to specify a longer mixing time, perhaps 15 minutes after adding the small scale mix, to be more certain that enough mixing has taken place.

6.2.6: Dispersion of furnace black

One possible explanation of the behavior we have observed is that the furnace black, which in most commercially available grades acts as an antioxidant, became less aggregated on soaking in the lower viscosity ink (as the solvents in the small scale mix permeated throughout the ink and were absorbed by the furnace black). With the furnace black acting as an antioxidant and in more intimate contact with the ink, the peroxyl radicals which lead to ink curing would be trapped and hence the ink would cure more slowly. A study documenting this effect was published by J. T. Gruver and K. W. Rollmann ("Antioxidant properties of carbon black in unsaturated elastomers. Studies with cis-polybutadiene", J. Appl. Polym. Sci., 8, 1169-1183, 1964). Lyon and Stoy showed that furnace black aggregates easily and is difficult to disperse (F. Lyon and W. S. Stoy, "Properties and ink applications of carbon black", Paint Manuf., 36, 36, 1966).

Estimations of the degree of dispersion of the carbon black could be based on rate of sedimentation of the solid filler from a solution of the ink or determination of turbidity by UV-visible spectrometry (see K. C. Yang and R. Hogg, "Estimation of particle size distributions from turbidimetric measurements", Anal. Chem., 51, 758-763, 1979).

6.2.7: Critical pigment volume considerations

An alternative explanation to the antioxidant nature of furnace black being the determining factor may be derived from the well-known absorption of ink and paint vehicles by filler. The critical pigment volume concentration is a very important concept in paint formulation and manufacture (see, for example, G. P. Bierwagen and T. K. Hay, "The reduced pigment volume concentration as an important parameter in interpreting and predicting the properties of organic coatings", Progress in organic coatings, 3, 281-303, 1975).

Poorly dispersed filler contains more space between the components of the aggregates than the same filler would if it were broken up into smaller particles. Small particles which are completely solid can pack with reasonably high space-filling efficiency. The poorly dispersed material is in effect aggregated into honeycombed structures contain an appreciable amount of interior space and which can not rearrange themselves to pack efficiently. Liquid is drawn into the interior of the honeycomb structures by capillary action. More liquid is consumed in this way than would be if the particles in the aggregate were separated. Therefore, the mixture acts as though it is more highly filled with solid material than it actually is. This means that the viscosity of the mixture will be higher and that less setting of the liquid phase will be necessary to give such an increase in viscosity that the material will seem to be cured. In an ink containing less than the usual amount of liquid, and especially in the case of a very highly filled ink such as BK62 (see Table 2), this may be enough to make the ink unstable.

6.2.8: Drying (dehydration) of the ink

The development of the blue color during mixing is at least in part due to drying of the driers - the cobalt salt solutions which in theory decompose hydroperoxide groups in the setting ink to give more free radicals and hence a quicker setting action. The drier as delivered by the supplier and added to the ink is purple. Figure 12 shows the visible spectrum of drier as received and after drying. The absorbance shifts to longer wavelength as the cobalt ions in the cobalt drier dehydrate. The appearance to the eye is a shift from purple to blue because the red is increasingly absorbed from the transmitted light. This is visually the same blue as that seen in solutions of the ink. The silica filler is obviously acting as a desiccant, as it does in many domestic products which have to pour, as well as in factory packaging of electronic components, and is keeping the ink dry. Wet inks are expected to dissolve less oxygen. The role of oxygen in the drying of drying oils is only partially understood. Certainly, it is needed to form the hydroperoxide groups on which the driers act. Therefore, insufficient oxygen will reduce the rate of formation of the groups necessary for the generation of the free radicals which start the setting of the ink. However, it is well known that oxygen adds to hydrocarbon free radicals and thus greatly deactivates them, so too much oxygen may slow down the ink setting reaction. Variations in the oxygen content of inks because of variations in the drying ability of different silicas could be a source of significant variation in the performance of the ink on the presses.

7: Cure measurements

7.1: Introduction

The cure behavior of an ink is one of its most important properties, and depends on the interplay of many variables which are not well understood. As steps are made to introduce water, either as a wiping medium, or, more seriously, as a component of the solvent system, the interplay between variables which complicate the study of ink cure becomes the interplay between requirements which are almost mutually exclusive. Previous work in this program has examined the changes in mechanical properties such as viscosity which occur during cure. It is now desirable to complement these measurements with data from techniques which focus on chemical and other molecular level changes which take place during cure. To gain experience in the analysis of inks and the selection of the important variables in ink cure and the characterization of these variables, we have followed ink cure in several ways. The approach was to quickly use each technique to see how useful and feasible it was, and to gather information which, although incomplete because of the survey-type approach and the constraints of limited time and resources, would be pertinent to interpreting the course of ink cure on a fundamental level.

7.2: Ink cure on the rubber mill

"Cure" times were measured as previously described for ink specimens exposed to air on a rubber mill at 70C and the results have been given in Table 1. The cure behavior measured in this way follows changes in the viscosity of the material. It is well-known that the viscosity increases very sharply as the material approaches the gel point. We have shown in previous work that the cure time measured in this way is quite close to the gel time and is a good method of monitoring the cure time.

To carry out tests based on gel permeation chromatography and UV absorbance, we had to dissolve ink specimens in suitable solvents. Three specimens of ink (numbers 38, 44, and 59 in Table 1) were selected from those which had essentially completed the milling process. These specimens of ink were cured on a rubber mill at 70C. The two rollers on the rubber mill rotate at different speeds, with the net result that the ink is kept as a single film on one of the rollers. The mill was set to produce a film 0.012 inches thick (i.e., 0.3mm = 300 microns).

Small specimens of the ink were taken every minute during the curing of the inks and introduced into preweighed vials which were immediately reweighed. One of three solvents was added: cyclohexane, to allow measurements of the ultraviolet spectrum down to 190nm; methylene chloride, as a backup solvent; and tetrahydrofuran, to allow gel permeation estimates of the molecular size of the soluble part of the inks. Thus, the ink was sampled every three minutes for each of the techniques.

7.3: Film reflectance

In the initial stages of cure, the ink is fluid enough to be able to flow at the temperature (70C) of the rollers of the rubber mill. A lightly or insignificantly cured ink containing most of the original solvent very quickly reforms a disturbed surface and thus maintains a high reflectance. The ink appears glossy. As the solvent evaporates and the ink cures, the viscosity of the ink increases and the ink responds more slowly to the disturbances its surface suffers when it passes through the rollers. Thus, the glossiness of the ink decreases. Easily noticeable changes take place as soon as 15 minutes on the rollers. We have not pursued this approach, but note that it is a quick test which could be used to assay rates of drying of the ink.

An indication of the evaporation rate for an undisturbed film is given by the thermogravimetric weight loss curves in Figure 13, where there is an appreciable rate of weight loss from the surface of the ink in the first 12 to 15 minutes. This trend is then overpowered by a weight gain, presumably from the oxidation of the ink as it sets. The fact that the effect is independent of sample size shows that it is a surface effect, as expected for an undisturbed film.

7.4: Mill resistance as a measure of tack

A meter was installed to measure the current drawn by the mill as the ink cured. The current decreases to a steady value after about 20% of the cure time. This corresponds to about 7 minutes in Figure 13, i.e., where the rapid rate of weight loss from solvent evaporation falls off sharply. As solvent is lost from the ink, the tackiness of the ink decreases and the ink remains as a film attached to only one of the rollers rather than gluing the two rollers together.

7.5: Clumping of the ink in solvents

When the ink is introduced into a solvent, it dissolves with more and more difficulty as cure proceeds and eventually remains undispersed in the "solvent". The time of such "clumping" depends to some extent on the solvent used. Clumping took place after the ink had cured for about 20 minutes on the rubber mill when cyclohexane was the solvent. We have not followed this index more quantitatively.

7.6: Color intensity of drier

After the specimens of cured ink had been placed in the solvents and centrifuged, we noticed that the intense blue coloration characteristic of the early stages of cure was much less intense in the specimens of well-cured ink. This provides another index with which to follow the extent of cure. The mechanism is not clear. Presumably, the cobalt ions are being bound up in the cured ink, rather than existing in soluble form by being coordinated to an anion which is itself soluble in the solvents used. As cure proceeds, oxygen-containing and hence polar groups are formed in the ink. Therefore, the cobalt ions have many more possibilities for bonding, and the metal ions would be expected to be attached to polar groups, such as carboxylic acid groups, in the cured ink.

The relationship between removal of cobalt ions from solution and crosslinking in the ink is not known. It is reasonable to assume that crosslinking via ionic bonds to the cobalt ions occurs. If so, it may be possible to make the cobalt ions more available to the ink setting reaction by including some small fraction (say about 1%) of free fatty acid in the ink formulation. Presumably there are other sources of crosslinks than ionic bonds to the cobalt ions, so loss of such bonds will not be detrimental to the setting of the ink.

7.7: UV absorbances

The most obvious use of UV absorbance measurements is to follow the disappearance of the unsaturation in the tung oil as the ink sets. Tung oil has a characteristic set of three absorbances at 263, 271, and 283nm. The liquid components of ink are petroleum solvent and various natural and modified oils. The oils consist of fatty acids esterified with the trihydric alcohol glycerol. The ester groups in the oils absorb at 204nm in the UV spectrum. Therefore, the quantity of unreacted tung oil can be estimated and the total amount of oil can also be found. UV spectra of the soluble components of the ink are given in Figure 14. Cyclohexane was used as the solvent because it does not absorb much in the range of interest, and matched cells were used so the solvent spectrum is not included in the spectra shown in the Figures.

Figures 15 and 16 contain graphical representations of the consumption of tung oil as the ink sets. The ratio of tung oil to total oil is shown in Figures 17 and 18. After the 24 to 27 minutes of curing at which the viscosity of the curing ink increases sharply, about 3/4 of the tung oil has been consumed, as shown by both Figure 15 and Figure 16. The spectra were normalized to equal sample weights.

The quantity of drier in the solution was determined from its absorbance in the visible region at 660nm. The amount in solution increases slowly up to a cure time of about 17 minutes, To some extent, this is a consequence of evaporation of solvent from the ink. At the time at which the ink begins to lose the capability to reform the surface after it has been disturbed by the rollers of the rubber mill, the quantity of soluble drier begins to fall off sharply. After 23 minutes, the quantity of soluble drier has fallen to a very low value.

The setting reaction of the ink comes from the unsaturation in the ink. The three neighboring double bonds in tung oil are especially reactive. It is convenient to follow the degree of cure by following the absorbance of UV radiation at 271nm, the center of the tung oil absorbance. Figure 19 shows the UV absorbance spectrum of a thin film of tung oil. Almost all the detail is missing. Addition of a small quantity of a solvent such as cyclohexane brings back the characteristic tung oil absorbance. We tentatively ascribe this phenomenon to the lowering of the high viscosity of the neat tung oil by the added solvent. We currently do not know whether cure of ink films can be followed using UV spectra taken on films of the ink without using a solvent, although we note that there is solvent in the ink. Certainly, the viscosity will change greatly in the final stages of cure. The safest route will be to dissolve small quantities of a large film in a solvent. These results also suggest that in principle it should be possible to follow changes in viscosity using UV absorbance spectra of suitable probes, and, conversely, that the UV absorbance spectra of probes and photoinitiators may be affected by the viscosity of the medium.

7.8: GPC measurements

When a polymeric molecule is dissolved in a solvent, it assumes a size which is governed by how large the molecule is and how well the molecule is solvated by the solvent. The average size is called the hydrodynamic volume of the molecule. Hydrodynamic volume is related to molecular weight through the Mark-Houwink parameters, which must be determined for each type of polymer and each solvent. Gel permeation chromatography is a technique which determines the distribution of hydrodynamic volumes in a material. Polymeric materials are injected in very dilute solution into a stream of solvent which flows through a set of columns containing a distribution of holes. The largest molecules are able to enter few of the holes, and the smallest molecules are able to enter most of the holes. Therefore, the largest molecules come out of the columns before the smallest molecules. The columns are calibrated in terms of narrow molecular weight fractions of well-known polymers such as polystyrene and poly methyl methacrylate. Tetrahydrofuran is used as solvent.

Figure 20A contains a chromatogram of an ink specimen which had cured for 24 minutes at 70C on a rubber mill. The chromatogram for the same ink after only 30 seconds of cure is shown in Figure 20B. We are currently developing methods of quantifying and comparing such chromatograms. Figures 20C and D show essentially pictorial ways of adjusting the relative heights of two chromatograms and performing a subtraction to determine the difference chromatogram. The abscissa units in Figure 20 are elution volume, which are dependent on the set of columns used in the chromatograph. Only the elution volume range in Figures 20 C and D was characterized in terms of hydrodynamic volume. We calculate indices to quantify the misfit in the chromatograms, but these approachs are still in the early stages, and more experience in using the results will be necessary before we can have confidence that the development is reasonably complete.

Chromatograms of the liquid ingredients of BEP BK62 mod 3 are given in Figure 21. Figure 22 contains chromatograms of specimens taken at the cure times shown. High molecular weight material appears at elution volumes between 24 and 28mls as cure proceeds.

We have developed our own computer programs for the analysis of gel permeation chromatograms. The classical approach is to relate the time at which the material comes out of the columns to the molecular weight of the material. To do this, however, one needs the Mark-Houwink parameters. If the Mark-Houwink parameters are not known, or if the injected material is a mixture, the molecular weight distribution can not be obtained. We have therefore introduced the concept of characterizing materials through their distribution of hydrodynamic volumes, and have provided parameters, analogous to the various molecular weight averages, which give some idea of the shape of this distribution. Number average log hydrodynamic volumes and weighted average hydrodynamic volumes are given for the curing inks in Table 3. The changes in hydrodynamic volume as a function of cure time are shown in the chromatograms in Figures 23 and 24. The averages of log hydrodynamic volume attain a maximum value after 24 to 27 minutes. The setting times, measured in the same experiment, were all about 28 minutes, but are not precisely known. The trend of average log hydrodynamic volume with time is shown in Figures 25 for the three inks and in Figure 26 for specimen 38. From these figures, it is qualitatively clear that the amount of large molecular weight material in the curing ink grows perceptibly for about 27 minutes, the time at which the viscosity measurements indicate that the inks had cured. The size of the soluble material then decreases to a constant value at a cure time of about 40 minutes. From crosslinking theory, the decrease is a consequence of the larger molecules being linked together to form insoluble gel, leaving only the smaller molecules in solution.

7.9: Infrared absorbances

Infrared spectra of the liquid ingredients of the ink are shown in Figure 27. The spectra are fairly simple, and those of tung and linseed oil are very similar. The major difference is between cis (735 wavenumbers) and trans (965 wavenumbers) C-H out of plane deformations next to the double bonds. In addition, tung oil has an intense absorbance at 995 wavenumbers. This may be from the C-H groups in the double bonds. Interestingly, the special intaglio vehicle contains both the cis and the trans C-H absorbances but not the 995 wavenumber absorbance. The soya lecithin contains many O-H bonds. IR spectroscopy is known to be fairly insensitive. In the near infrared, water can be determined at 5160 wavenumbers as a combination band, but our specimens were too thin for us to be able to see this absorbance. A large quantity of work has already been published on IR studies of the oxidation of the isolated pure fatty acids and esters which make up the drying oils. It remains to be seen to what extent the oxidation of pure fatty acid esters parallels the oxidative curing of an ink contains metal drier salts and furnace black antioxidant.

A specimen of ink placed on a sodium chloride plate was allowed to cure at room temperature, and the infrared spectrum taken at intervals, as shown in Figure 28. The difference spectra show that little change is seen up to 42 hours. Some of the OH absorbance at 3500 wavenumbers is at first lost (in the down direction in Figure 28) and then regained. After 5 days, the ink cracked on its support, as shown by the overall smaller signal it gave and the less intense absorbance of the background. It is obvious that extremely precise spectra will be required to show details in which one can have confidence. The IR spectra in Figure 28 were taken on the ink itself, and little energy was transmitted through the ink to the detector. In addition, the tung oil vehicle was only a small fraction of the total absorbing species. Features such as the C-H stretch next to the double bonds can be seen clearly at 3010 wavenumbers, and the trans and cis C-H bends can be seen at 965 and 735 wavenumbers, respectively. The carbonyl region at 1735 wavenumbers contains only the ester group absorbance. We will examine the feasibility of taking IR spectra on specimens of ink which we have dissolved in some solvent, probably cyclohexane, and relating the results to those found earlier on pure compounds by other workers.

8: Conclusions

Alkyds were recommended as the most practical new resin system to polymerize in air. The alkyd should have a well-chosen molecular weight distribution and be dispersible in a water-containing solvent system. UV irradiation of the newly printed currency paper can probably be used to skin the ink rapidly and prevent blocking, especially if a photoinitiator system is added to the formulation. This may allow printing of both sides of the currency paper in one pass. Replacement of the various pigments and fillers currently in use by dyes attached to the backbone of an organic polymer, either in water-soluble form or in the form of a glass should be investigated.

A rapid method of analysis using thermogravimetry to determine solid residues left after an ink has been ashed has been developed. Analysis time is 15 minutes. The reproducibility of one determination is roughly 0.3%. The method showed that specimens from one ink sample had on the average 0.3% more liquid than specimens from the other (this average value was obtained from 25 determinations and hence has an uncertainty of about 0.06%). UV spectroscopy showed that the second ink sample contained more tung oil. Cure time studies showed that it cured more quickly.

Several interesting results arise from the study of the variation of cure time variation with extent of mixing and milling. First, both the variations in properties within a batch and between the two batches were less than our earlier work on these inks had led us to expect. These two ink samples clearly do not show the width of variation that exists in intaglio inks. When we examine more inks in the future we may find other differences. Even so,our results are very informative. Four points are worth noting:

1) The inks were fairly homogeneous on a scale of about 0.1 milligrams yet showed significant differences in curing behavior.

2) The time of cure increased with grinding, rather than decreasing as would be expected if the ink cured somewhat during the grinding process.

3) The addition of the small scale mix, which contains the driers, had little or no effect on the cure time for the second ink until the ink had been milled.

4) The intensity of the blue color in the liquid-extracted portion of the ink changed with extent of cure.

Dispersion of the solids in the ink seems to be critical. An explanation for the variation of cure time with extent of mixing is that the solids remain aggregated, or at least poorly dispersed, and therefore absorb more liquid inside the aggregate by capillary action than they would if the aggregates were well dispersed and the liquid were merely absorbed on the separated particles. The ink then acts as though it were more highly filled than it really is. With a highly filled ink such as BK62 mod 3, this may make the ink unstable. The phenomenon is well known in the manufacture of paints.

Carbon black acts as an antioxidant in most of its forms. Thought should be given to omitting the furnace black from the ink formulation and using a volatile antioxidant instead. This will give good storage properties and perhaps better control of cure since furnace black is known to aggregate easily and to be difficult to disperse. A volatile antioxidant would evaporate from the ink on the press and allow the setting reaction to proceed from that point on.

The technique of gel permeation chromatography was developed to provide distributions and averages of these distributions in terms of log hydrodynamic volume. This is a new way of classifying molecular size for systems which are mixtures of materials. The average log hydrodynamic volume of the soluble part of the vehicle is a useful index with which to follow the cure of the ink.

9: Figure legends

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Figure 2. Comparison of thermogravimetry curves of specimen weight versus temperature for two runs of a specimen of the same sample of a BEP BK62 mod 3 black ink.

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Figure 5. Thermogravimetry curves and qualitative spoilage records for BEP green inks 4717 RCA Mill #5 heated in oxygen.

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Figure 20. Gel permeation chromatograms for two ink specimens cured for 24 minutes (20A) and 30 seconds (20B). Figures C and D show two possible ways of subtracting the chromatograms from each other to show the effect of cure. In Figure 20C, the two chromatograms have been equalized at the peak corresponding to unpolymerized oil/varnish/solvent. In Figure 20D, they have been equalized at a point between the non-polymerizing component and the high molecular weight material.

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Figure 23. Chromatograms of a curing ink transposed into terms of log hydrodynamic volume. The high molecular weight material formed during curing appears at log hydrodynamic volumes higher than 4. Cure times as shown.

Figure 24. Superposition of selected chromatograms of a curing ink. The times cover the time at which the viscosity of the curing ink suddenly increases. The curve for 27 minutes is

lowest near 2 in log hydrodynamic volume and highest near 5. The curves for 21 minutes and 33 minutes are highest near 2 and lowest near 5. The other two curves are intermediate.

Figure 25. Change in average log hydrodynamic volume with cure as determined from GPC chromatograms. The log hydrodynamic volume passes through a maximum just before the viscosity of the curing ink suddenly increases. (Only the soluble portion of the ink is characterized in this way.)

Figure 26. Log hydrodynamic volume versus time of cure for a specimen of BEP BK62 mod 3. The maximum in log hydrodynamic volume is shown clearly. "Cure time" for this ink specimen was 32 minutes, based on increase of viscosity.

Figure 27. Infrared spectra of the liquid components of BEP BK62 mod 3 spread on a sodium chloride plate. The spectral range is from 4000 wavenumbers (left) to 800 wavenumbers (right).

Figure 28. IR spectra of an ink curing on a sodium chloride plate taken at several long cure times at room temperature. The spectral range is from 4000 wavenumbers (left) to 800 wavenumbers (right).

Table 1: Average log hydrodynamic volumes, sample numbers, cure times and TG residues for specimens of BEP BK62 mod 3 selected during the mixing and milling process.

	mix 4	mix 5	mix 4	mix 5	mix 4	mix 5	mix 4	mix 5	mix 4	mix 5
	hydrodynamic volume averages		sample #	sample #	temperature, C		cure times minutes		TG residues percentages	
MIXING										
before		2.53		16		50				67.18
top		2.51		22				21.3		69.03
middle		2.52		21		54		21.3		69.08
thick		2.56		23				19.7		69.22
thin		2.58		24				20.6		69.06
after										
top	2.46	2.43	19	26		52	30.8	20.5	67.64	67.20
middle	2.48	2.41	18	25	47		26.5	20.0	67.59	67.23
thick	2.43	2.43	20	27			29.7	22.0	67.48	67.74
thin	2.47	2.47	17	28			25.5	22.3	67.65	67.29
						average =	28.1	21.0	67.51	68.23
						std dev of single determination =		2.8	.92	.20
						std dev of average value =	1.3	.3	.09	.33
MILLING										
1st grind										
pumping										
begin	2.43	2.45	29	46	40	49	27.0	26.4	67.62	67.38
5 min		2.50	30	47		48	29.1	26.6	67.72	67.29
15 min	2.47		34				31.7		67.56	
end	2.54	2.45	35	51	55	51	31.3	26.7	67.73	67.53
rollers										
left	2.65	2.48	33	50			33.8	30.5	67.68	67.38
middle	2.43	2.50	31	48	61		34.7	27.4	67.66	68.00
right	2.45	2.45	32	49			28.2	30.1	67.83	67.02
2nd grind										
pumping										
begin	2.58	2.41	36	52	54	54	32.7	28.6	67.91	67.44
5 min	2.54	2.41	37	53	57	53	34.2	29.0	67.90	67.30
10 min	2.47	2.41	41	57	56	48	38.3	31.6	67.83	67.39
end	2.44	2.43	45	58	48		33.5	31.4	67.91	68.12
rollers										
left	2.45	2.46	40	56			33.6	27.2	67.96	67.95
middle	2.59	2.40	38	54		65	32.2	29.2	67.15	67.38
right	2.47	2.43	39	55			32.6	27.7	67.93	67.60
rollers										
left	2.44	2.52	44	61			33.5	27.9	68.18	67.39
middle	2.46	2.43	42	59		60	30.9	28.7	68.06	67.75
right	2.48	2.41	43	60			33.7	28.4	67.91	67.26
bottom		2.70		62		40		31.7		67.31
average	2.48	2.47				average =	32.2	28.8	67.80	67.50
std dev	.05	.07				std dev of single determination =	2.3	1.76	.23	.30
std dev of average	.01	.01				std dev of average value =	.6	.4	.06	.07

Table 1

Table 2: Compositions in terms of weights and weight percents for several BEP intaglio inks

ingredients	BK-3280 373K IRO	BK-62 RCA mod 3a	G4716 MRE	G4717 RCA	BK3280	BK62	G4716	G4717
					percentages of ingredients			
tung	25	25.60		14	4.93	6.36		3.43
pet solv	20	2.22			3.94			
blk FeOx	150	128			29.57	31.81		
Fe blue	10	10			1.97	2.48		
C blk	10	17.40		14	1.97	4.32		3.43
Silica	20	10	5.20		3.94	2.48	2	
CaCO3	100	53.40	78	80	19.71	13.27	30	19.61
BaSO4		96		160		23.85		39.22
Co drier	7.50	1.78	3.90	2	1.48		1.50	.49
Pb/Mn	7.50	.67	3.90		1.48		1.50	
Clove	2.50				.49			
atlas	4.80				.95			
aq varn	150		104		29.57		40	
sp int vh		22.80				5.67		
solv varn		28.80		36		7.16		8.82
syn grn			18.20				7	
hi gloss		2.22						
blk tint			7.80				3	
min spts			5.20				2	
TiO2			5.20	38			2	9.31
y FeO			28.60				11	
luna yell				24				5.88
phth blue				12				2.94
epo 370				4				.98
thix E				4				.98
corn stch		2.89		20				4.90
soya		.67						
ss sc alx		10				2.48		
total wt	507.30	402.44	260	408	100	100	100	100
wiping:	water	paper	water	paper	water	paper	water	paper
ss so alx		weights	x		x	x	x	x
hi gloss		96	22.22	ash:air	45.73	66.64	30.69	60.86
pet solv		76.80	17.78	liquids	42.83	19.18	55	28.43
corn stch		124.80	28.89	solids	57.17	80.82	45	71.57
soya lthn		28.80	6.67	ash:N2	47.41	55.16	30.69	47.26
Co drier		76.80	17.78					
Pb/Mn dry		28.80	6.67					
total wt		432	100					

Table 2

Table 3: Averages based on hydrodynamic volume as a function of cure for three specimens of BEP BK62 mod 3 intaglio inks curing at 70C on a rubber mill.

time,m	hv38	lhv38	nlhv38	wlhv38	hv44	lhv44	nlhv44	wlhv44	hv59	lhv59	nlhv59	wlhv59
.80	165	2.22	2.38	2.52	168	2.22	2.39	2.54	166	2.22	2.38	2.50
3	161	2.21	2.36	2.48	168	2.22	2.39	2.54	166	2.22	2.39	2.53
6	170	2.23	2.40	2.53	171	2.23	2.41	2.58	173	2.24	2.41	2.56
9	174	2.24	2.41	2.56	172	2.23	2.40	2.54	176	2.25	2.43	2.59
12	178	2.25	2.43	2.58	173	2.24	2.40	2.53	181	2.26	2.45	2.60
15	186	2.27	2.48	2.69	179	2.25	2.44	2.59	186	2.27	2.47	2.62
18	190	2.28	2.49	2.64	186	2.27	2.47	2.64	193	2.28	2.52	2.76
21	194	2.29	2.51	2.68	190	2.28	2.49	2.67	203	2.31	2.59	2.88
24	204	2.31	2.60	2.92	199	2.30	2.55	2.80	208	2.32	2.62	2.98
27	202	2.31	2.58	2.86	214	2.33	2.64	2.97	199	2.30	2.57	2.90
30	201	2.30	2.59	2.95	202	2.31	2.60	2.96	181	2.26	2.47	2.66
33	195	2.29	2.55	2.89	196	2.29	2.56	2.89	182	2.26	2.47	2.65
36	189	2.28	2.52	2.77	184	2.27	2.48	2.67	188	2.26	2.47	2.65
39	185	2.27	2.50	2.74	183	2.26	2.47	2.67	188	2.28	2.51	2.78 blue
42	188	2.27	2.52	2.79					189	2.28	2.52	2.78 blue
45	187	2.27	2.51	2.77								
hpv	302	2.48	3.07	3.71								
siv	175	2.24	2.41	2.55								
bto	145	2.17	2.32	2.48								
av	172	2.24	2.39	2.51								
[illegible]	245	2.39	2.84	3.38								

Specimen numbers are 38, 44 and 59.

hv = average hydrodynamic volume

lhv = average log hydrodynamic volume

nlhv = number average log hydrodynamic volume

wlhv = weight average log hydrodynamic volume

Table 3

Table 3

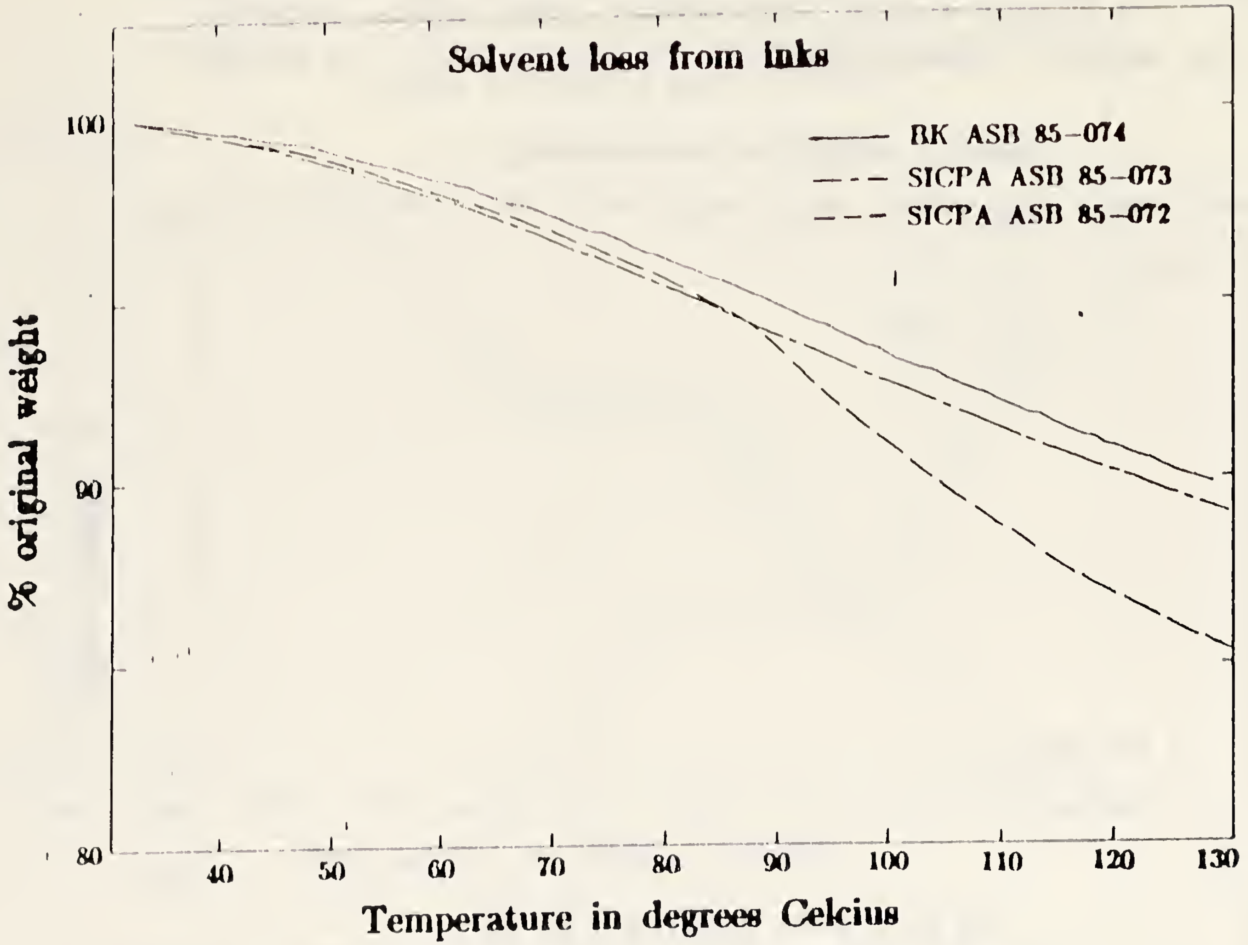

Figure 1. Weight loss of BEP inks as marked, showing the influence of evaporation of solvent.

Figure 1

Figure 1

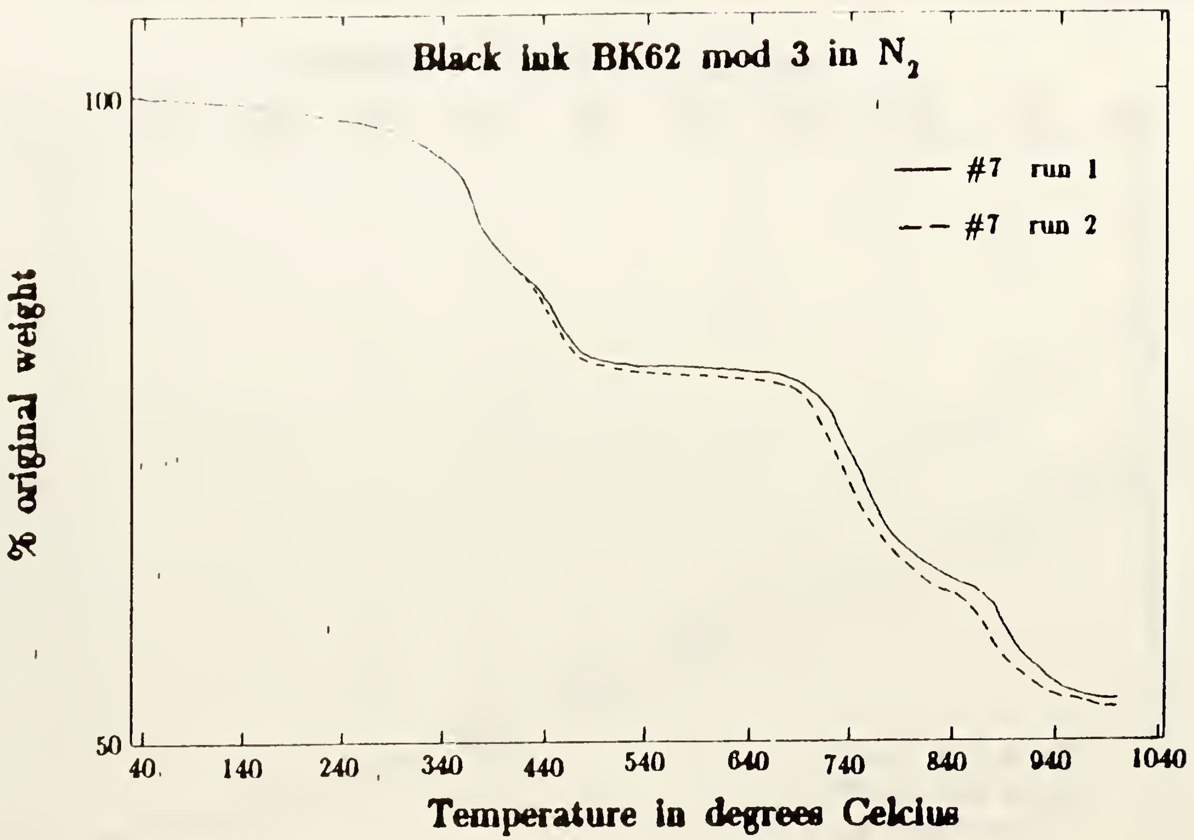

Figure 2. Comparison of thermogravimetry curves of specimen weight versus temperature for two runs of a specimen of the same sample of a BEP BK62 mod 3 black ink.

Figure 2

Figure 2

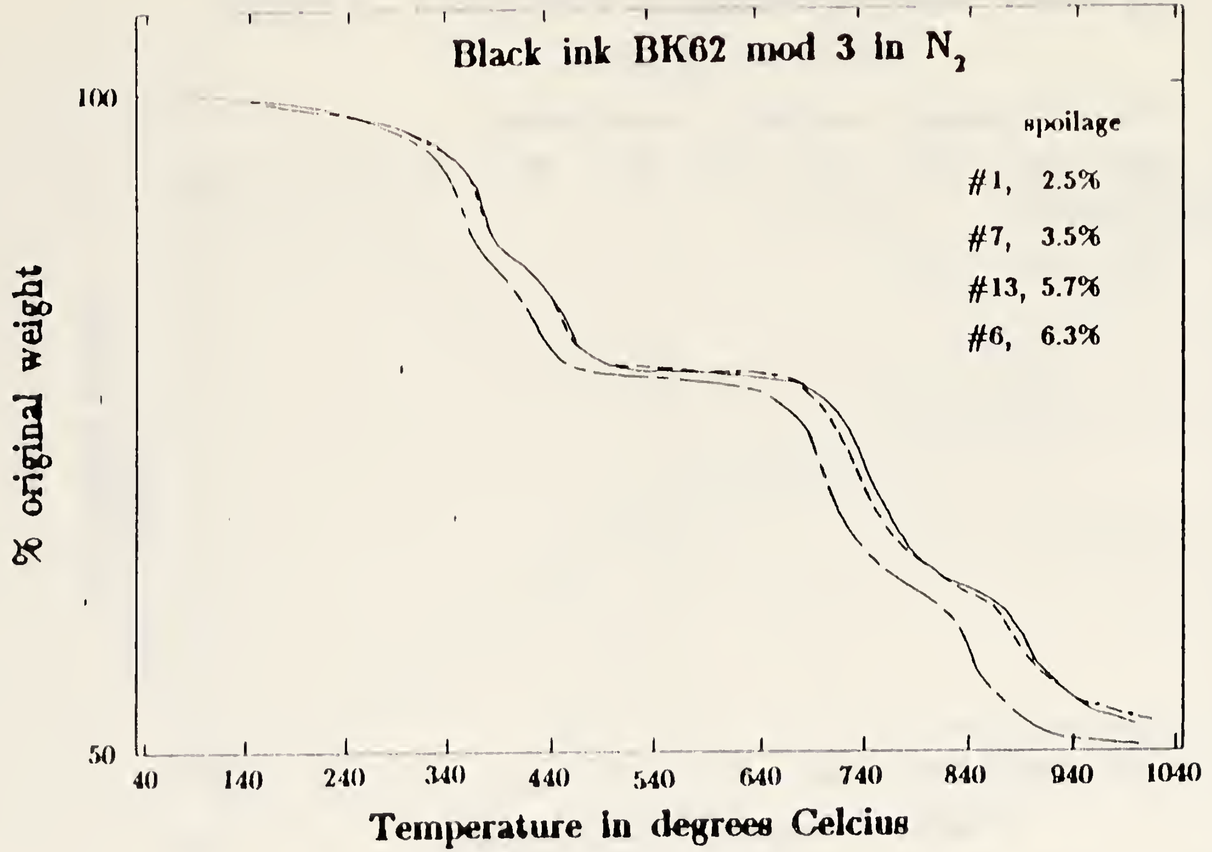

Figure 3. Thermogravimetry curves and spoilage records for several BEP BK62 mod 3 black inks heated in nitrogen.

Figure 3

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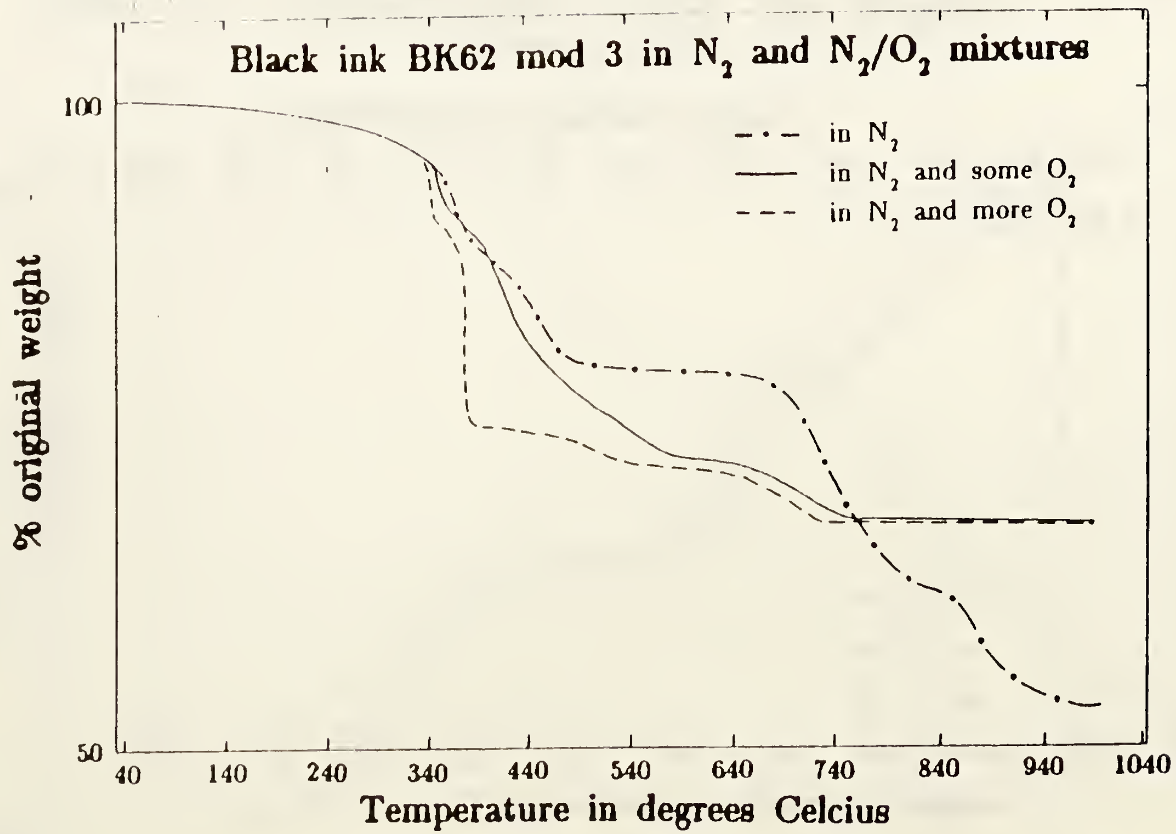


Figure 4. Comparison of thermogravimetry curves for specimens of BEP BK62 mod 3 black inks heated in oxygen and nitrogen, as indicated.

Figure 4

Figure 4

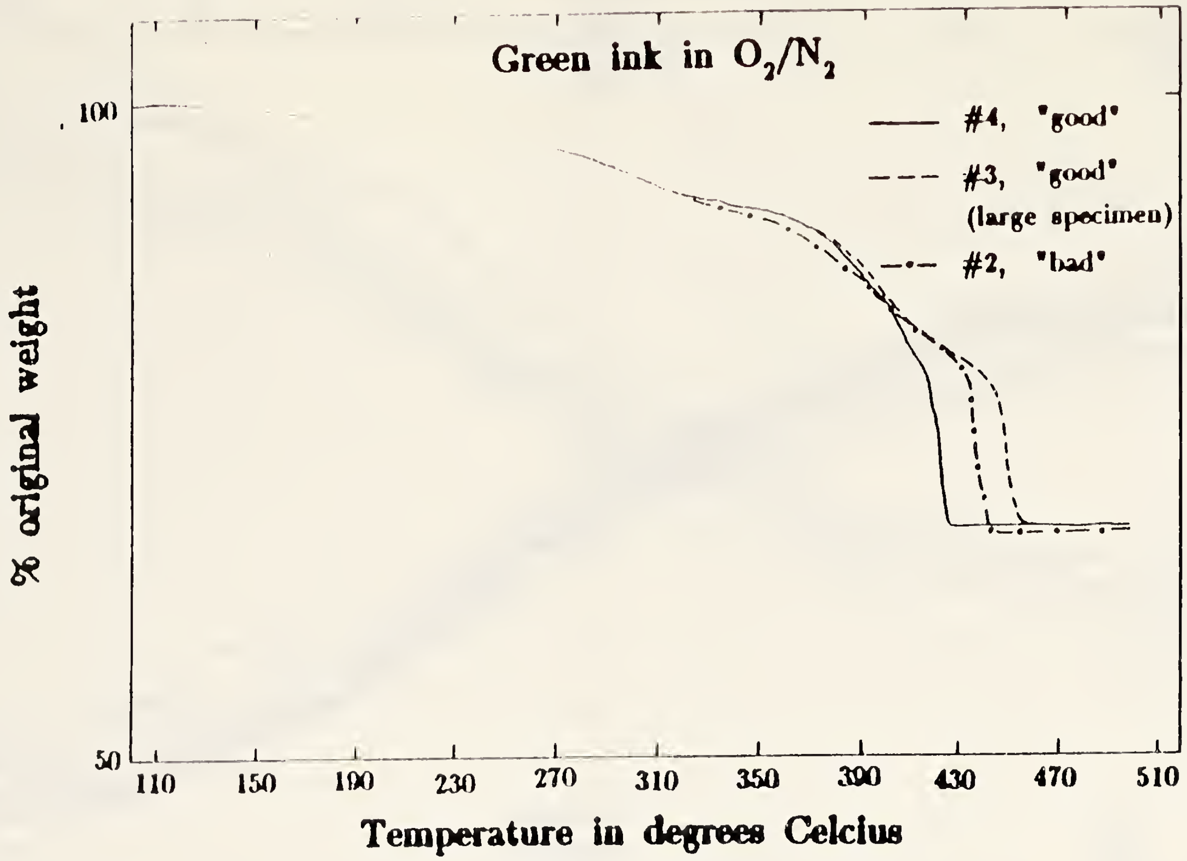


Figure 5. Thermogravimetry curves and qualitative spoilage records for BEP green inks 4717 RCA Mill #5 heated in oxygen.

Figure 5

Figure 5

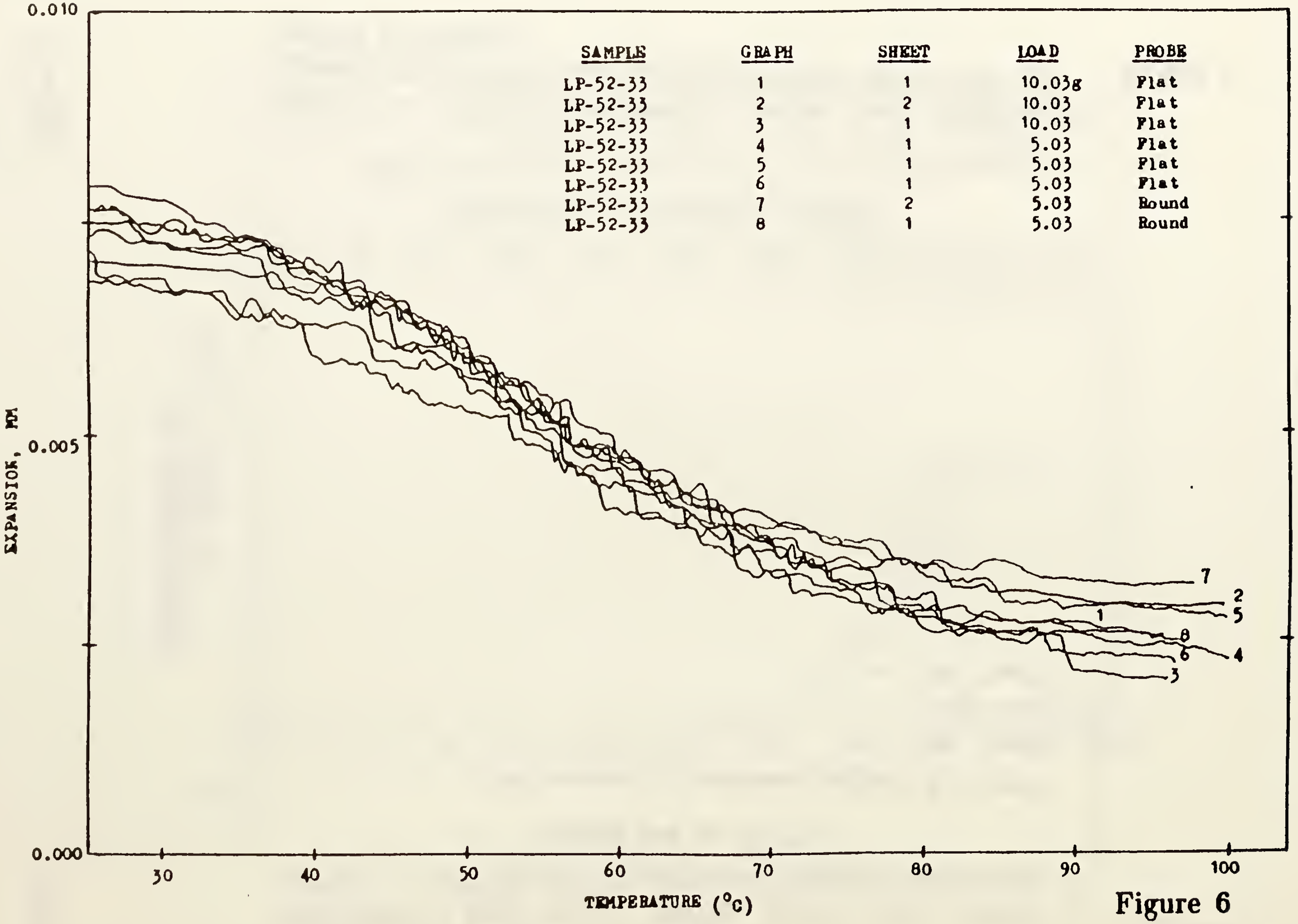


Figure 6

Figure 6. Decrease in thickness with heating to 100C for various specimens of LP–52–33.

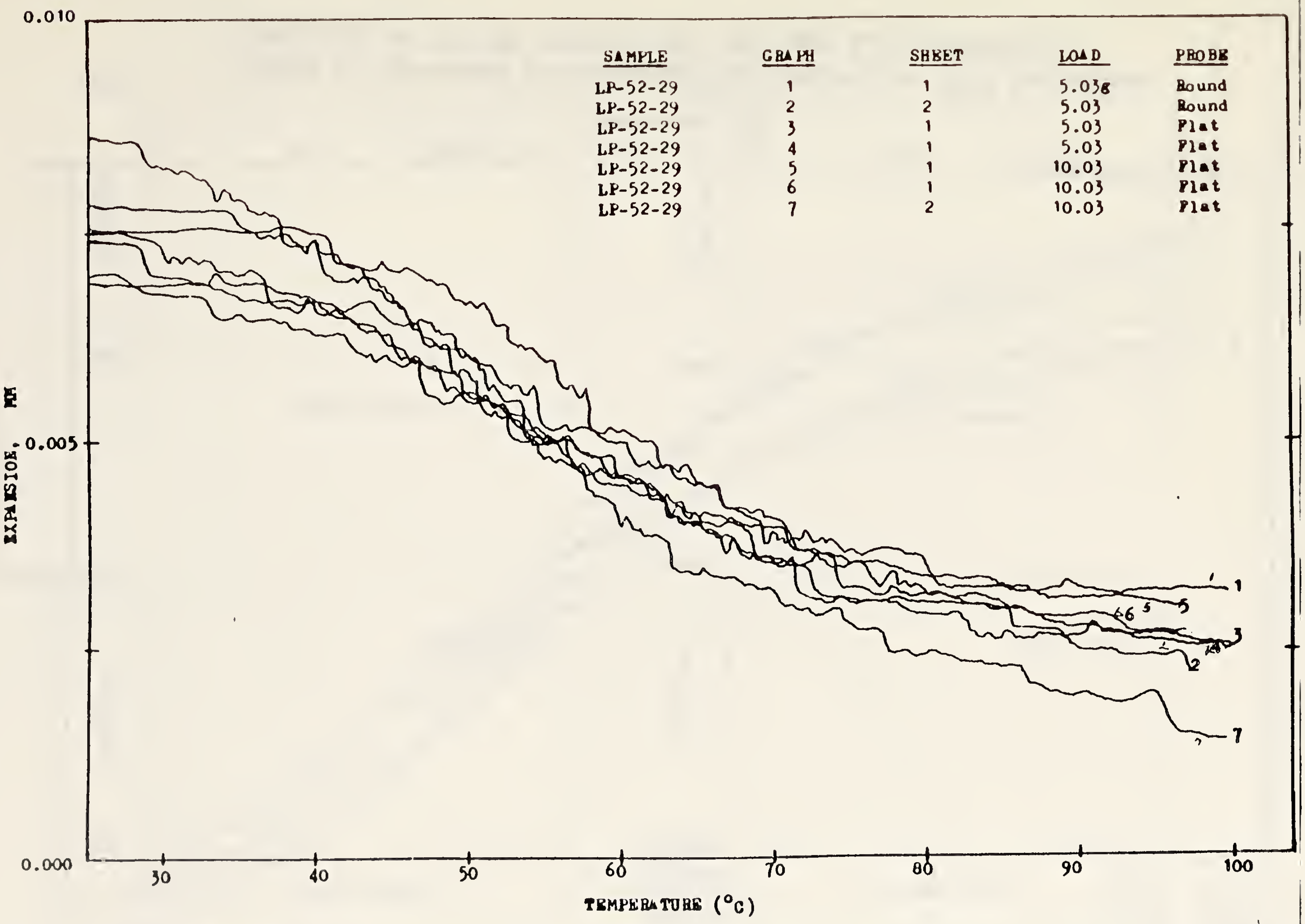
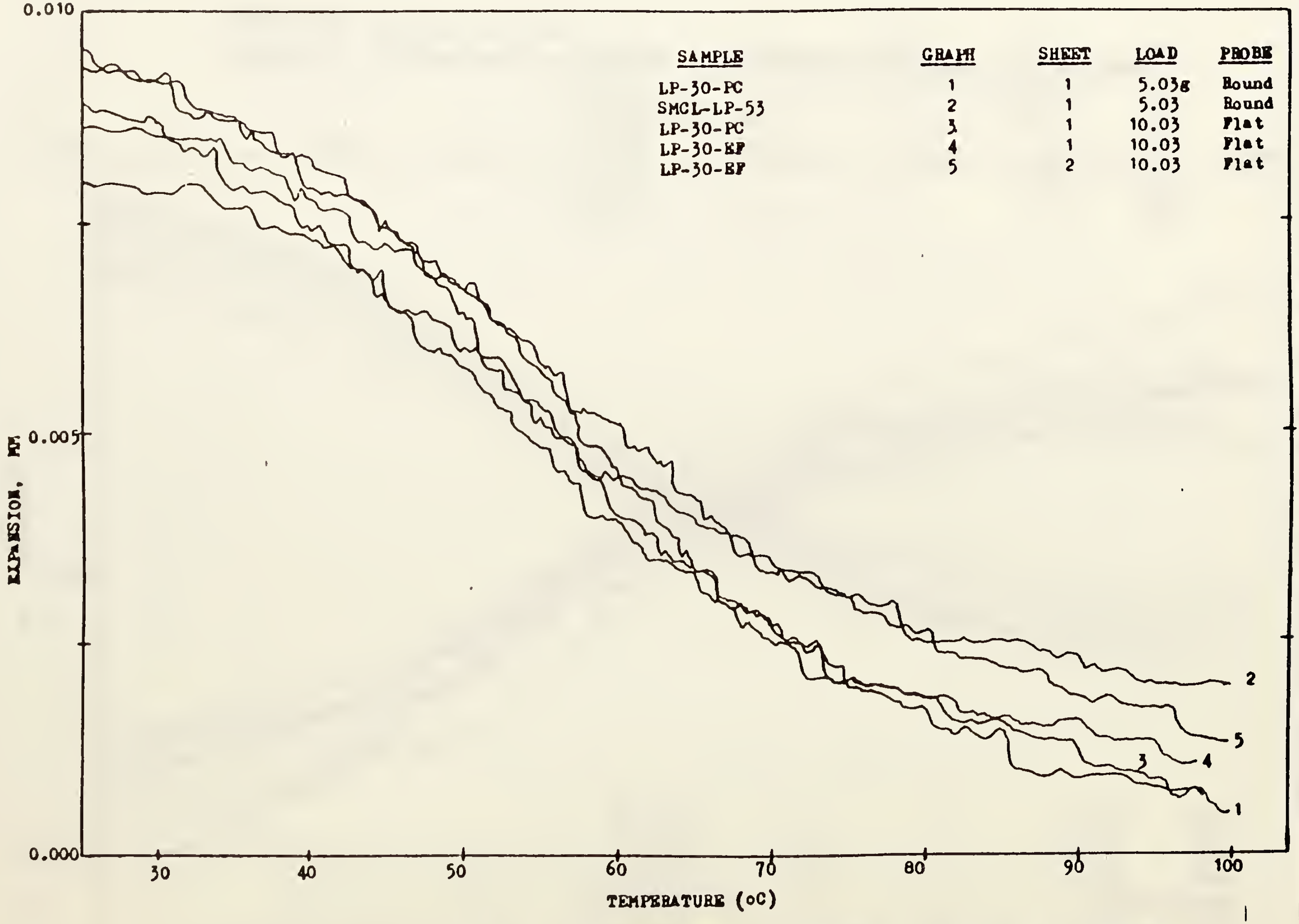


Figure 7. Decrease in thickness with heating to 100C for various specimens of LP–52–29.



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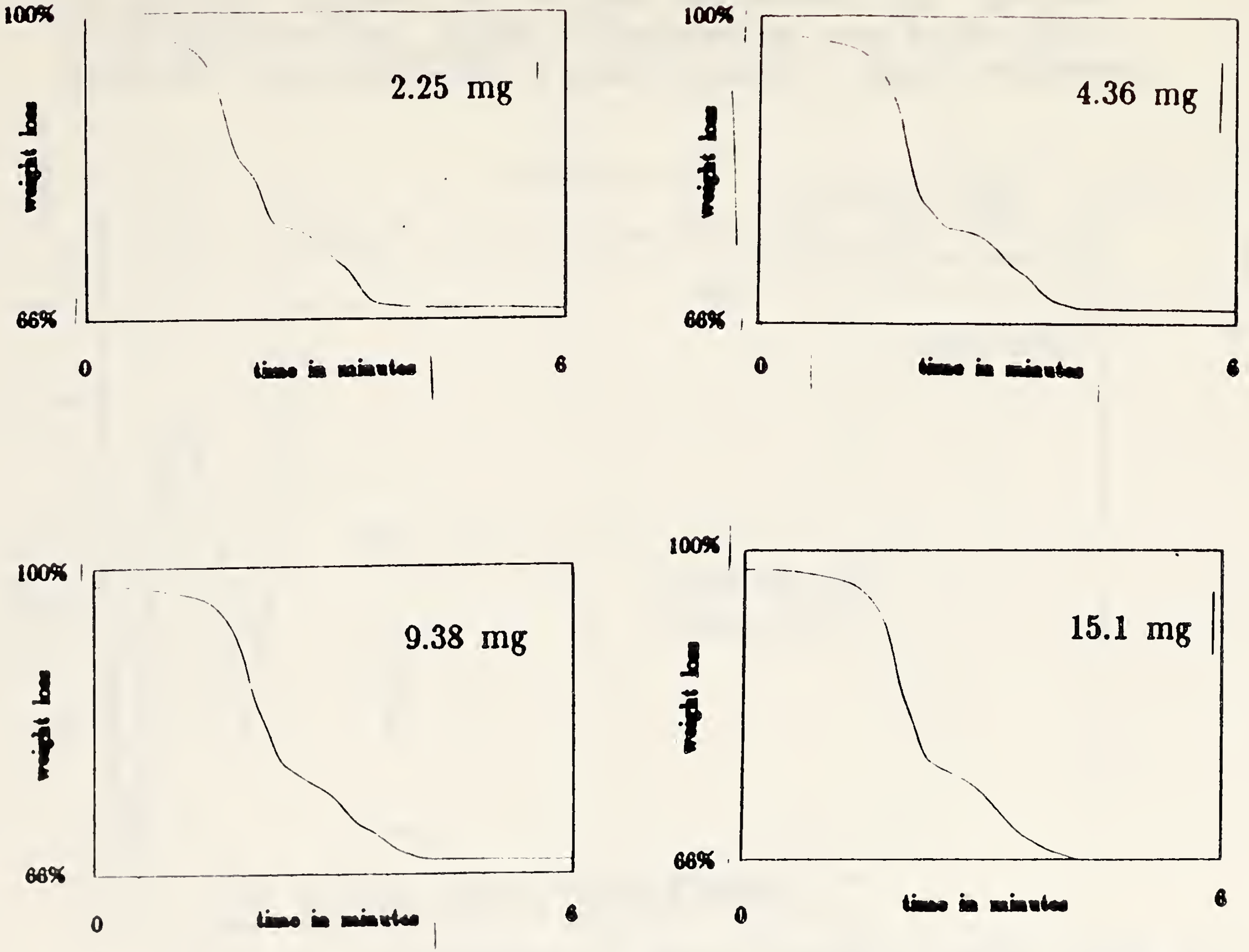

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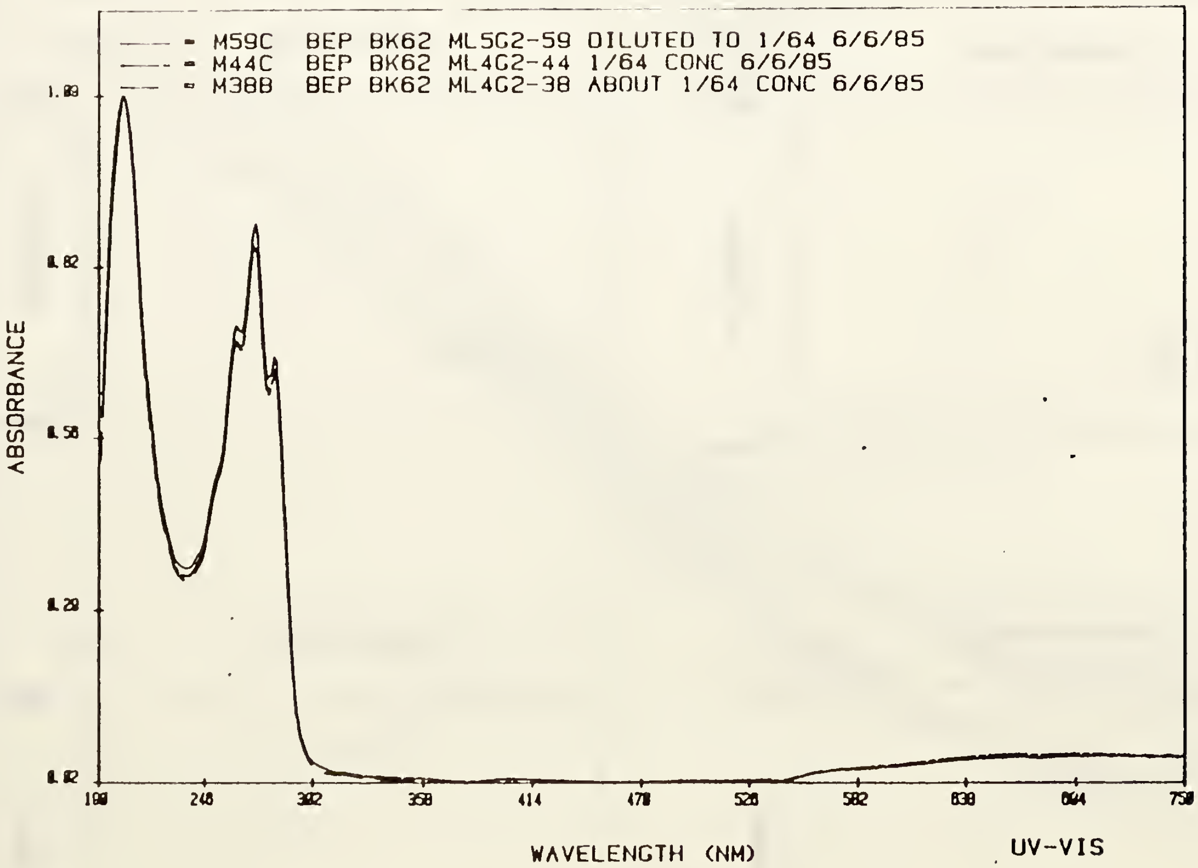

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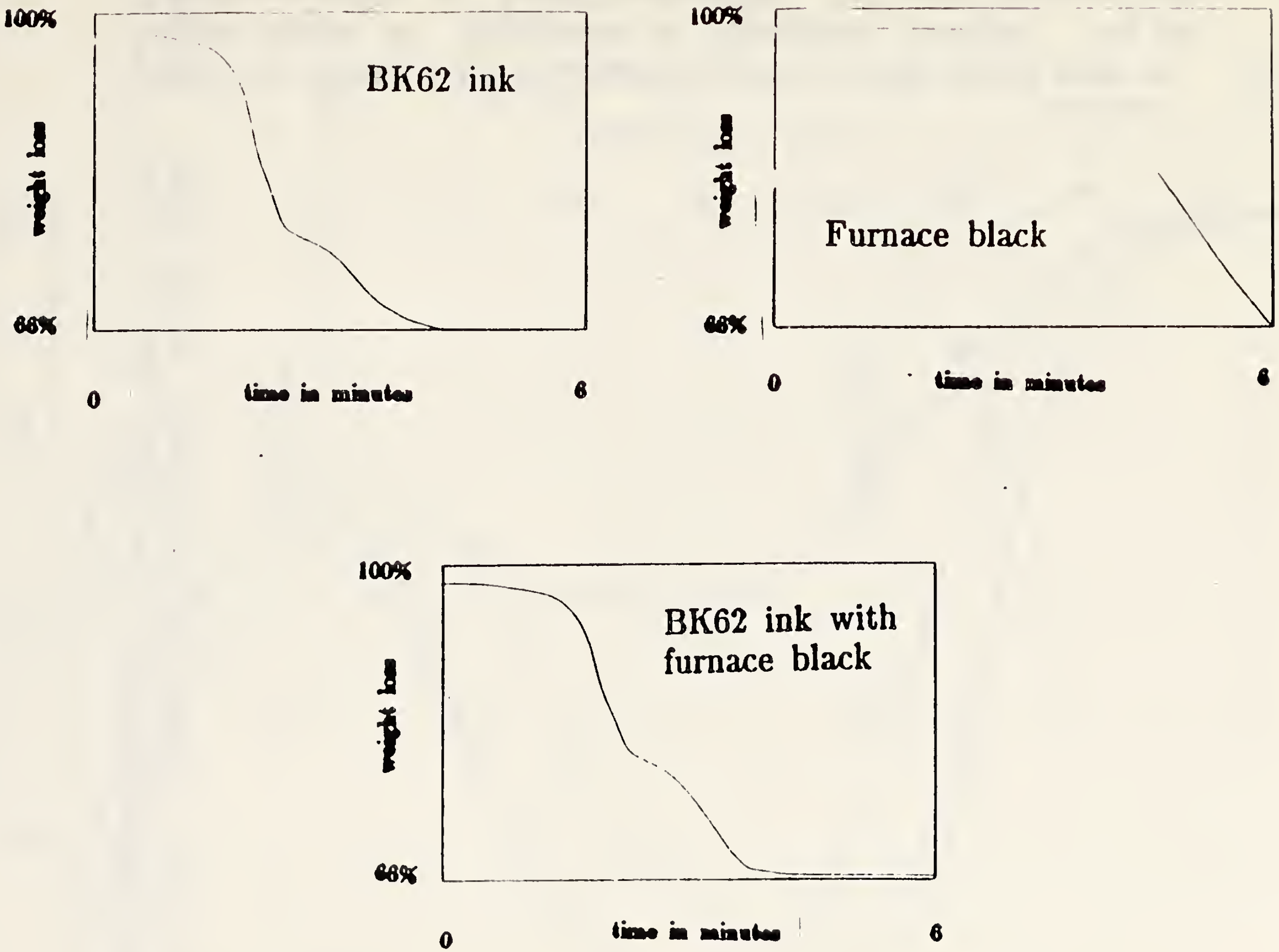

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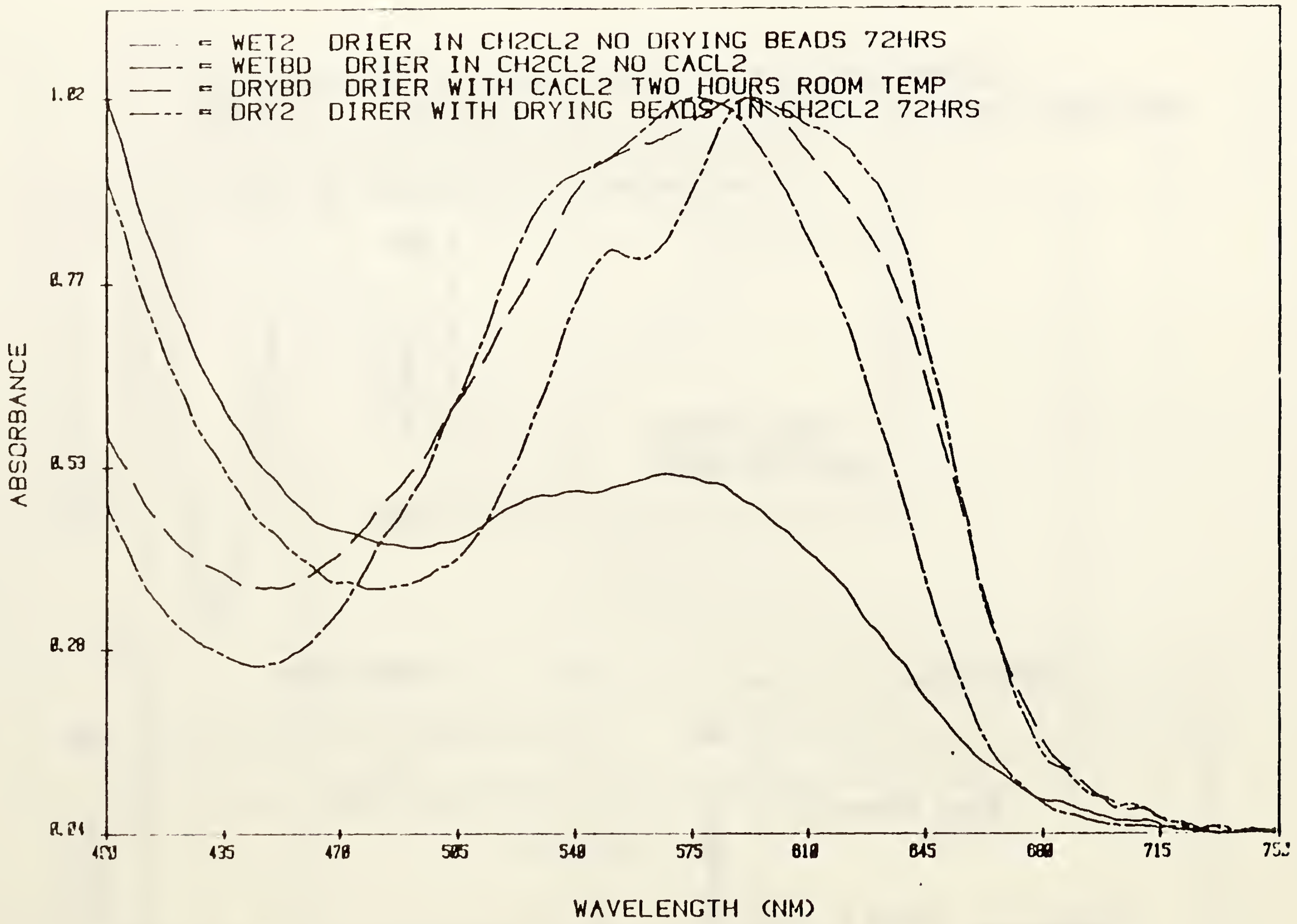

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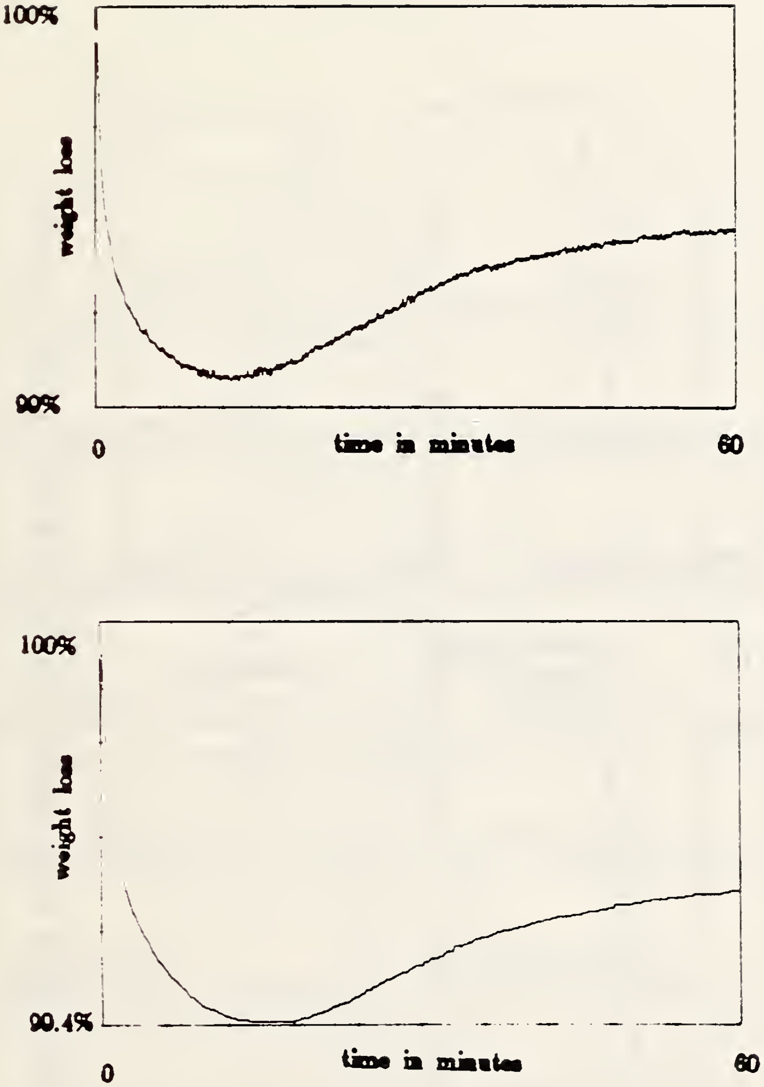

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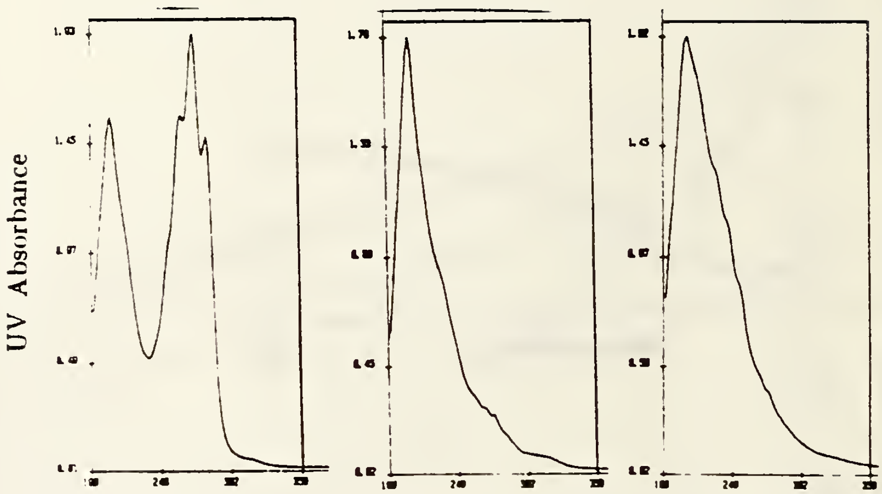
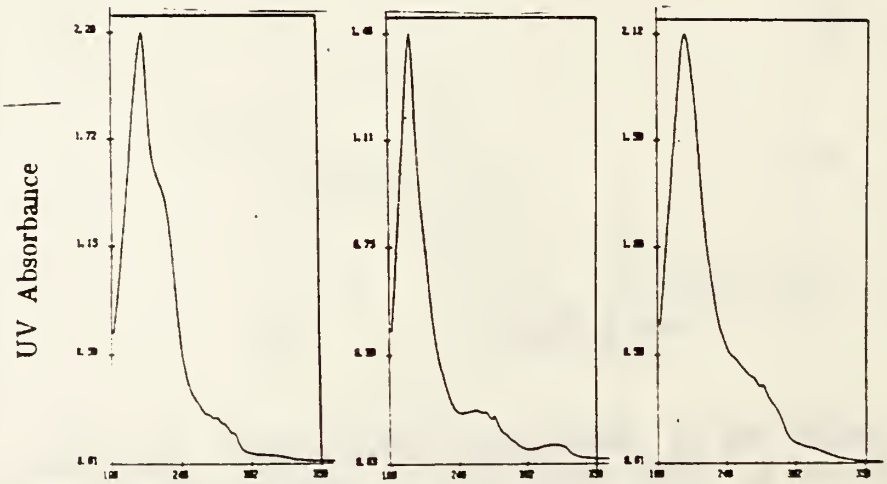


Bodied tung oil

special intaglio vehicle

cobalt drier

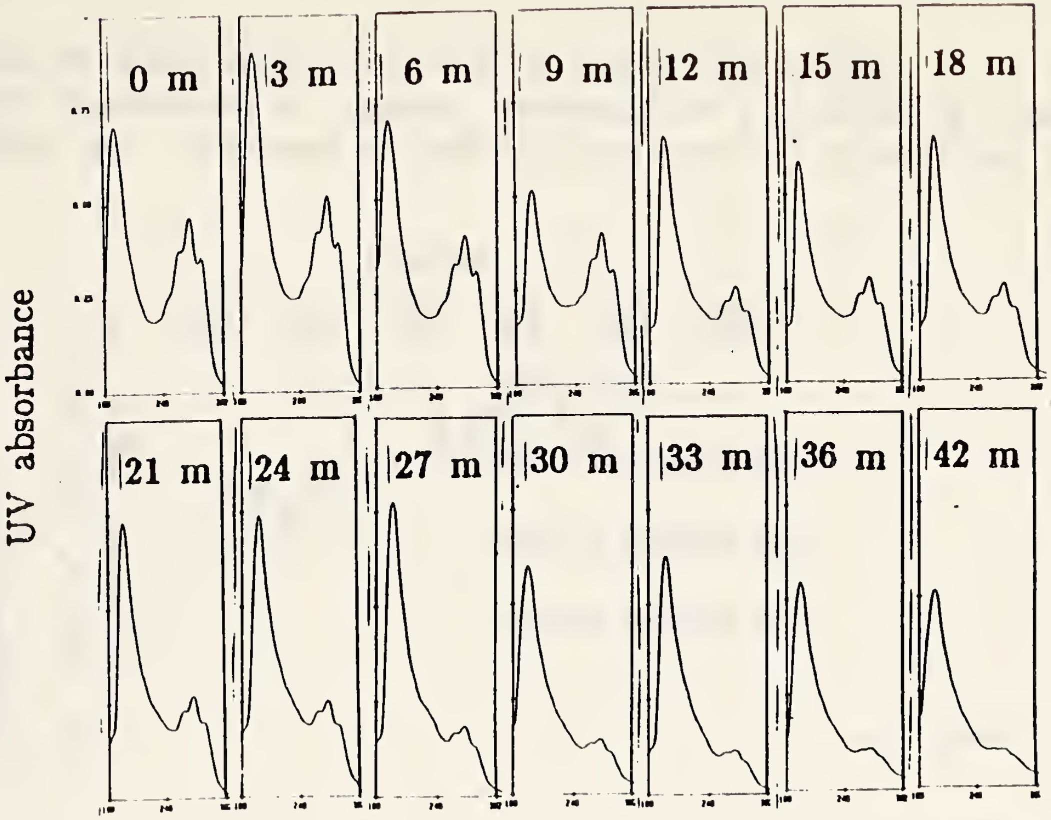


solar varnish

soya lecithin

high gloss varnish

Figure 14. UV absorbance spectra of the liquid components of BEP BK62 mod 3 intaglio ink.



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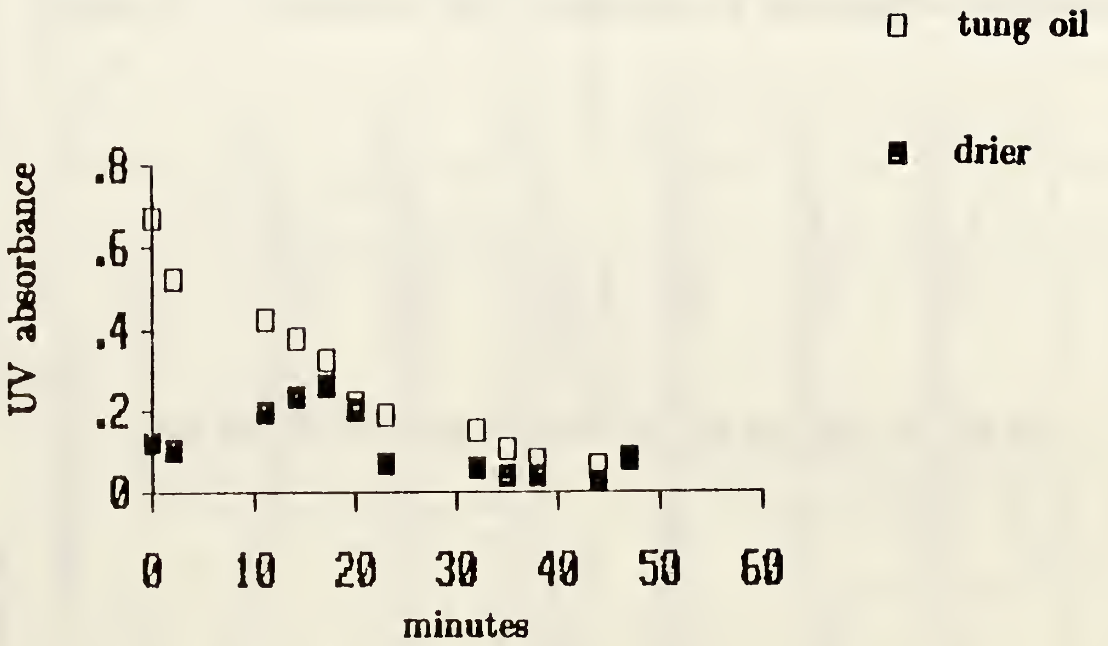

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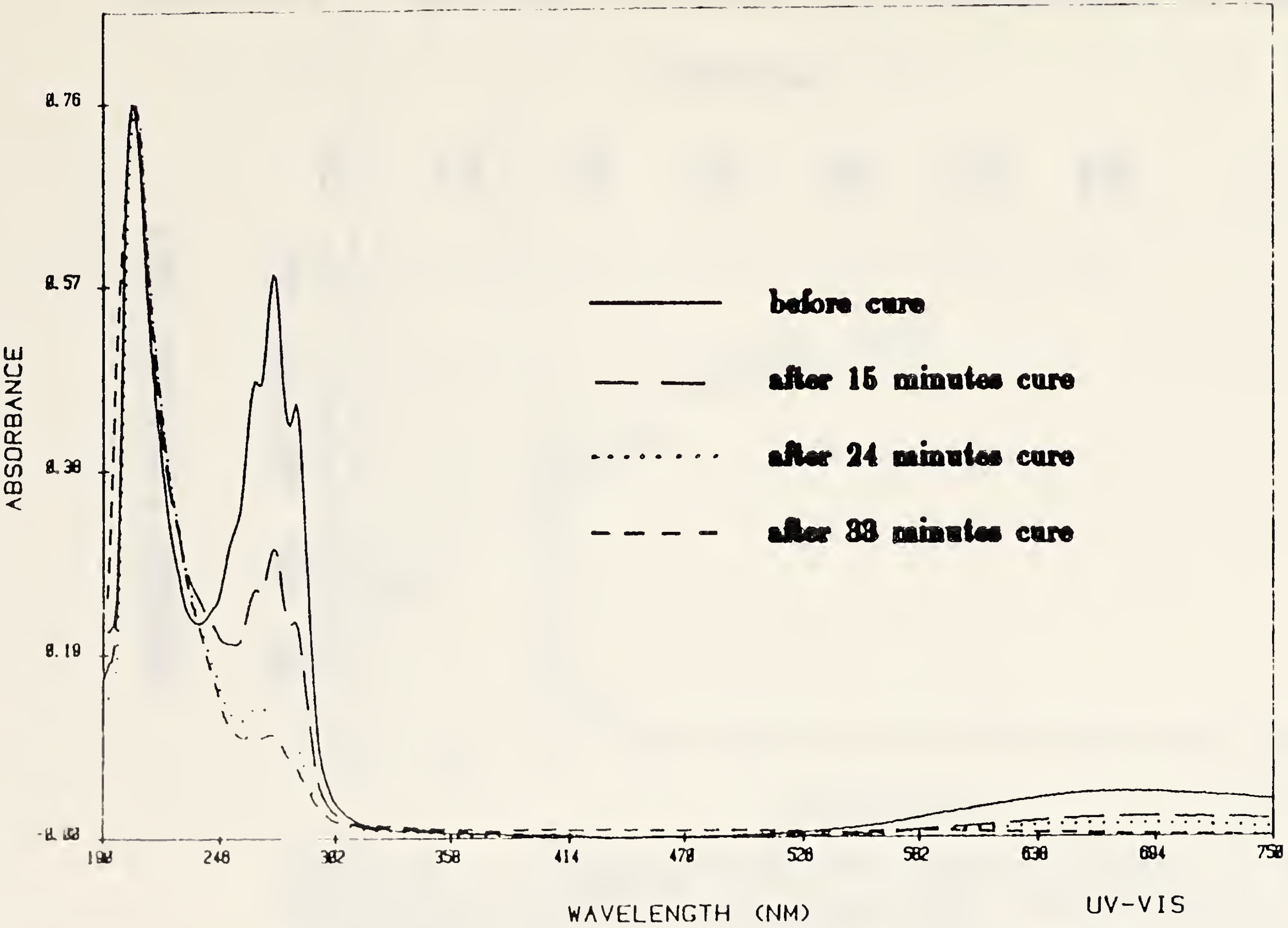

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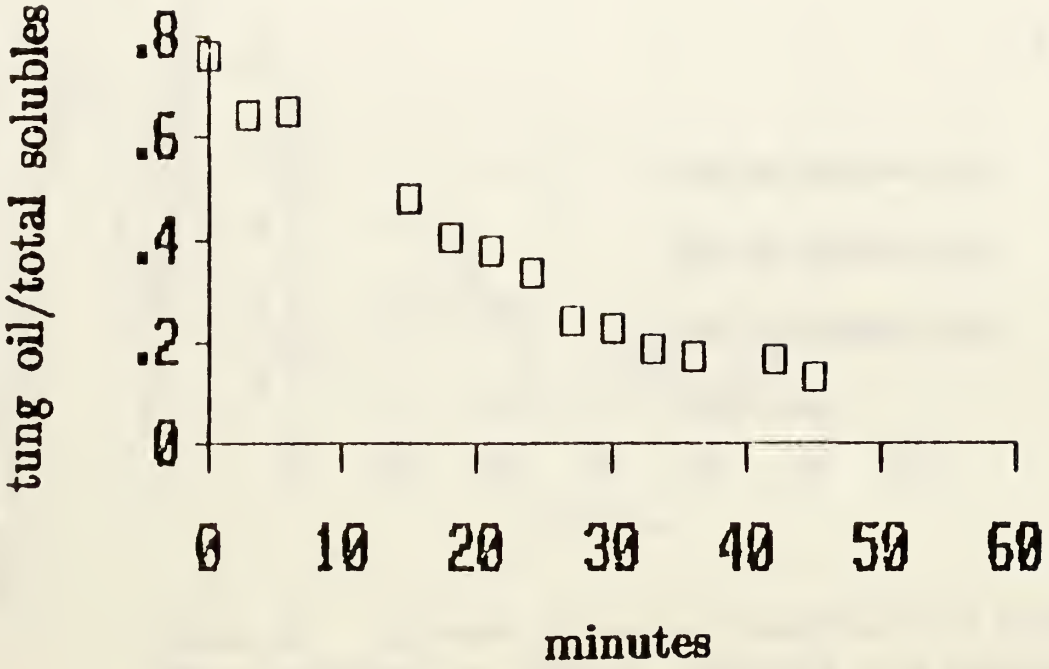

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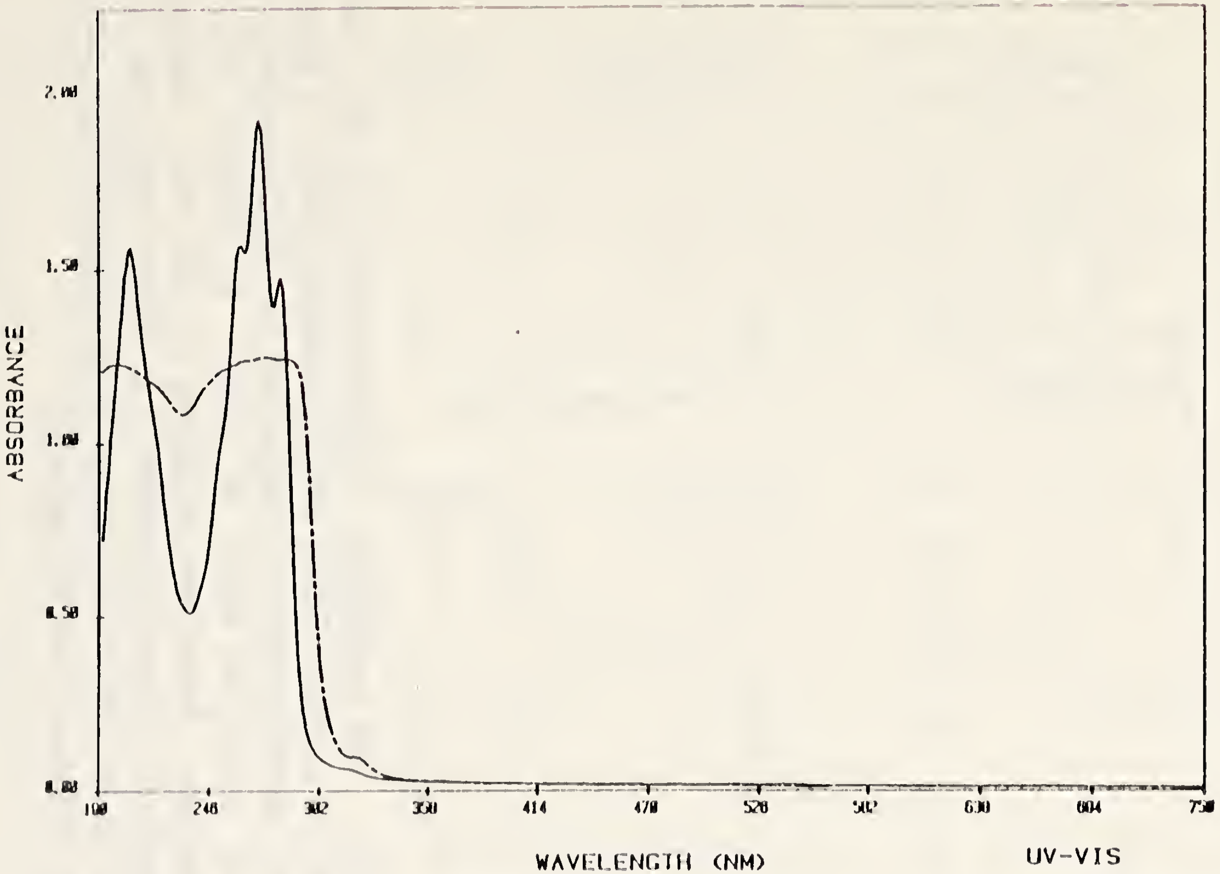

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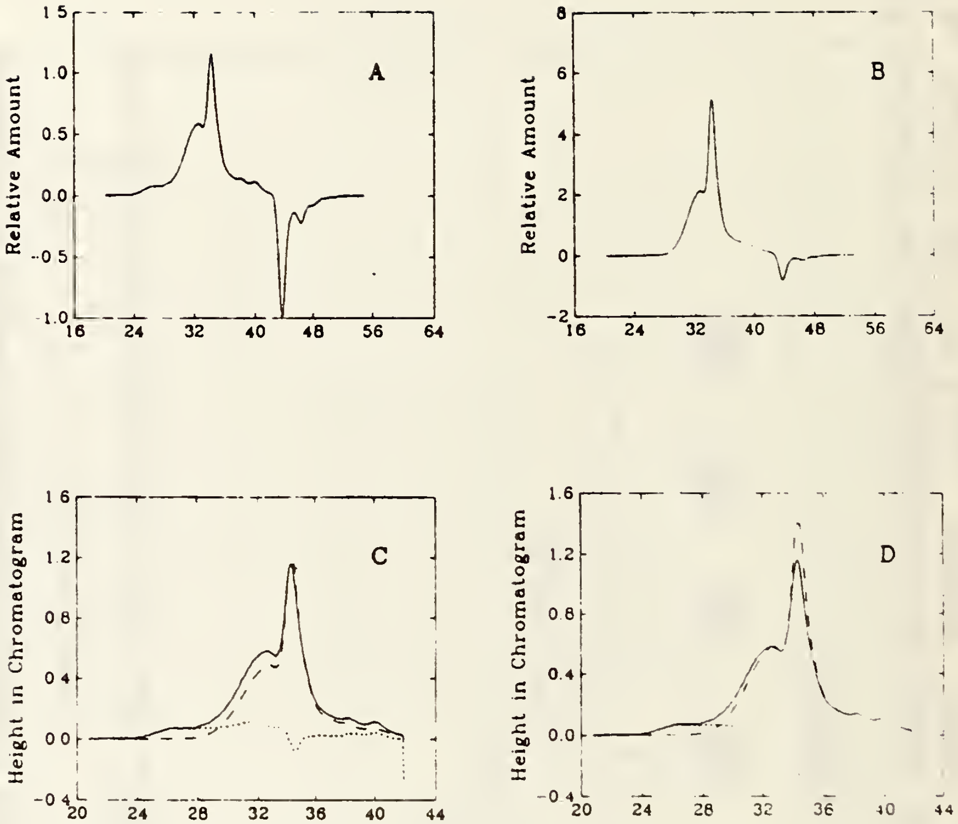

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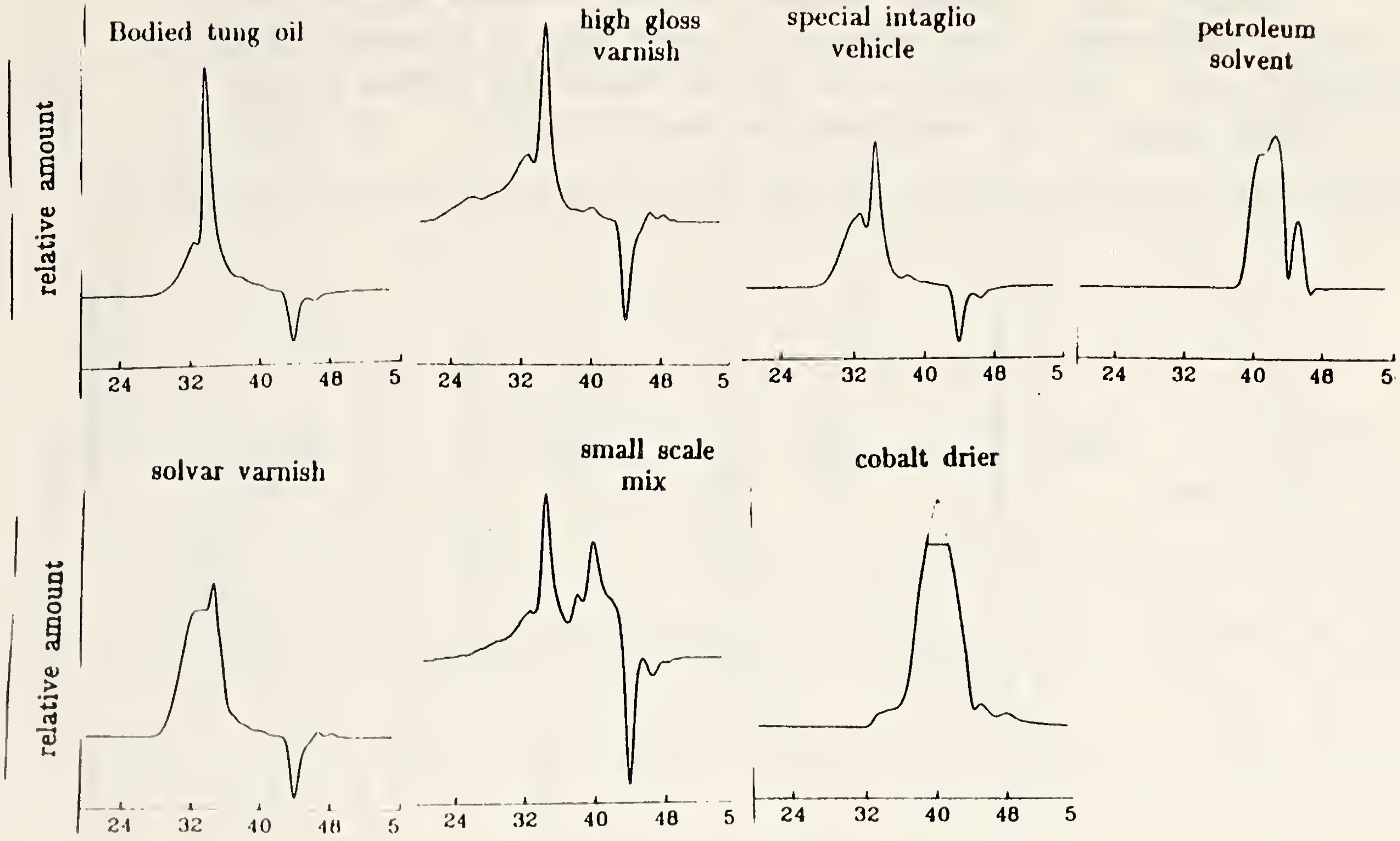
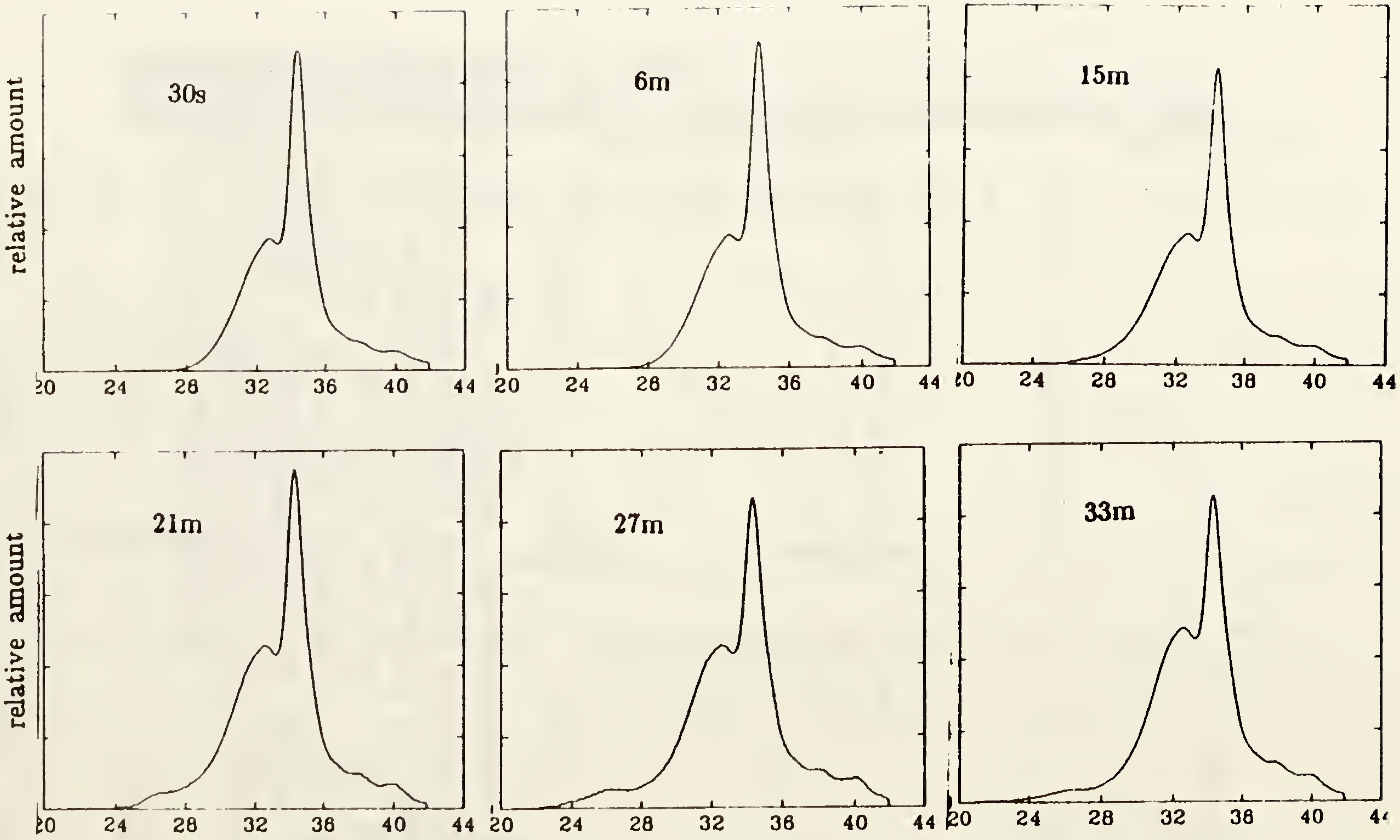


Figure 21. Chromatograms of the liquid components of BEP BK62 mod 3 intaglio ink in THF.



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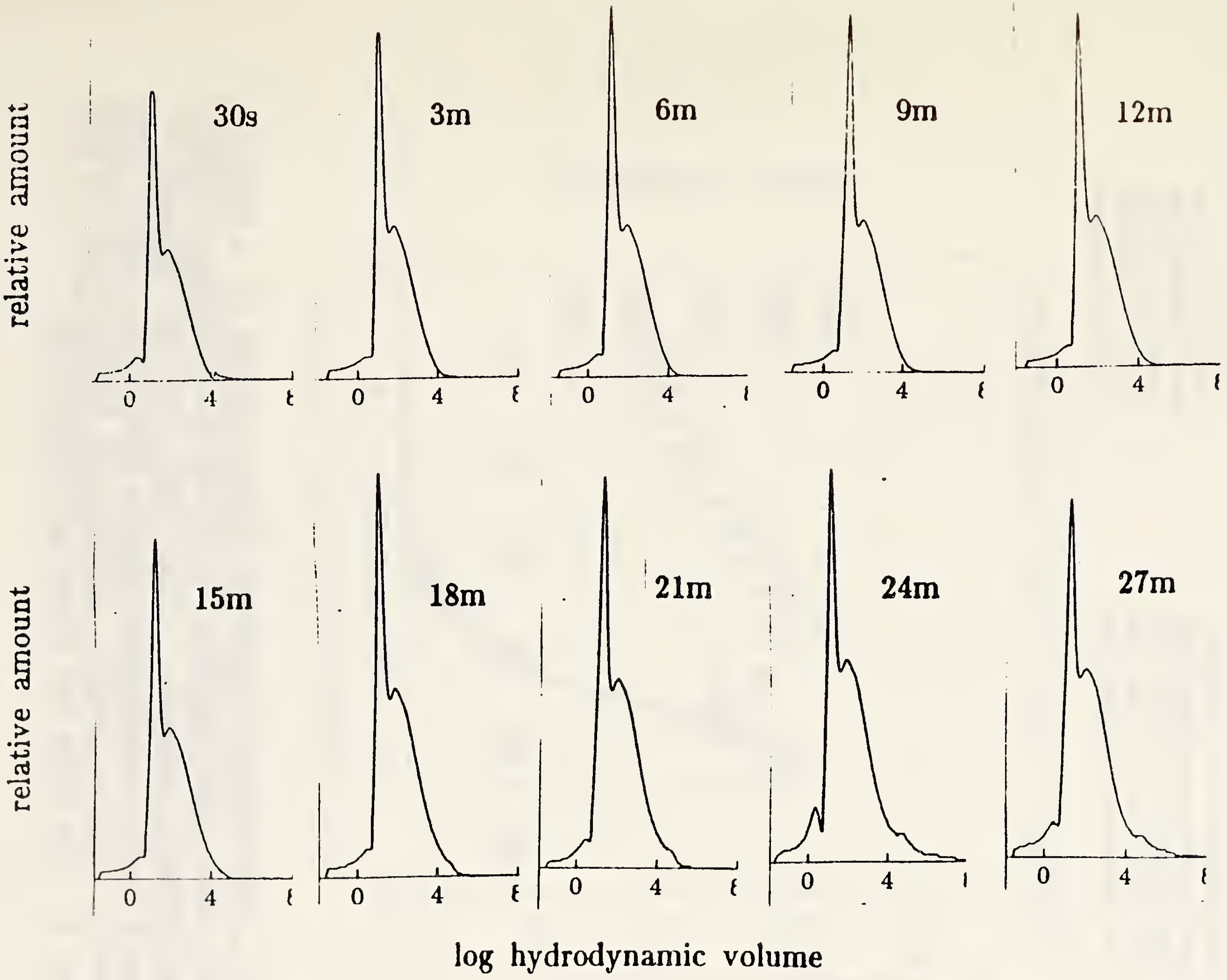


Figure 23. Chromatograms of a curing ink transposed into terms of log hydrodynamic volume. The high molecular weight material formed during curing appears at log hydrodynaimc volumes higher than 4. Cure times as shown.

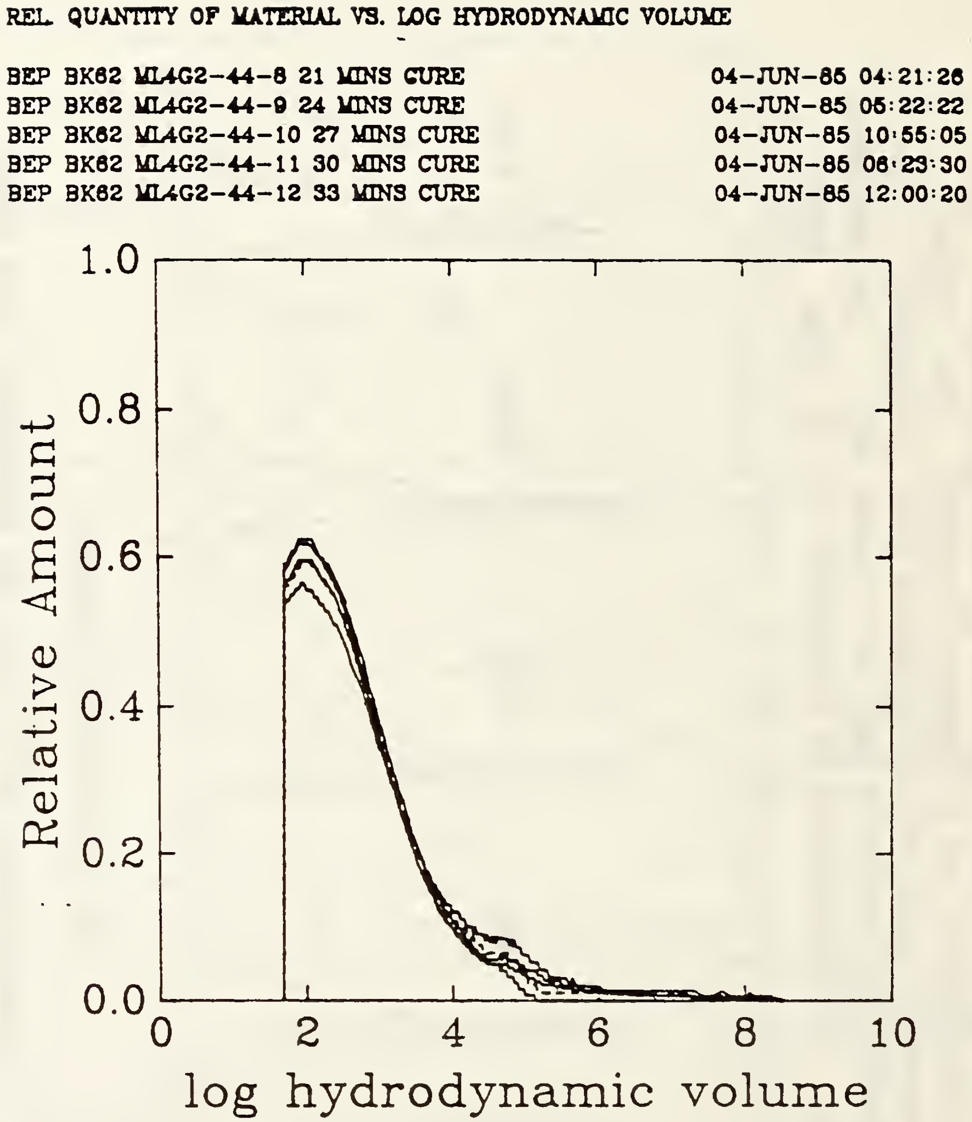


Figure 24. Superposition of selected chromatograms of a curing ink. The times cover the time at which the viscosity of the curing ink suddenly increases. The curve for 27 minutes is lowest near 2 in log hydrodynamic volume and highest near 5. The curves for 21 minutes and 33 minutes are highest near 2 and lowest near 5. The other two curves are intermediate.

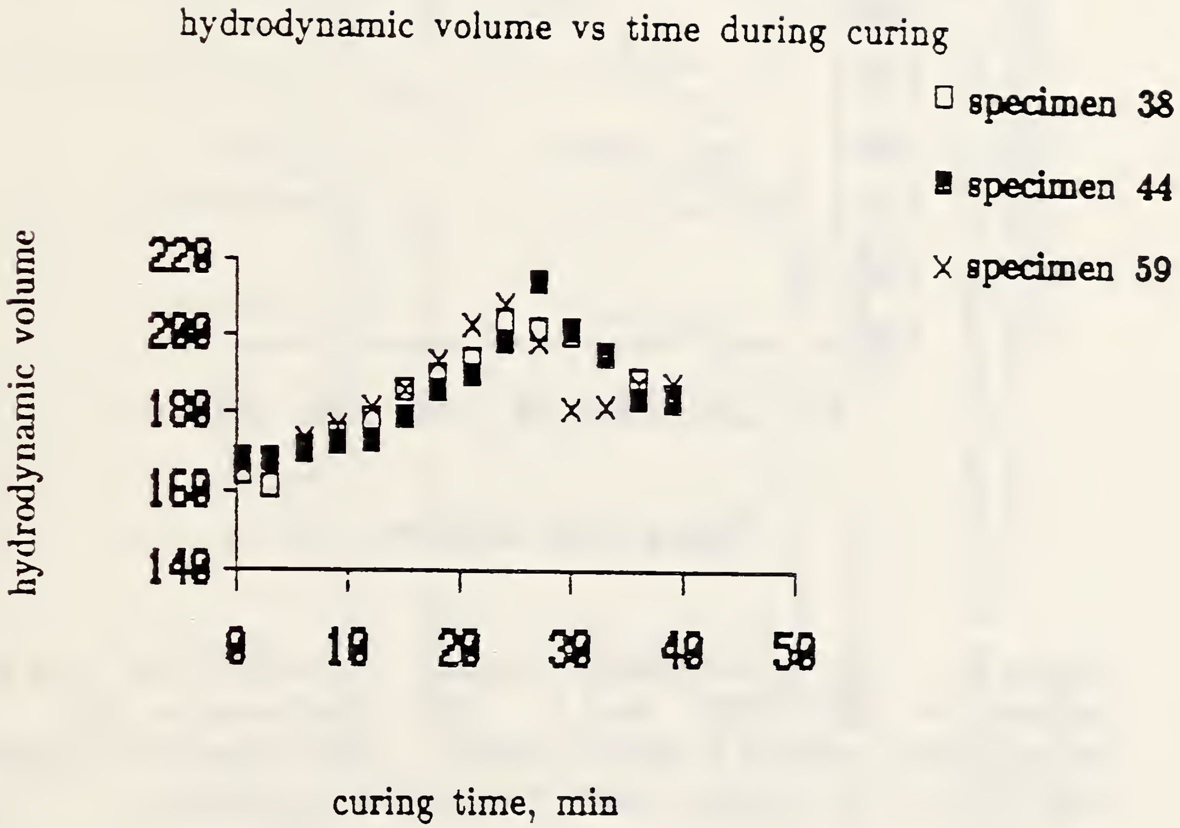


Figure 25. Change in average log hydrodynamic volume with cure as determined from GPC chromatograms. The log hydrodynamic volume passes through a maximum just before the viscosity of the curing ink suddenly increases. (Only the soluble portion of the ink is characterized in this way.)

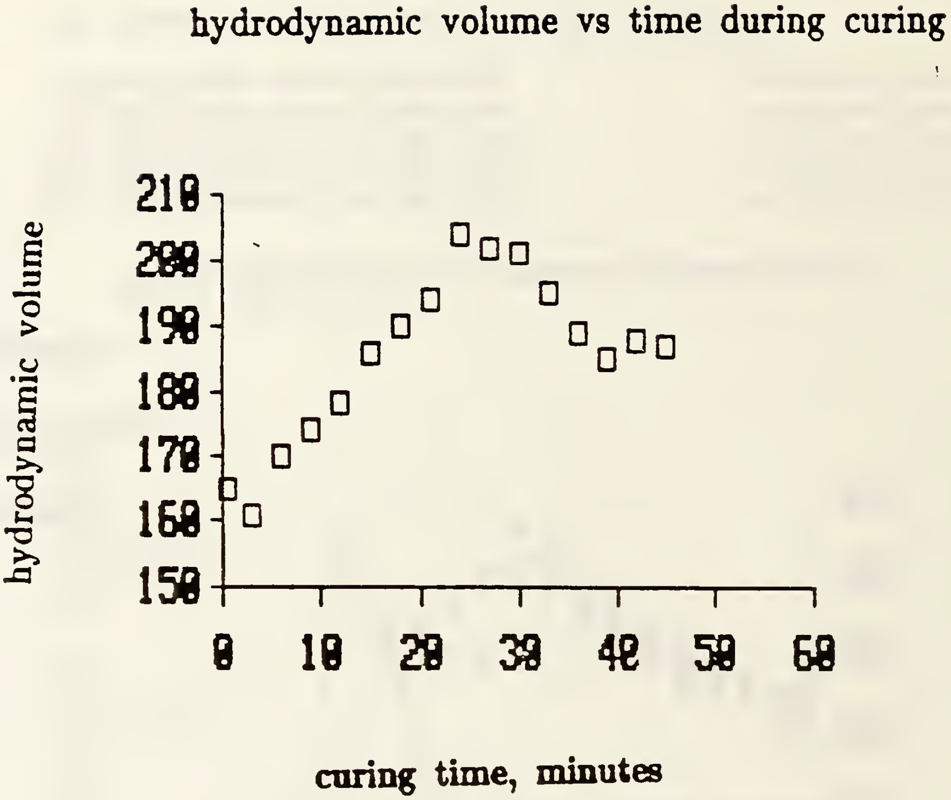
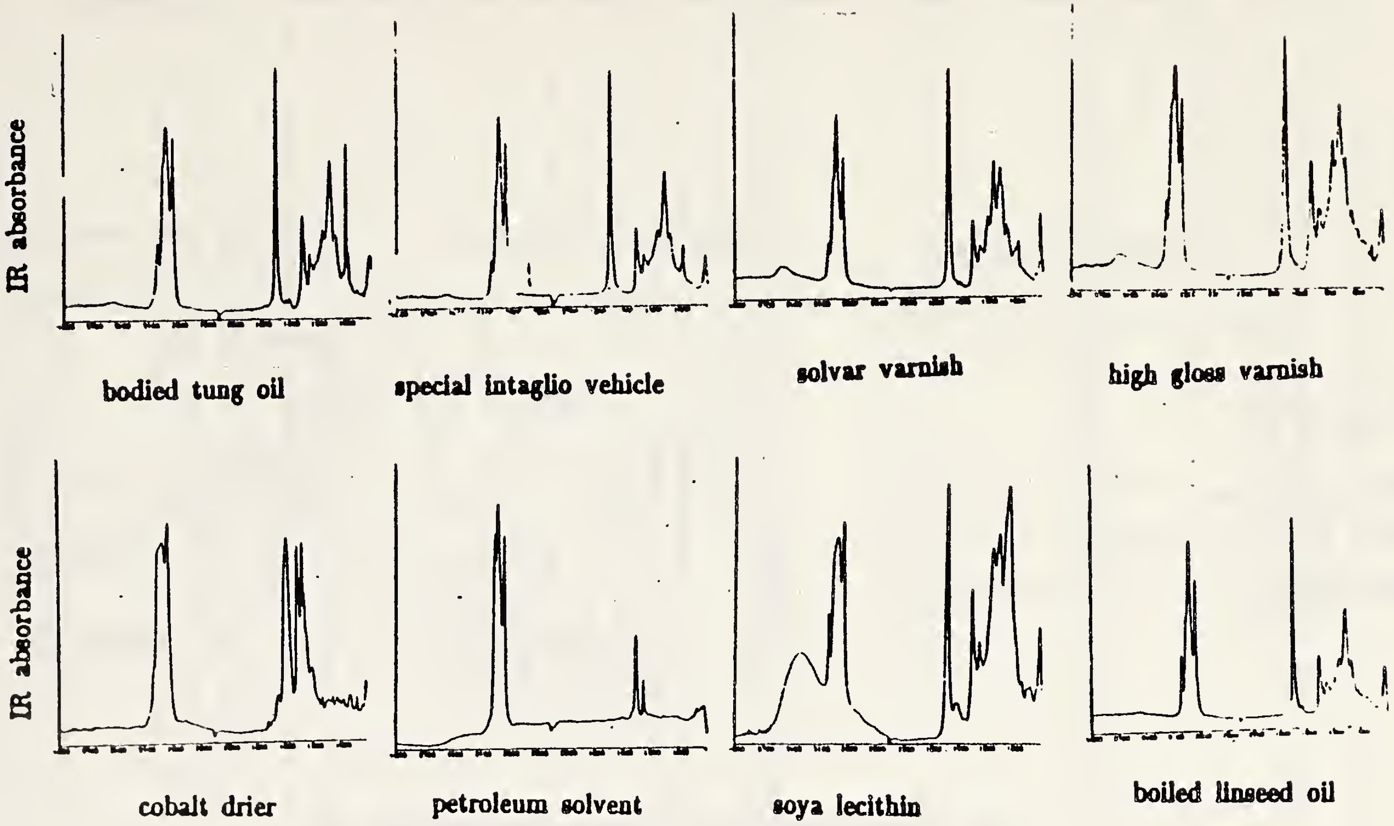


Figure 26. Log hydrodynamic volume versus time of cure for a specimen of BEP BK62 mod 3. The maximum in log hydrodynamic volume is shown clearly. "Cure time" for this ink specimen was 32 minutes, based on increase of viscosity.



bodied tung oil

special intaglio vehicle

solvar varnish

high gloss varnish

cobalt drier

petroleum solvent

soya lecithin

boiled linseed oil

Figure 27. Infrared spectra of the liquid components of BEP BK62 mod 3 spread on a sodium chloride plate. The spectral range is from 4000 wavenumbers (left) to 800 wavenumbers (right).

IR absorbance spectra of BK62 mod3 ink

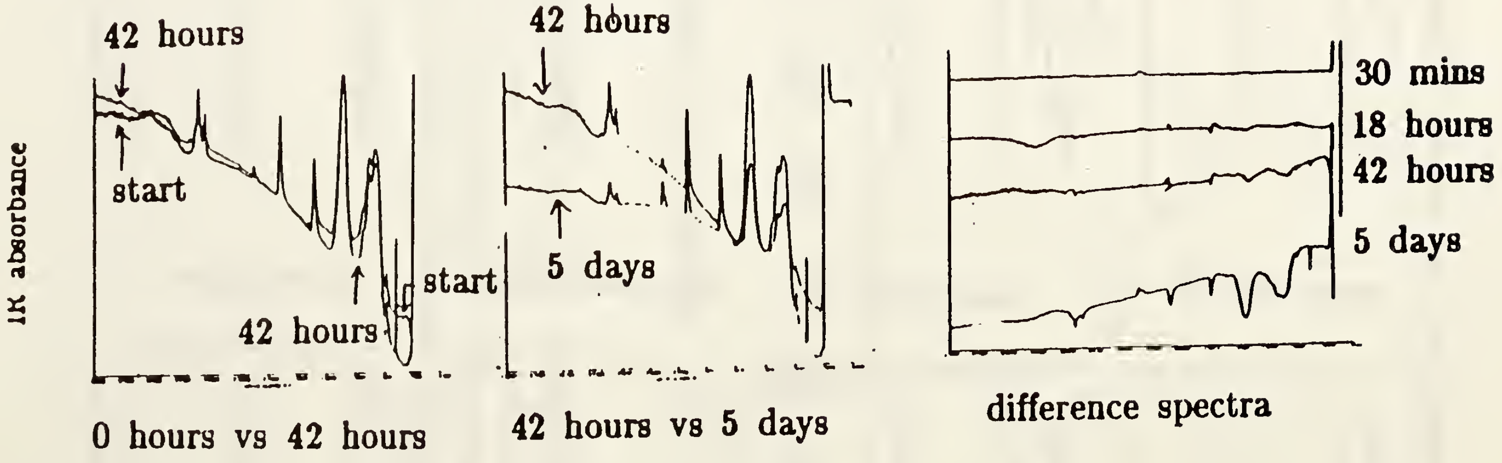


Figure 28. IR spectra of an ink curing on a sodium chloride plate taken at several long cure times at room temperature. The spectral range is from 4000 wavenumbers (left) to 800 wavenumbers (right).

Figure 28

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11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

This report covers the period October 1, 1984 to September 30, 1985. A report discussing principles important in formulating intaglio inks and giving several recommendations was provided to BEP and is reviewed here. Other reports on evaporation from intaglio inks, on a short thermogravimetric study of correctness of weighing out the ingredients in the inks, and on a thermomechanical study of gummed paper were provided to BEP but are also included here.

Two intaglio inks were sampled during mixing and milling at BEP and characterized in terms of cure times, ash residues, ultraviolet absorbance spectra measurements, and gel permeation chromatographic measurements. The results show that even when mixing to homogeneity on the scale of fractions of milligrams has been accomplished, the state of dispersion on a scale much finer than this may be critical. Cure times, ultraviolet absorbance measurements and gel permeation chromatography measurements have been used to follow ink cure. Refinement and application of the techniques developed in these studies are expected to lead to data which will help greatly in understanding the variables which influence the air-cure of intaglio inks. Application of these techniques and the development of new techniques as the needs arise will help in the design of improved inks.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Alkyds; analysis; formulation; gel permeation chromatography; intaglio printing inks; milling; mixing; thermogravimetry; UV absorbance.

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