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The effects of common solvents on different types of flexographic printing plates

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THE EFFECTS OF COMMON SOLVENTS ON DIFFERENT TYPES OF FLEXOGRAPHIC PRINTING PLATES

by

Jack D. Jenkins

A thesis submitted in partial fulfillment of the
requirements for the degree of Master of Science in the
School of Printing in the College of Graphic Arts and Photography
of the Rochester Institute of Technology

May, 1985

Thesis Adviser: Chester J. Daniels

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The conception and subsequent development of an idea always represents the work of many people. I owe my sincerest thanks to those persons who lent their expertise and support toward the completion of this project, including my wife Mary for her tireless support and concern; my adviser Chester Daniels for his help and guidance; and for his early encouragement, my dear friend Bruce W. Capriotti, without whom this idea would never have come to realization. Also, I wish to thank the many faculty who have given me the inspiration to finish this task, namely Dr. Robert Hacker, Dr. Julius Silver, and Professors Joseph Noga and Charles J. Weigand.

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School of Printing
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Rochester, New York

CERTIFICATE OF APPROVAL

MASTER'S THESIS

This is to certify that the Master's Thesis of

Jack D. Jenkins

with a major in Printing Technology has been approved by the Thesis Committee as satisfactory for the thesis requirement for the Master of Science degree at the convocation of

May 1985

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THE EFFECTS OF COMMON SOLVENTS ON DIFFERENT TYPES OF FLEXOGRAPHIC PRINTING PLATES

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An Abstract

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ABSTRACT

A dynamic development which has sparked flexography is the introduction and use of photopolymer plates. These plates have simplified flexographic printing by reducing the amount of time and effort needed to prepare plates for press and makeready. An experiment was conducted to determine the effect of commonly used solvent mixtures on flexographic plates. The plates tested include those using natural rubber, Buna N, and various photopolymers. The experiment specifically studied change in hardness of these plate materials due to immersion in different solvent mixtures over time. Noticeable differances in the degree of softening of plates was observed after 24 hours of immersion.

Differences in the degree of softening were found in the plates after soaking in different percents of solvents. It was also discovered what percents of different lactol spirits and normal propyl acetate added to alcohol would affect the plates the most. Further, these differences were detectable at different periods of time.

Most plates softened with time. One plate softened to such a degree with the solvent of this experiment that it was difficult to determine which solvents had a significant effect. This, of course, is due to the fact that solvents compatible with this plate were not used in this experiment.

All photopolymer plates performed poorly in acetates, but it would be possible to use acetates with these plates over short periods of time on small press runs.

When using flexographic plates of the composition tested in this experiment it is recommended that the practitioner use less than five percent of lactol or ten percent normal propyl acetate for a minimum affect on these plates over a short period of time.

Abstract approved: Chester J. Daniels
thesis advisor
Senior Technologist
title and department
April 26, 1985
date

CHAPTER I

INTRODUCTION

Flexography is a high-speed method of relief printing from which a fluid ink is transferred, using rotary actions, from a rubber printing plate onto a moving web of substrate.[1] Historically the process has been considered capable only of printing low quality images, such as might be found on bread bags, in great volume. The process actually offers unique advantages to the printer, converter, and customer. Flexography is capable of printing on just about anything that will run through a press, including cellophane, fabric, linerboard, film, and newsprint.[2] Technological developments are improving flexographic printing, enabling it to faithfully reproduce fine-line images and halftones. Printing plates are both inexpensive and durable, with some having the capacity to print up to 6,000,000 impressions. Ink-distribution systems of newer presses include automatic ink-viscosity controls incorporated into their ink pumps.

Graphic arts processes, including letterpress, offset lithography, gravure, and screen printing use rubber or rubber substrates at some point in their process. Flexography uses these materials in the part of the printing process crucial to the successful transfer of an image--the plate.

Flexographers know that the application of toluene to a natural rubber plate or Methyl Ethyl Keytone (MEK) to a Buna N synthetic rubber plate will swell low spots in these plates. These are often used in an attempt to change plate thickness. The practice of swelling low spots to make the plate thickness more uniform reduces the need to print with excessive pressure, a situation that could lead to poor image definition, bad ink transfer and excessive wearing of the press gears. Because these solvents affect the plate materials so greatly, inks using toluene or MEK are unsuitable when printing with natural rubber and Buna N plates, respectively.

Flexographers are therefore confronted with a dilema: they must use inks formulated to adhere to a given substrate even though the inks are reducible only with a solvent that swells the plate. This dilemma is intensified by the fact that high-quality flexographic printing, like that demanded by emerging flexographic markets such as newspaper printing, rely on the degree to which plates made from rubber and rubber substitutes, such as photopolymeric materials like the Cyrel plate, can resist swelling caused by these reducing solvents. Unfortunately, little understanding exists concerning the effects of these solvents on flexographic plates, and little research has been done in this area.

FOOTNOTES FOR CHAPTER I

[1] Howard K. Sheldon, ed., Flexography: Principles and Practices. (Brooklyn, New York: Flexographic Technical Association, 1970) p.1.

[2] Victor Strauss, The Printing Industry. (Washington: Printing Industries of America, 1967) p.31.

CHAPTER II

REVIEW OF THE LITERATURE

A review of the procedures required to produce molded rubber and photopolymer plates, including chemical structure, and some printing and platemaking problems common to both is expected to result in a better understanding of the two plate systems. Differentiating between rubber plates and photopolymer plates is technically incorrect because both are composed of similar polymers. Instead, the plates should be distinguished on the basis of both the process used to form the image area and the chemical reactions which occur during the platemaking process. More specifically, the production of rubber plates begins with the manufacture of the desired image onto a pattern plate, which is usually a photoengraving made out of zinc, magnesium, or copper. For this reason rubber plates are actually members of a class of relief plates known as duplicate plates.[1] Photoengravings which have good shoulder angles, no pimples, and no scum--requirements for a good mold for a duplicate rubber plate--are a tedious, time consuming and expensive process. To make a photoengraving the following procedure is normally applied.

1. Prepare a high contrast negative of the image that is to appear on the plate.
2. Coat the metal from which the photoengraving will be made with an ultra-violet (UV) sensitive coating.
3. Place the negative in contact with the plate and expose it to actinic light which is rich in UV radiation.

4. Etch the image after the exposure using either thermal or chemical methods.
5. Descum, or wash, the plate with a solvent and etch it in a powderless etching bath.
6. Hand tool the plate after etching to remove imperfections like pimples[2].
7. Place a piece of molding board, which is a paper board impregnated with a phenolic thermosetting resin, on the lower platen of a molding press.
8. Place the photoengraving atop the molding board. The thickness of the floor of the matrix is governed by the positioning of bearers on either side of the matrix-engraving assembly.
9. Close the platens of the molding press to squeeze the matrix board and photoengraving together under high pressure and at a temperature of 300 to 310 degrees Fahrenheit. (The amount of pressure required for a particular mold will vary depending on the nature of the original and its area. If the original is a type form, no more that 300 PSI should be used. If an engraving is used, pressures may be necessary up to 1000 PSI. The pressure required to mold the engraving varies proportionally with the amount of solid area to be molded.)[3]
10. Cure the plate for ten minutes by allowing the matrix board and photoengraving, now squeezed into one piece, to rest undisturbed in ambient room conditions.
11. After curing strip the matrix from the photoengraving.

12. Place the matrix face up on the lower platen of a molding press.
13. Place a charge, or piece, of unvulcanized rubber atop the matrix.
14. Position bearers on either side of the assembly. The height of these bearers will determine the height (thickness) of the finished plate.
15. Close the platens of the molding press to squeeze the matrix board and rubber charge together under high pressure and at a temperature of 300 - 310 degrees Fahrenheit. (Pressure requirements vary according to the type of rubber being used, the plate thickness and plate construction. Pressure required to mold rubber plate can be as high as 600 to 1000 PSI.)
16. Allow the rubber-matrix to cure about eight to ten minutes. The exact curing time is determined by the particular rubber compound used.
17. Strip the rubber and matrix apart at the end of the cure. The excess rubber, or flash, is trimmed off the edges of the plate.[4]
18. Check the plate for thickness in several areas with a micrometer. If the plate is .001" too thick, or the thickness is not uniform, the back should be ground on a grinding machine removing unwanted plate material. The plate is then ready for mounting onto the plate cylinder.[5]

Besides being time consuming to make, this type of plate can lose image fidelity because of the many steps and kinds of materials required for its preparation.

In contrast to the preparation of a rubber plate, the manufacture of a photopolymer plate is simple. Rubber plates are chemically created through a process known as vulcanization, where heat and pressure are used to mold the image area. Photopolymer plates are made by an addition photopolymerization process, where the desired image area of the plate is exposed to and hardened by actinic radiation while the unexposed non-image area is washed out with a solvent. Platemaking is outlined by the following:

1. Place a sheet of factory-prepared photopolymer plate material face down in an exposure unit and expose it through the back. This exposure produces the thickness, of the plate floor, which is the area below the relief image area.
2. Turn the plate face up and lay a previously prepared high-contrast negative on top of the plate material.
3. Bring the negative and plate material into intimate contact using a vacuum.
4. Expose the plate and negative assembly to a UV light source for a predetermined amount of time.
5. Remove the plate from the exposure unit. Place it in a solvent washout unit to remove the non-image areas of the photopolymer materials not hardened by the actinic light.
6. Bake the plate in an oven at 300 degrees Fahrenheit for about 45 minutes to evaporate any solvents retained from the washout process.
7. Give the plate a short post exposure or chemical treatment to reduce its surface tackiness.

The methods used to produce either the molded or the photopolymeric plates suggest that these substances, although consisting of similar polymers, may have potentially different chemical reactions to heat, pressure, and light. It is possible to speculate that the required catalyst is determined by the chemical makeup of the various polymers used for each respective plate type. A linear polymer is likely to be different from a block copolymer. An understanding of the chemical and physical nature and structure of these polymeric components is therefore useful in comprehending the chemical reactions occurring during the platemaking process.

Polymers exist in different physical states although they lack a gaseous state and exhibit properties of both a liquid and a solid when in a solid state.[6] See Figure 1.

According to one source:

> At sufficiently high temperatures, a linear polymer is an amorphous, rubbery melt. . . . At sufficiently low temperatures, the same polymer is a hard, rigid solid. Besides having varying physical states, polymers harden in two different ways.
> The change from a liquid to a solid for polymers is also unusual, because there are two completely distinct mechanisms by which they can solidify upon cooling: they can crystallize and form a rubber-like material or vitrify, and form a glass.[7]

Often when a polymer solidifies it has both a degree of crystalinity and a degree of glassiness. The ratio of these solid states will vary from polymer to polymer and helps determine, along with the type of polymer, the properties of the polymeric material.[8] Polymers with high percentages of crystalinity are rigid and brittle while those having high percentages of glassy solids are rubbery and soft. Figure 1 graphically illustrates this concept.

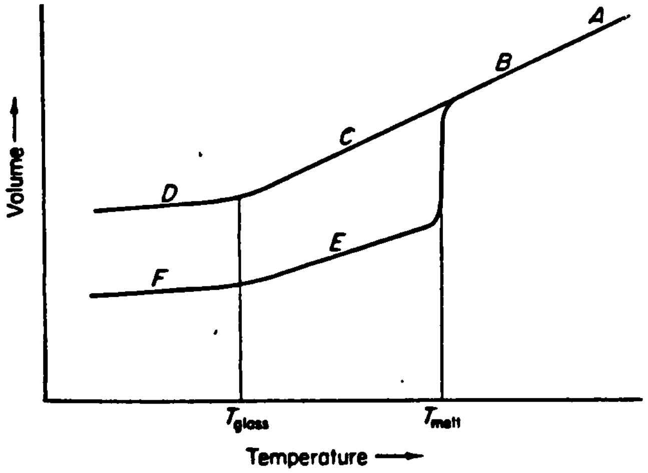


Figure 1. Volume-temperature curves for a crystalline polymer. (A) Liquid region, (B) Liquid with some elastic response, (C) Rubbery region, (D) Glassy region, (E) Crystallites in a rubbery matrix, and (F) Crystallites in a glassy matrix.

A polymeric structure is created from monomers. By definition a polymer is:

> an organic compound comprising very large molecules ranging in molecular weight from 10,000 to 10,000,000 Atomic mass units. All of them have recurring structural units that are repeated many times within each large molecule. Since these recurring structural units are usually formed from, or derived from, simpler organic chemicals, it is customary to call the simple starting materials monomers to indicate that they contain only one unit of the chemical structure recurring hundreds or thousands of times in each large molecule.[9]

Products such as synthetic fibers, flexible films, proteins, plastics, and rubbers are formed from polymers.

The main structural types of polymer can be arranged into four general classes: linear, branched chain, moderately cross-linked and highly cross-linked. These do not form four separate distinct classes of polymers. Actually one might consider these classes as transitional, a continum with parts of one structure that may contain certain parts of another. The linear involving true thermoplasts may be considered at one end of the scale and the highly cross-linked thermosets at the other end with rubbers elastomers falling in between. This is illustrated in Figure 2.

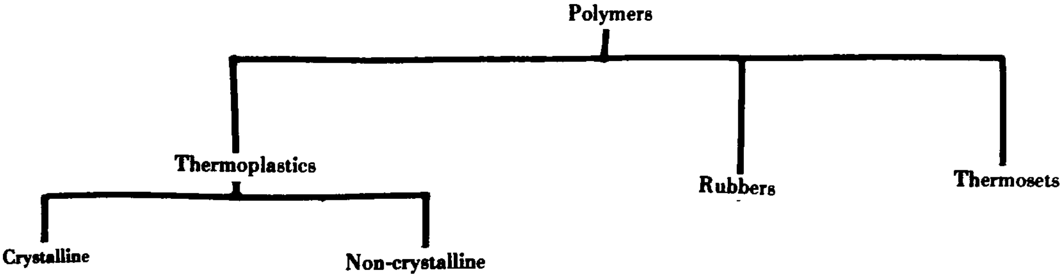
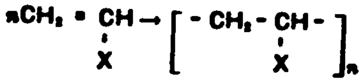


Figure 2. Physical properties of common polymeric materials.

The linear polymer is:

> a recurring structure, shown in the brackets, that is linked with other exactly similar structures at both ends until a long chain consisting of hundreds or thousands of such units results.[10] . . . the subscript 'n' at the end of the bracket indicates the number of times the monomer units is repeated.[11] This concept is shown in Figure 3.



$$n\mathrm{CH_2} = \underset{X}{\mathrm{CH}} \rightarrow \left[-\mathrm{CH_2}-\underset{X}{\mathrm{CH}}- \right]_n$$

Figure 3. Diagram of a linear polymer.

An example of a material made using linear polymers is polyethylene, or polystyrene-polyisoprene chains of crude rubber.

Unlike the linear polymer, some monomers polymerize in such a way that branches grow out of the parent chains.[12] These branch chains may be very small, compared to the parent molecule, or they may be nearly as large as the parent. The properties, and specifically the solubility, of a molecule with short branches will not differ much from the properties of the monomer.[13] However, if the branches are long, properties such as solubility will be greatly reduced because chemically it is more difficult to move one chain past another.[14] Butadiene is a material made with branched chains. Figure 4 shows such a polymer.

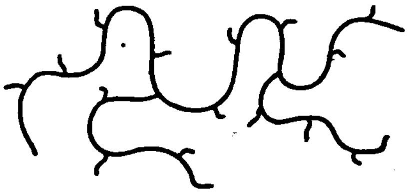


Figure 4. Diagram of a Branch Polymer.

A third basic type of polymer, and one more important to the graphic arts, is the moderately cross-linked polymer, also called a loose network. A moderately cross-linked polymer is a thermoset where there are at least two distinct polymers chemically linked together. Linear polymers are held together by carbon bonds; in this structure the molecular chains are connected by primary valences.[15] Moderately cross-linked polymers, such as vulcanized rubber, occur when:

> the number of cross-linkages per chain is not great. This structure is usually built up by cross-linking existing polymers by means of a chemical reaction. Linear chains are first formed by a polymerization reaction and then joined together by establishing cross linkages. This occurs when rubbers are vulcanized, and the structure is typical of vulcanized rubber.[16]

Like branching, cross-linking affects polymeric properties. In particular, cross-linked linear polymers are difficult to dissolve in solvents, while non-cross-linked linear polymers are easy to dissolve. This occurs because a solvent is unable to overcome the cross-linked polymer's strong intermolecular binding forces and break apart the chain of monomers. However, solvents can overcome the relatively weak intermolecular forces within a linear polymer. These different abilities to resist solvents are significant to printers, because the plates made using linear polymers dissolve when exposed to solvents, while those made using cross-linked polymers only swell.[17]

A fourth type of polymer, in addition to plain and branched linear polymer and the moderately cross-linked polymer, is the highly cross-linked polymer. This polymer has many cross-linkages per chain and is characterized by rigidity, insolubility, low extensibility, and high strength. An example of this material would be a thermosetting resin, such as urea phenol-formaldehyde.[18]

Different types of polymers can be combined to give a resulting material a combination of properties. For example:

> Mixtures of more than one vinyl monomer can often be copolymerized to yield polymer chains composed of two or more types of units (copolymers).
>
> One special type of copolymer of interest to us is the block copolymer.
>
> Block copolymers are polymer chains composed of two different types of units, in which long sequences of one type alternate with long sequences of the other type. A block copolymer of A units and B units is represented schematically by the structure
>
> -- -- --BBAAAAAAAAAAAABBBBBBBBBBBBBBAAA-- -- --[19]

The different methods by which polymers harden are often combined to give the resulting block copolymers hybrid properties. To illustrate:

> By combining high-melting poly-A blocks with low-melting poly-B blocks, it is possible to combine a high crystalline melting point (contributed by the A-component) with a low glass transition temperature (contributed by the B-component). Consequently, it is possible to achieve property combinations with block copolymers which are not attainable with Class 1 homopolymers or with random copolymers.[20]

The different polymeric physical states, hardening mechanisms, and structures all have important effects on the different types of reactions causing polymerization. One reaction commonly used in the graphic arts is addition polymerization:

> Polyaddition reactants, which are used to imitate this process, are usually ethanic compounds, while the polymerization reaction itself involves carbon-carbon double bonds. Many of the raw materials employed in the formation of polymers by this reaction are vinyl compounds.
> The addition of polymerization reaction is actually composed of the four different reactions of initiation, propagation, transfer, and cessation. Transfer reactions, although not required to explain the formation of addition polymers, do play an important role in determining the molecular weight. These four reactions may be simply represented as follows, where M represents an ethenic monomer, X a solvent molecule of a chain transfer agent, and the asterisk indicates an activated monomer or growing chain:

Figure 5 illustrates this phenomena.

1. Initiation or activation

$$M + \text{energy} \rightarrow M^{\bullet}$$

2. Propagation

$$M^{\bullet} + (n-1)M \rightarrow M_n^{\bullet}$$

3. Transfer

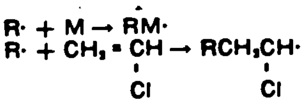
$$M_n^{\bullet} + M \rightarrow M_n + M^{\bullet}$$
$$M_n^{\bullet} + M_m \rightarrow M_n + M_m^{\bullet}$$
$$M_n^{\bullet} + X \rightarrow M_n + X^{\bullet}$$
$$X^{\bullet} + M \rightarrow X + M^{\bullet}$$

4. Cessation

$$M_n^{\bullet} + M_m^{\bullet} \rightarrow M_{n+m}$$
$$M_n^{\bullet} + M_m^{\bullet} \rightarrow M_n + M_m$$

Figure 5. Typical polymerization reaction

> Transfer reactions also can be considered to be cessation reactions in the sense that they terminate the growth of that particular chain, but they have no effect on the over-all rate of polymerization because a new active nucleus is produced as each growing chain is terminated. However, they may play a very important role in the formation of branched chains.
>
> Unsaturated bifunctional compounds differ greatly in their tendency toward polymerization. The simple olefinic hydrocarbons do not readily polymerize but will react in the presence of catalysts. Thus ethylene is made to polymerize to polyethylene, but catalists and pressure are required.... A wide variety of catalysts have been used to initiate addition polymerization reactions. One class consists of free-radical formers.....
>
> The mechanism of the initiating reaction has been a subject of much discussion and investigation since it usually is the controlling factor in the over-all rate of reaction and may play an important part in determining the average molecular weight of the product. It is now well established that many polymerizations can be initiated by free-radical mechanisms, and this method of activation has become the most widely used for addition polymerizations.
>
> The active center is transferred continually to the end of the chain, permitting monomers to add on a rapid succession until the cessation reaction stops the growth.[21] This is illustrated in Figure 6.
>
> The free radical then is capable of adding on to a monomer to provide the nucleus for the growing chain:



$$\begin{array}{l} R\cdot + M \rightarrow RM\cdot \\ R\cdot + CH_2{=}\underset{Cl}{CH} \rightarrow RCH_2\underset{Cl}{CH}\cdot \end{array}$$

Figure 6. Diagram of a free-radical adding on to a monomer.

The preceding information about plate making and photopolymer chemistry helps explain the various reactions flexographic plates have to solvents. In essence, vulcanization of rubber is an addition -

polymerization reaction using heat and pressure to bring about the moderate or heavy cross-linking of linear polymers. Before the rubber is molded into a printing plate it consists of a linear-type polymer containing a number of double bonds. Vulcanization occurs when the presence of both heat and pressure causes the opening of these double bonds and the polymers that were in linear chains cross-link. The most important changes occurring in a rubber plate during vulcanization are a reduction in plasticity while elasticity is maintained. Vulcanized rubber has a greater strength and less surface tackiness. Therefore, because it is moderately cross-linked, the structure resists being dissolved by solvents, although, as described earlier, solvents recommended by the plate material manufacturers will swell the structure.[22]

Both United States and foreign patents as well as technical papers indicate that most photopolymer plates contain three major ingredients. The first of these is usually a block copolymer, while the second is a mixture of an addition photopolymerizable polyunsaturated ester, derived from an acrylic or methacrylic acid, and an addition photopolymerization initiator such as benzophenone.[23] A third material, such as soft rubber or other plasticisers may be added to alter the finished plate properties.[24]

Patents indicate that the three chief differences among photopolymer plates are reaction to solvents by either swelling or dissolving; the glass transition temperature; and the number of cross-linking sites available.[26]

For example, a cross-linked block copolymer such as nitrile rubber will resist dissolution or swelling in aliphatic hydrocarbons like naphtha and lactol spirits.[27] However, a block copolymer, such as styrene isoprene styrene, which resembles natural rubber (Dupont's Cyrel plate) will be dissolved by such a solvent, making this type of block copolymer unsuitable for use with inks using hydrocarbons.

A second difference in properties, namely the polymer's transition temperature, is illustrated by the fact that a block copolymer like crystalline polymer can have a glass transition temperature of 25 degrees Centigrade while another might have a much higher transition point.[28] An example of a plate using the first type of block copolymer is the Econo Etch Plate (Goodrich patent 3798035), which is made using a crystalline polymer having a relatively low crystalline melting point. The use of this block copolymer makes the plate unsuitable for operations requiring higher temperatures.

A third difference in properties due to various types of block copolymers is the number of sites in the molecular chains where cross-linkages can occur.[29] Some block copolymers have many cross-linking sites while other types, may have only a few. A plate made from a block copolymer with many cross-linking sites will produce varying levels of durometers, which is a measure of hardness, catalyzed by different exposure times. In contrast, plates made from block copolymers with few cross-linking sites can only have a low durometer. Although the type of block copolymer is the most important cause of hardness, molecular cross-linking, and the hardness of the plate's ceiling is also affected by the amount and the area of reactive monomer put into the plate compound.[30]

The number of plate property differences caused by differences in the type and amount of block copolymer content is indeed limitless. A skilled chemical engineer would be able to create hundreds of plates, each with different properties, by modifying the amount of block copolymer content in the plate material.

The exposure and processing of a photopolymer plate--either natural rubber or man made--can cause a variety of chemical reactions. These may be listed as follows:

1. The photoinitiator absorbs the actinic radiation.
2. The energy provided by the radiation opens up the multiple bonds in the polyunsaturated ester comprising the plate material.
3. The ester joins linear or block copolymer to linear or block copolymer after these double bonds open to form a cross-linked structure. This reaction continues as long as there are monomers, or nodes, available for cross-linking or as long as actinic radiation is available.[31]
4. After exposure the plate is treated in a solvent, (usually a chlorinated hydrocarbon with a cohesive energy density similar to that of the plate)[32] to dissolve the unexposed linear and block copolymers.

It is interesting to note that none of the photopolymer plate manufacturers recommend a high ester content in a printing ink for use with their plate.

These descriptions of rubber and photopolymer reactions apply to all plates using these materials, but there are significant differences among the plate brands available to the flexographic industry.

The Cyrel Plate, manufactured by the E. I. Dupont deNemours and Co., was the first flexographic photopolymer plate to appear on the market. The following remarks about this plate are taken from a paper presented by Dr. William J. McGraw to the 1976 Annual Meeting and Technical Forum of the Flexographic Technical Association. He stated:

> The photopolymer plate is initially exposed through the back to activate the photopolymer. After removing the protective cover sheet, the negative and plate combination are exposed in a vacuum exposure unit. After the exposure is complete the plate is processed, then dried. A finishing solution changes the plate surface to a dry non-tacky finish, followed by a general post-exposure.
>
> The Cyrel photopolymer plates are being improved, so that flexographers using well maintained presses will find an improvement in the line quality they can print. Larger plate sizes, improved solvent resistance, more exposure lattitude are among the areas that will result in this line quality improvement.[33]

James W. Messerly of B. F. Goodrich Company spoke about Goodrich's unbacked Econo Etch plate.

> The unbacked photopolymer plate cannot delaminate, has a repeatable shrinkage factor for negative compensation, and little or no tendency to cup. These unbacked plates can maintain finer lines and dots due to the dimensional stability resulting from the higher hardness of the plate.
>
> The magnified surface of the photopolymer plate is smooth whereas the rubber plate has a rough surface. Less ink will be picked up by the smooth surface and more ink actually transferred to the substrate, resulting in a significant increase in print quality. The smoother plate surface causes the plate to run cleaner resulting in reduced washup time.
>
> Econo etch plates are designed to run water base, alcohols, alcohols with 20% acetate, and cellosolve inks, but are not recommended for use with inks containing high concentrations of hydrocarbon solvents. These plates can be stored indefinitely without cracking or showing any detrimental effects.[34]

Mr. Gene J. Mirolli of Hercules Inc. described a somewhat different plate system from the preceding two. He stated that the Hercules plate uses

> ....a liquid resin which has the consistency of honey is placed in a bucket which is attached to a mechanically driven carriage....[35]

Further, this system uses a developing unit to remove unreacted resin and a post exposure unit to further harden the processed plate and remove surface tack.[36]

> The negative is positioned on the glass, emulsion side up. A thin cover film is placed over the negative and held by vacuum. The carriage is moved into position and filled with resin. A doctor blade smooths and levels the resin, while placing a transparent backing sheet over it.
>
> A background exposure is made thru the backing sheet for the desirable base layer, controlling the relief height of the plate, and binding the backing sheet to the photopolymer. This background layer is instrumental in the formation of fine highlight dots and wide tonal range.
>
> The relief exposure is made thru the negative by a UV light source below the glass, to determine the character's shape and structure.

Mr. Mirolli also stated that the Hercules plate was developed by washing the exposed plate in water and detergent mixture. This solution, he claimed, is completely biodegradable and may be flushed down any public sewer with no ill effects. Further, he claimed that this water washout development system leaves the plate completely unswollen.[37]

The Hercules plate system allows a choice among several varieties of liquid resins. These are divided into type FA, which should be used with alcohol reducible inks, the type FCS, which should be used with water based and hydrocarbon-based ink systems. The hardness of the plate can be varied by the selection of the appropriate resin. As mentioned earlier durometer is a measure of hardness. The type FA resin is available in 40, 55, and 70 durometers. The type FCS is available in 50 and 70 durometers.[38]

Finally, Mr. Michael L. Heckaman of Unrioyal -- U.S. Rubber Co. made the following remarks about his company's flexographic printing plate.

> Perchlorethylene is used to render the uncured material removable by brushing, without affecting the cured areas, resulting in fine line and halftone capabilities, less swelling, and quickly restored plate caliper during the drying process. The removed polymer, being insoluable in perchlorethylene is easily removed from the solvent, allowing the solvent to be recycled.[39]
>
> Solvent resistance for these plates is excellent for water, glycol-ether, alcohol and oil-based ink systems but aromatic hydrocarbons and organic esters in high levels should be avoided.[40]

This description of differences in both plate chemical composition and reaction to solvents suggests that it is important to experimentally determine the sensitivity of available plate materials to commonly used solvent mixtures. This thesis will consider the period of time these materials can remain in contact with solvent mixtures. The response which appears to be significant and which shall be considered in this study is change in plate hardness as measured by durometer.

FOOTNOTES FOR CHAPTER II

[1] Victor Strauss, The Printing Industry. (Washington: Printing Industries of America, 1967) p.20

[2] Ibid., p. 212 - 218.

[3] Joe W. Cotton,ed., Flexography: Principles and Practices. (Brooklyn, New York: Flexography Technical Association, 1980) p.157.

[4] Ibid., pp. 157 - 164.

[5] Victor Strauss, Ibid., p.234.

[6] Turner Alfrey and Edware F. Gurnee, Organic Polymers (Englewood Cliffs, NJ: Prentice Hall, 1967) p. 12.

[7] Ibid., p. 12.

[8] Ibid., p. 13.

[9] Charles C. Winding and Gordon D. Hiatt. Polymeric Materials. (New York: McGraw-Hill Book Company, Inc.) 1961 p. 1.

[10] Ibid., p. 7.

[11] Ibid., pp. 7 - 8.

[12] Ibid., p. 9.

[13] Ibid.

[14] Ibid.

[15] Ibid., pp. 9 - 10

[16] Ibid.

[17] Ibid., pp. 10 - 11

[18] Ibid., pp. 11 - 12

[19] Charles C. Winding and Gordon D. Hiatt, Ibid., pp. 30 - 31.

[20] Turner Alfrey and Edware F. Gurnee, Ibid., pp. 45 - 46.

[21] Charles C. Winding and Gordon D. Hiatt, Ibid., pp. 21 - 23.

[22] Charles C. WInding and Gordon D. Hiatt, Ibid., pp. 354 - 356.

[23] Robert L. Lauchlan; Stephen Vamvaketis; and MacLean R. Hess, *'Photosensitive Compositions'*, Canadian Patent 977,202; Granted to Uniroyal, Inc., New York, U.S.A., Filed April 21, 1971; issued; Nov. 4, 1975 p. 6.

[24] *Ibid*.

[25] *Ibid*., p. 8.

[26] Donald M. Kurtz, "Method of Making Flexible Printing Plates". United States Patent 3,658,531. Assigned to B. F. Goodrich Company, New York, New York, Filed: Oct. 29, 1070, Granted: April 25, 1972.

Robert L. Lauchlan; Stephen Vamvaketis; and MacLean R. Hess, *Ibid*.

Floyd L. Ramp, "*Ploymeric Printing Plates*". United States Patent 3,615,469. Assigned to B. F. Goodrich Company, New York, New York, Filed: June 2, 1969, Granted: Oct. 26, 1971.

Richard S. Varga and Thomas R. Szezpanski, "*Method of Making Flexible Printing Plates*." United States Patent 3,789,035. Assigned to B. F. Goodrich Company, New York, New York. Filed: Oct. 6, 1972, Granted: March 19, 1974.

[27] Robert L. Lauchlan; Stephen Vamaketis and MacLean R. Hess, *Ibid*., p.4.

[28] Uniroyal, Inc., British Patent 1,395,822. Granted May 29, 1975.

[29] Robert L. Lauchlan; Stephen Vamaketis; and MacLean R. Hess, *bid*., p. 6.

[30] *Ibid*.

[31] *Ibid*.

[32] *Ibid*., p. 4.

[33] William J. McGraw, "*An Introduction to Photopolymers*". Flexographic Technical Association. Report of the Proceedings of the 18th Annual Meeting and Technical Forum, (Chicago, Conrad Hilton Hotel, April 27 - 29) pp. 86 - 91.

[34] James W. Messerly, "*Unbacked Photopolymer Plates, A New Porduct for the Flexo Printing Industry*". Flexographic Technical Associaiton. Report of the Proceedings of the 18th Annual Meeting and Technical Forum. *Ibid*.

[35] Gene J. Mirolli, "The Merigraph Photopolymer Platemaking System". Flexographic Technical Association. Report of the Proceedings of the 18th Annual Meeting and Technical Forum. Ibid., p. 97.

[36] Ibid., p. 97 - 98.

[37] Ibid., p. 98.

[38] Ibid., p. 98 - 99.

[39] Ibid., p. 100.

[40] Michael L. Heckaman, "Uniroyal Flexlite Photopolymer Plate". Flexographic Technical Association. Report of the Proceedings of the 18th Annual Meeting and Technical Forum. Ibid. pp. 101 - 102.

[41] Ibid., pp. 103 - 104.

CHAPTER III

THE PURPOSE OF THIS RESEARCH

As was mentioned in the Review of the Literature, different solvents are expected to affect different polymers to a varying degree due to the theoretical considerations already discussed.

Different types of polymers and co-polymers will swell to different degrees depending on the type of solvents to which they are exposed.

Also, the degree to which the polymer is cross-linked will determine its solvent resistence to a great extent.

Exposing a polymer to solvent may affect its properties in other ways. Chemicals added to the compound such as plasticizers, are often leeched out of a polymer over a period of continued exposure to solvent. The removal of such plasticizers would usually harden such a polymer.

Synthetic rubbers such as nitrile type compounds have excellent resistance to aliphatic hydrocarbons and water. They are swollen to some degree by most alcohols and to a much greater degree due to acetate esters after immersion. The degree of swelling and the length of time they remain a useable material is dependent upon the concentration of these materials in solvent and ink compounds to which they are exposed.

On the other hand, compounds containing natural rubber or isoprene are known to have good resistance to most alcohols and acetate esters but very limited resistance to aliphatic hydrocarbons.

Again, the degrees of swelling and the length of time they remain a useable material is dependent upon the concentration of these materials in solvent and ink compounds to which they are exposed.

Other polymers have different degrees of solvent resistance, or lack of it, to different classes of solvents.

Some appropriate measures of solvent attack on polymers are changes in compounds, Shore A hardness, changes in weight, and change in thickness. The amount and rate of change in these properties is a good indication of the useability of a particular compound with a particular solvent or combination of solvents in a printing application.

Certain polymers may be used without hesitation with a certain solvent or mixture of solvents, while another may be totally unsuitable. Other polymers used in this application may be used, but only with caution or for only a limited amount of time.

On the basis of the chemical composition and the physical-chemical properties described it is expected that the various materials used for flexographic platemaking will react in varying degrees to commonly used solvents found normally in flexographic inks. The research question therefore is, do the various plate materials used for flexography change weight and/or hardness after exposure to commonly used solvents and is exposure time also critical.

The purpose of this research is to examine a number of photopolymers and molded flexographic plates by exposure to different solvents and mixtures of solvents for a number of time intervals and infer the effect of solvent, time and the interactions of these two factors. The response variable is Shore A hardness and weight change.

Statement of the Hypothesis

Using statistical methods the following mathematical model of a two factor experiment twice replicated, describes the experiment:[1]

$$X_{ijk} = \mu + A_i + B_j + (AB)_{ij} + e_{k(ij)}$$

where $u =$ population average of all factors and levels under study, usually estimated by $\bar{\bar{X}}$, the grand average of all observations in the experiment

$A_i =$ effect of factor placed in rows

$B_j =$ effect of factor placed in columns

$(AB)_{ij} =$ effect of interaction of main factors

$e_{k(ij)} =$ effect of random error estimated from replicates.

The statement of hypothesis properly takes the null form;[2] there is no significant difference in the flexographic plate hardness or weight change due to various selected solvents and time.

Footnotes for Chapter III

[1] Albert D. Rickmers and Hollis M. Todd, "_Statistics: An Introduction_", New York, New York, McGraw Hill, 1967 pp. 168 - 174.

[2] _Ibid_., pp. 62 - 200.

CHAPTER IV

METHODOLOGY

The experimental design applied here is known as a complete factorial or crossed experiment.[1] In this case each level of each factor is tested against every level of every other factor. Analyzing data generated by a crossed experiment not only allows insight into how much each factor, such as the solvent, influences a response, such as durometer, but also shows how one factor can directly and indirectly influence the effects caused by other factors. In order to obtain an estimate of experimental error the entire experiment was also designed to be replicated, or repeated, using fresh solvents and samples. In this experiment the three factors under test were the:

1. Type of plate.
2. Type of solvent.
3. Amount of time each plate was in contact with each solvent.

A measurement, or response, of the plate hardness explained as Shore A durometer, and weight, was made for each plate-solvent-time combination.[3]

Seven types of flexographic printing plates were used in the experiment, five of which were made using photopolymer materials and two of which were molded using rubber compounds. The seven types were:

1. A photopolymer plate composed of a styrene isoprene styrene Block copolymer.

2. A photopolymer plate composed of a crystaline polymer with a low crystaline melting point.
3. A photopolymer plate composed of an acrylonitrile butidine copolymer.
4. A photopolymer plate produced from a liquid resin system. (The resin and plate were advertised as being compatible with alcohol-based inks. The chemical composition is unknown.)
5. A photopolymer plate produced from a liquid resin system. (The resin and plate were advertised as being compatible with only water-based and hydrocarbon based inks, but their chemical composition was also unknown.)
6. A molded natural-rubber plate.
7. A molded Buna N (nitrile) plate.

These plate samples were immersed into ten different solvents or mixtures of solvents. The solvents and mixtures were:

1. Water.
2. Water and soap.
3. Normal propyl alcohol.
4. A mixture consisting of 90% normal propyl alcohol and 10% normal propyl acetate, which is an ester.
5. A mixture consisting of 80% normal propyl alcohol and 20% normal propyl acetate.
6. A mixture consisting of 70% normal propyl alcohol and 30% normal propyl acetate.

7. A mixture consisting of 95% normal propyl alcohol and 5% lactol spirits, which is an aliphatic hydrocarbon.
8. A mixture consisting of 90% normal propyl alcohol and 10% lactol spirits.
9. A mixture consisting of 80% normal propyl alcohol and 20% lactol spirits.
10. A mixture consisting of 70% normal propyl alcohol and 30% lactol spirits.

These plates and solvents were chosen because they reflect materials currently used by flexographic printers. The plates will be referred to by number for the remainder of this study at the request of the material donors.

Large processed sheets of all seven types of plate materials were obtained for use in the experiment, with each sheet being .125 inches thick. To insure that all samples would be both measured for thickness and exposed to the solvents equally, any existing polyester backing on these materials was removed. Because the entire experiment, which would be replicated, required two plate samples each time, four one-inch by two-inch samples were cut from the large sheets.

One hundred fourty (140) bottles with plastic caps were obtained from the Rochester Institute of Technology Chemistry Department so that the different plates could be immersed into the different solvents. These bottles, each of which holds 4 ounces of fluid, are used to distribute chemical samples to chemistry students.

Master batches of each solvent solution were prepared. Two bottles were filled with each solvent or solvent mixture because the experiment would be replicated. Two pieces of each plate were then placed into one bottle of each solvent and allowed to soak for time periods of 30 minutes, 4 hours, 8 hours, and 24 hours.

After each of these periods had elapsed the samples were removed from the bottles and wiped dry with a towel. Because a piece of material with a thickness of at least .250 inches is required for durometer testing,[1] the two .125 inch thick samples were laid on top of each other when the sample durometer was measured. One of the two samples from each bottle was then weighed on a Metter balance and its results recorded. All data were recorded on prepared data sheets and the samples returned to the bottle from which they were taken to soak for the next time interval, at which time measurements were made again.

The experiments therefore yielded a total of two measurements for any one plate-solvent-time combination. The data gathering sheet is shown in Figure 7.

Plate ____________ Solvent ____________

Responses	0	1	2	3	4
Durometer					
Weight Change					
Thickness Change					
Highlight					
Middletone					
Shadow					

Figure 7. Sample form that was used to record different responses of information before it was transferred to the RIT computer system.

FOOTNOTES FOR CHAPTER IV

[1] Albert D. Rickmers and Hollis M. Todd, "Statistics: An Introduction", New York, McGraw Hill, 1967, pp. 167-178.

[2] Owen L. Davis, "The Design and Analysis of Industrial Experiments", New York: Hafner Publishing Company, 1956.

CHAPTER V

ANALYSIS OF THE DATA, PART I

After the data were collected during the experiment, each hardness and weight response for a given plate, solvent, and time combination was recorded in the appropriate data table.

After these responses were tabulated, they were subjected to the Analysis of Variance, hereafter referred to as ANOVA[1]. When a factor, such as the solvent, was found to cause a significant response the different levels of this factor were subjected to further analysis by a technique known as the multiple range test[2]. This test gives insight into which levels of the significant factors made large contributions to a significant effect and which did not. For example, solvents may have no effect after 30 minutes but a significant one for every other time period; a second possibility is that it has a significant effect after 30 minutes and then no effect from then on. Although the data for each response was intended to be analyzed as a three-factor experiment and subjected to an Anova as such, plates had markedly different durometers varying by a large number of points at the start of the experiment. For example, one particular plate had an initial hardness of 54 points while another had an initial hardness of 78 points; any comparison of these plates for subsequent durometer would be affected by these initial values. Therefore, the durometer response was treated as a separate two factor experiment, which meant that the effects of solvent and time were considered for every plate durometer but that the plate durometers were not compared to each other. Also, some plate samples exhibited large weight changes in short periods of time while others exhibited large weight changes after a long period of time. It was therefore decided that only the total weight change for each sample in a 24-hour period would be considered as the response, and the only factors truly considered were the type of solvent and the type of plate.

The data was then analyzed using the RIT computer system after which significant interactions were graphed. In most cases the data for each factor were plotted. Figure 8 illustrates the data sheet for the ANOVA.

Source	Sum of Squares	df	Means Squares	F Ratio (Calculated)	F Ratio (Table)	Significant* Not Significant (N.S.)
Solvent						
Time						
Interaction						
Total Error						

Figure 8. Sample form that was used to record the results used in the ANOVA Tables.

FOOTNOTES FOR CHAPTER V

[1] Albert D. Rickmers and Hollis M. Todd, "Statistics: An Introduction", New York, McGraw Hill, 1967, pp. 154-157.

[2] Ibid., pp. 223-224.

CHAPTER V

ANALYSIS OF THE DATA, PART II

Analysis of Weight Change

The first data analyzed was the percentage weight gained after soaking the plates in the solvents for a 24-hour period. The ANOVA Summary Table for this experiment indicates that both Factor B Plates and Factor A Solvents, as well as the interaction between the two, are significant (Table 1).

An examination of the plotted data in Figure 9, which shows plate

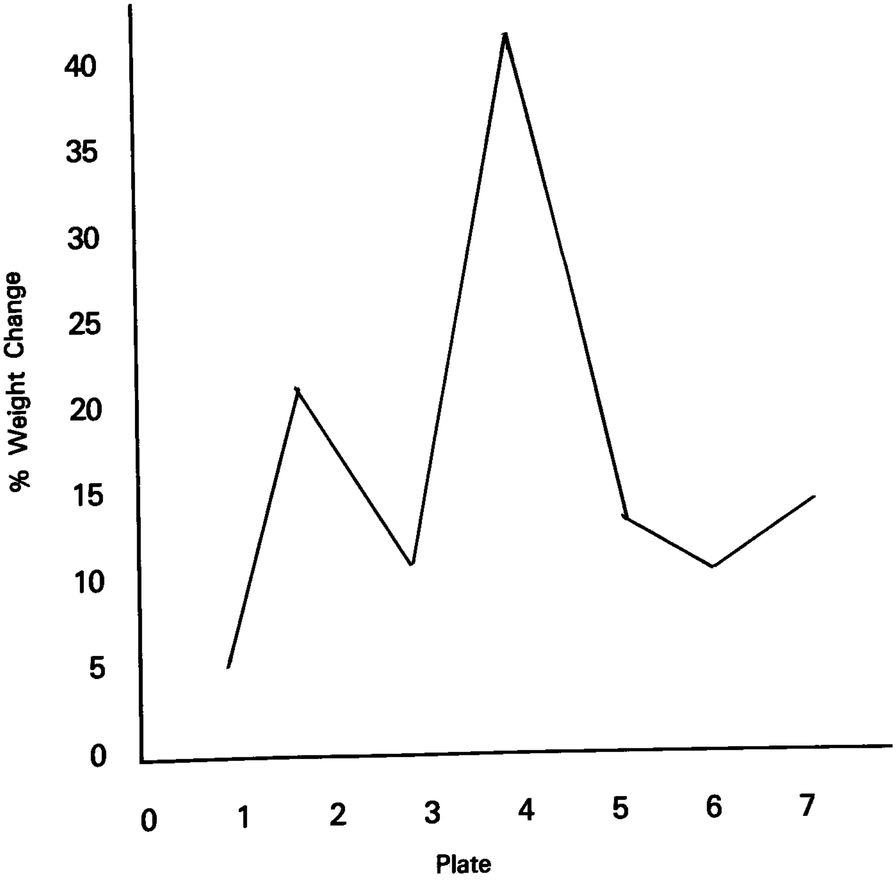


Figure 9. Plot of the data, plate vs. percent weight gain, overall solvents.

Source	Sum of Squares	df	Means Squares	F Ratio (Calculated)	F Ratio (Table)	Significant* Not Significant (N.S.)
Solvent	13282.83203	9	1475.87012	17.34843	1.7380	*
Plates	17691.71875	6	2948.61963	34.66019	1.8238	*
Interaction	10102.51953	54	187.08369	2.19912	1.3952	*
Total Error	5955.05639	70	85.072223			

Table 1. ANOVA Summary Table for percent of weight gained by soaking the plates in the solvents for a 24 hour period.

sample vs. percent weight gain for all of the solvents, suggests all plates gained weight as a result of contact with the solvents. Plates 2 and 4 in particular gained much more weight than others tested.

Examination of the multiple range test for this factor in Figure 10 shows that Plate 4 is unique in terms of the percent weight gained, which means that statistical analysis supports the plotted data shown on Figure 9. The multiple range test for this factor also indicates there is no significant difference between plates 2 and 7 and plates 2 and 5, results that are also confirmed by the data plotted in Figure 9. The remainder of the measurements, from plates 5 to 1, form a homogeneous group when arranged in a descending order of weight (Figure 10).

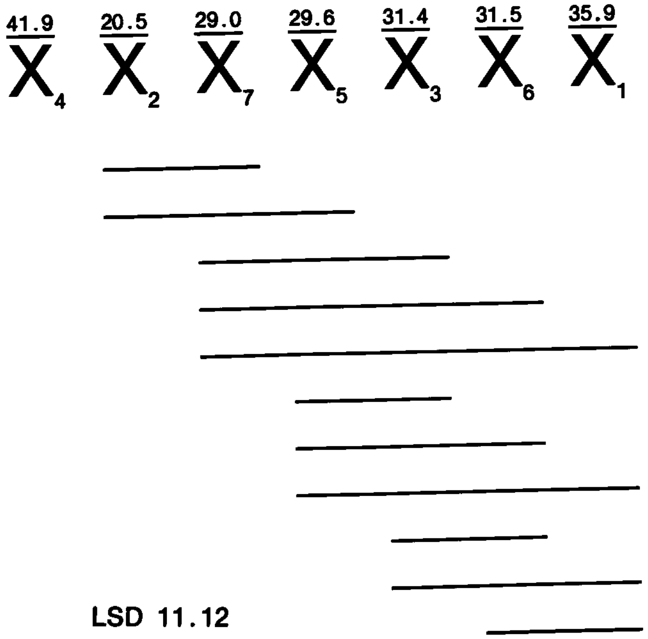


Figure 10. Multiple Range Test for Factor B plates. (The plates with no significant difference are underlined.)

An examination of Factor A Solvents via a graph where solvent type is plotted against percent weight change (Figure 11) reveals that Solvent 1, which is water, does not affect the weight of any of the plates. However, Solvent 2, a mixture of water and anti-foam, and Solvent 3, which is 100% normal propyl alcohol, a component of the remaining solvents have some effect on weight gain. Solvents 4, 5, and 6, which are propyl alcohol mixed with increasing amounts of normal propyl acetate, indicate increased weight with increasing acetate concentration. The same trend is shown by Solvents 7, 8, 9 and 10, which contain increasing amounts of lactol spirits mixed with normal propyl alcohol. The greater the amount of normal propyl alcohol or lactol, the greater the gain in plate weight.

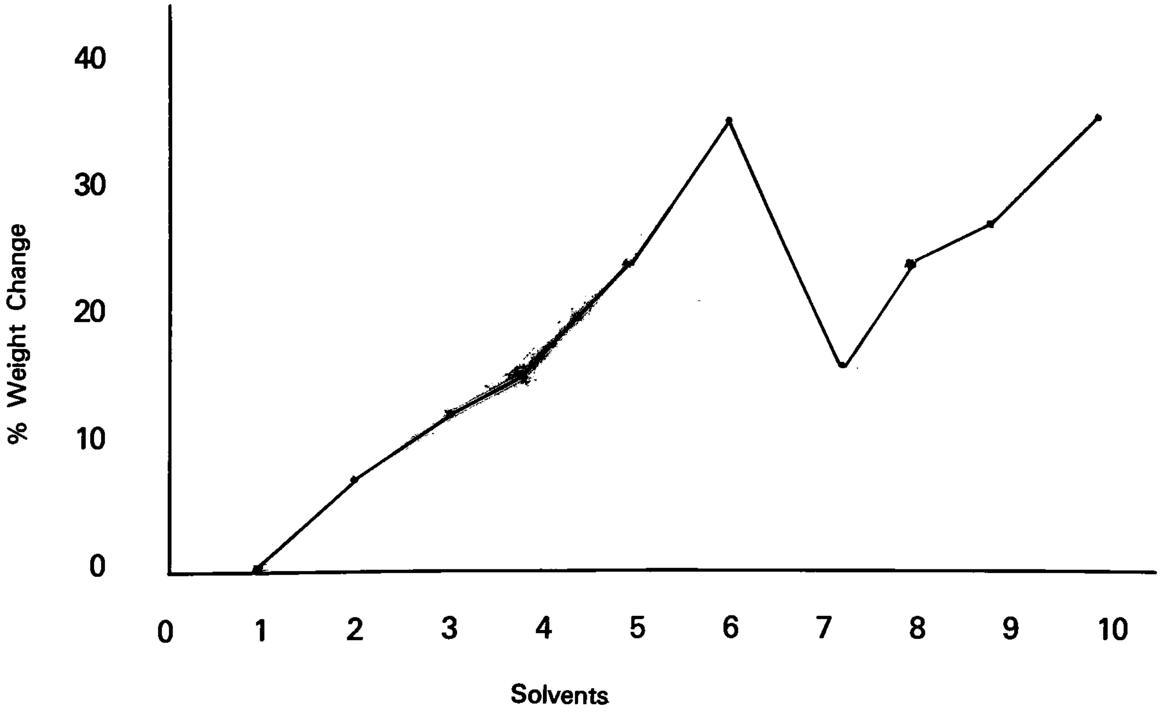


Figure 11. Plot of the data, solvents vs. percent weight change, overall solvents.

The multiple range test of Factor A Solvents (Figure 12) shows that an increasing amount of lactol spirits and acetates have a statistically significant effect on the plates in terms of the percent weight gained.

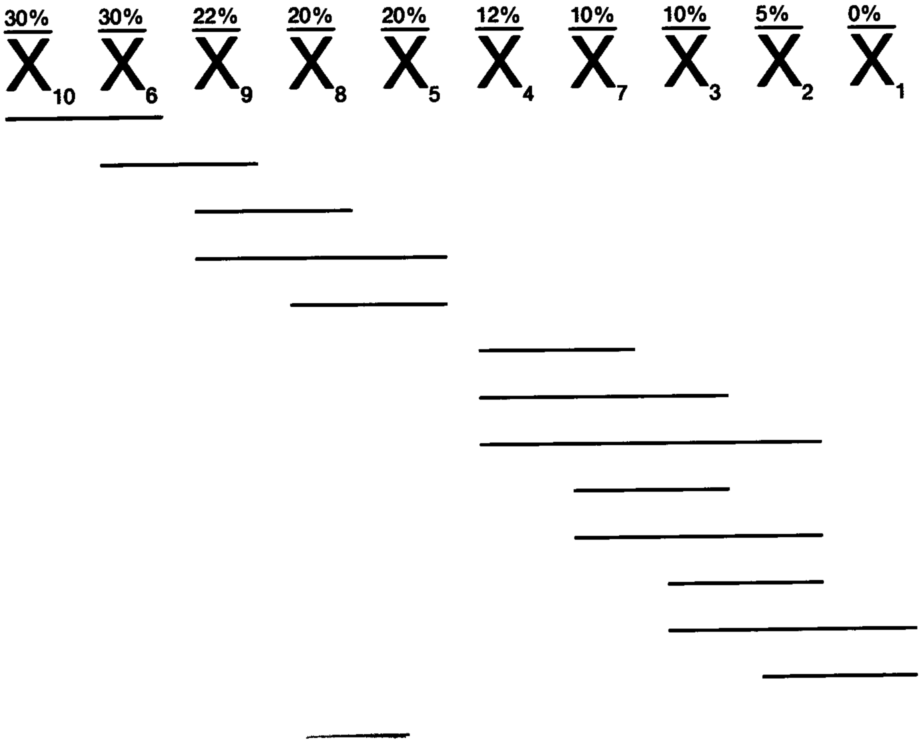


Figure 12. Multiple Range Test for Factor A Solvents. (The solvents with no significant difference are underlined.)

Analysis of Change in Plate 1 Hardness

The results of the experiment involving Plate 1, which are described in the ANOVA Summary Table for this experiment (Table 2), show that Factor A Solvents, Factor B Time, and the interaction between the two are all significant. A simple plot (Figure 13) of all the levels of Factor A Solvent in this experiment show there is little softening of this plate caused by water, alcohol, soap, and solvents containing small quantities of lactol spirits and normal propyl acetate. High levels of lactol spirits and normal propyl acetate soften Plate 1 considerably. The multiple range test (Figure 14), for this factor indicates there are no significant difference due to water, a water and soap mixture, 100% normal propyl alcohol, a normal propyl alcohol and 10% normal propyl acetate mixture, normal propyl alcohol and 5% lactol spirits mixture, and a normal propyl alcohol and a 20% lactol spirits mixture. However, the remaining solvents form a homogeneous group, all having a softening effect on the plate.

The multiple range test for Factor B Time (Figure 15) shows that there are no significant differences between Times 1 and 3, indicating that Plate 1 could be used with all solvents, except those causing extreme swelling, such as solvents containing 30% lactol spirits or 20% and 30% normal propyl acetate mixture for up to 4 hours. The interaction graph (Figure 16) for the two factors Time and Solvent shows pictorially that Times 1, 2 and 3 permit the same amount of plate softening with all solvents while Times 4 and 5 show extreme departures from this norm and greatly soften the plates.

Source	Sum of Squares	df	Means Squares	F Ratio (Calculated)	F Ratio (Table)	Significant* Not Significant (N.S.)
Solvent	483.83984	9	53.75998	20.01251	1.76545	*
Time	205.84000	4	51.45999	19.15632	2.06595	*
Interaction	381.55981	36	10.59888	3.44550	1.47145	*
Total Error	134.31596	50	2.68632			

Table 2. ANOVA Summary Table for Plate 1

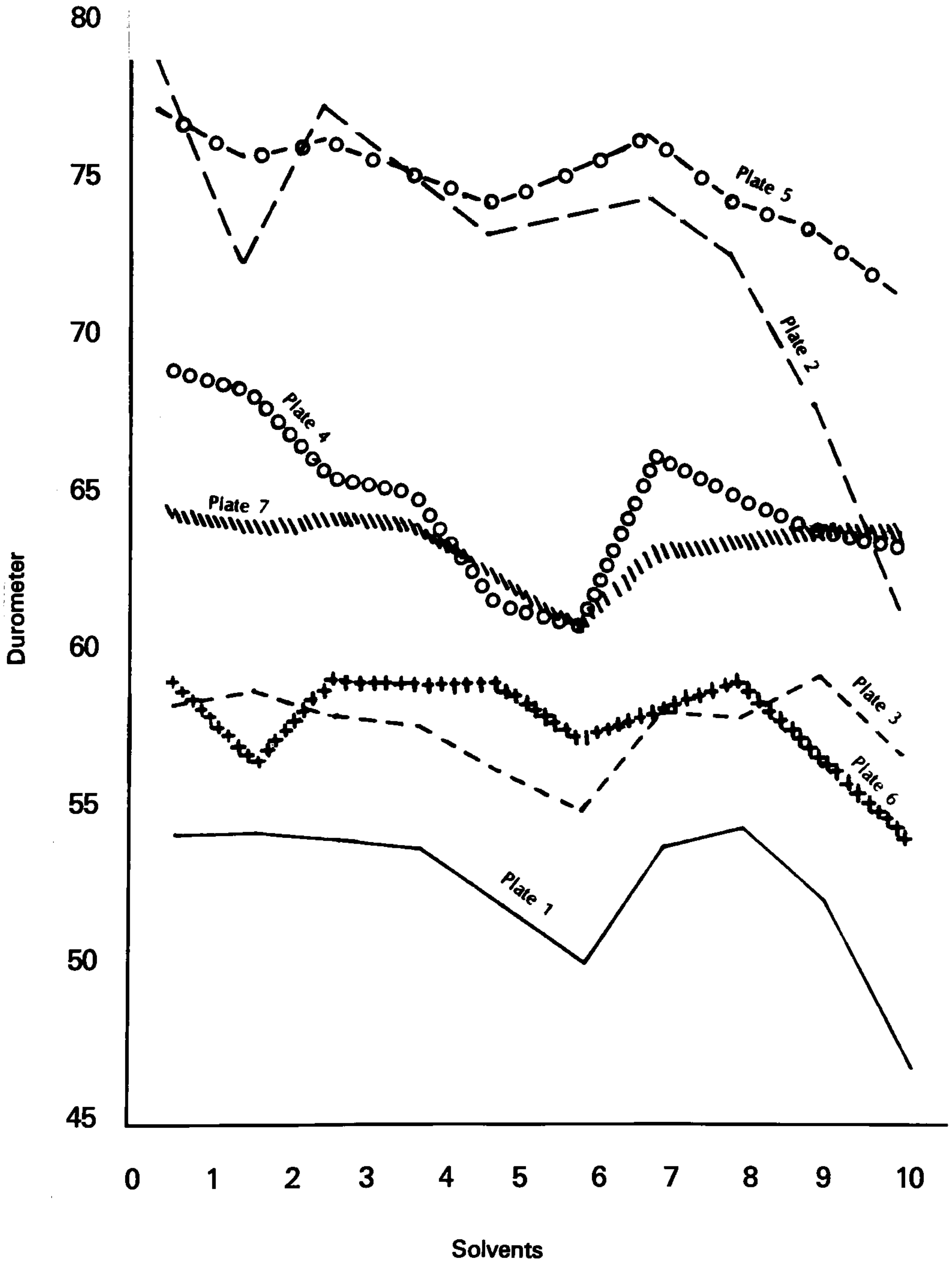


Figure 13. Plot of the data, solvents vs. durometer, plates 1-7.

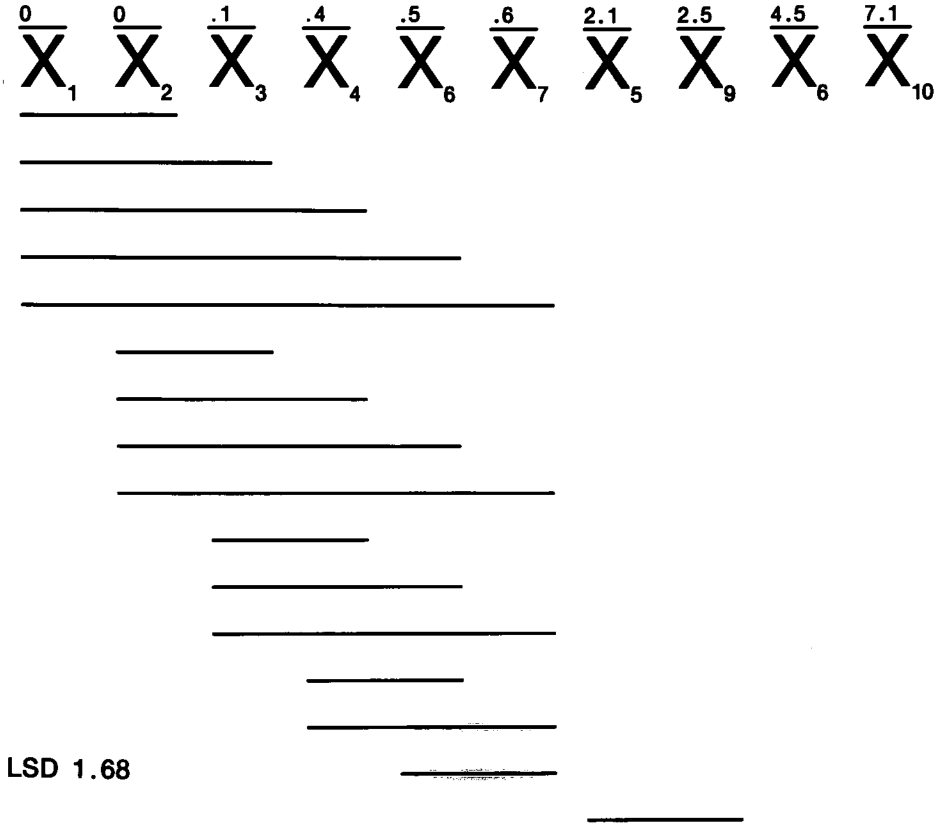


Figure 14. Multiple Range Test for Factor A Solvent, Plate 1. (The solvents with no significant difference are underlined.)

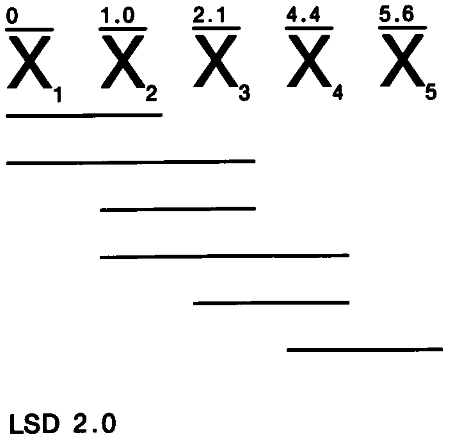


Figure 15. Multiple Range Test for Factor B Time, Plate 1. (The times with no significant difference are underlined.)

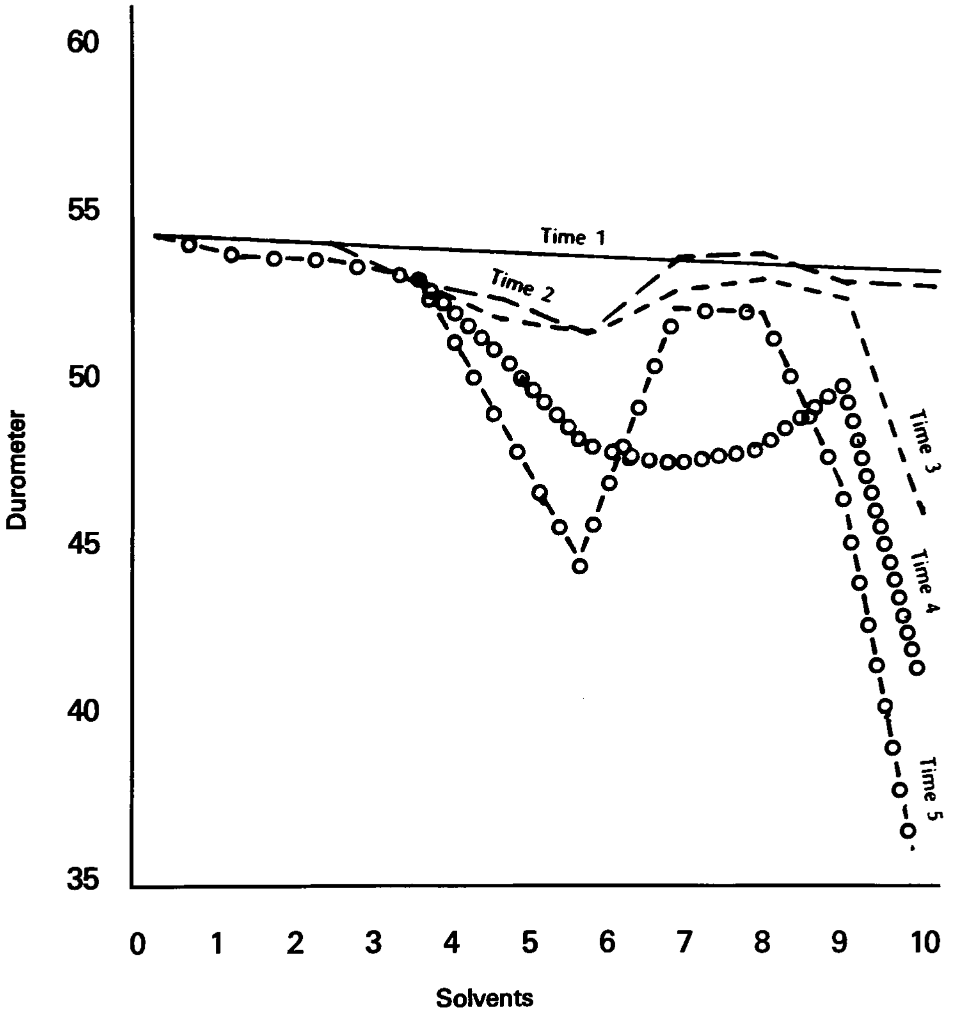


Figure 16. Interaction plot of data, Time vs. Solvent, Plate 1.

Analysis of Change in Plate 2 Hardness

For Plate 2 the ANOVA Summary Table (Table 3) indicates that both factors and the interaction have a significant statistical effect. The plot of the effects that individual solvents have on this plate (Figure 17) shows that Plate 2 softens very little when immersed in water and alcohol. However, all of the other solvents affect the plate significantly. The multiple range test for this factor confirms the graphic analysis that this plate was not affected by water, 100% normal propyl alcohol, a mixture of normal propyl alcohol and 5% lactol (Figure 18). The only two solvents not causing significant swelling were water and 100% normal propyl alcohol. The other solvents caused significant softening of the plate. In fact, the mixtures of normal propyl alcohol and 30% normal propyl acetate, normal propyl alcohol and 20% lactol spirits and normal propyl alcohol 30% lactol spirits all precipitated significant degrees of softening. The factor B Time plot for this plate (Figure 19), which is a plot of the five different levels of Time, indicates there is a rapid drop in durometer response (hardness) over time. The multiple range test for Factor B Time corroborates the plotted data (Figure 20).

Source	Sum of Squares	df	Means Squares	F Ratio (Calculated)	F Ratio (Table)	Significant* Not Significant (N.S.)
Solvent	2366.20996	9	262.91222	36.46494	1.73800	*
Time	1897.15991	4	474.28998	65.78225	1.82380	*
Interaction	863.03979	36	23.97333	3.32501	1.39520	*
Total Error	360.49997	50	7.21000			

Table 3. ANOVA Summary Table for Plate 2.

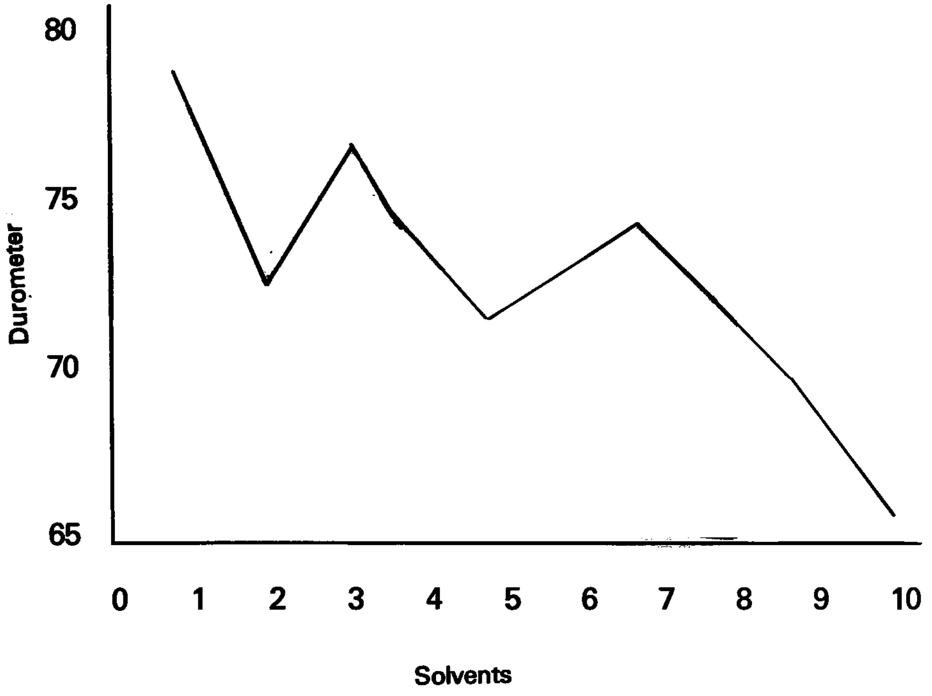
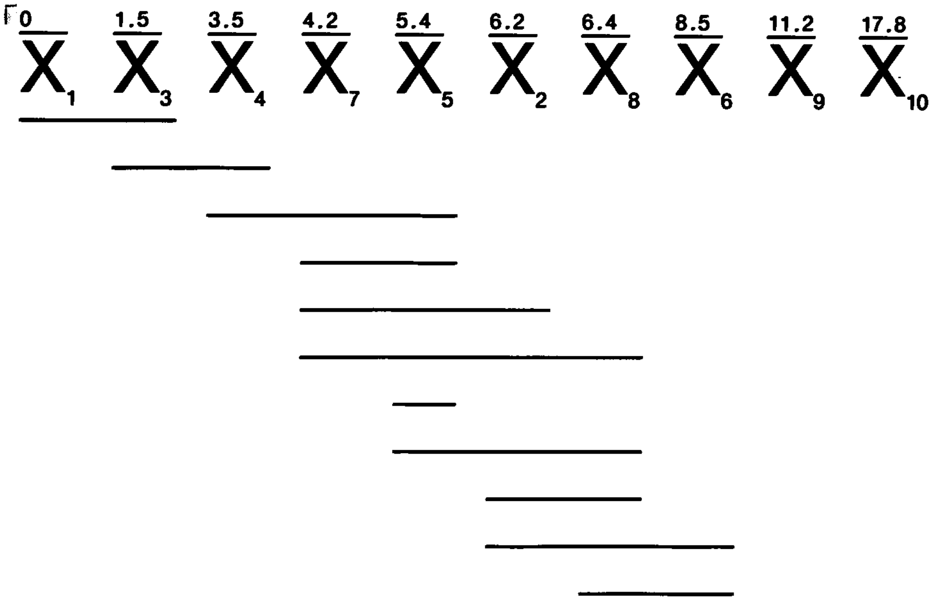


Figure 17. Plot of the data, solvents vs. durometer, Plate 2.



LSD 2.7

Figure 18. Multiple Range Test for Factor A Solvent, Plate 2. (The solvents with no significant difference are underlined.)

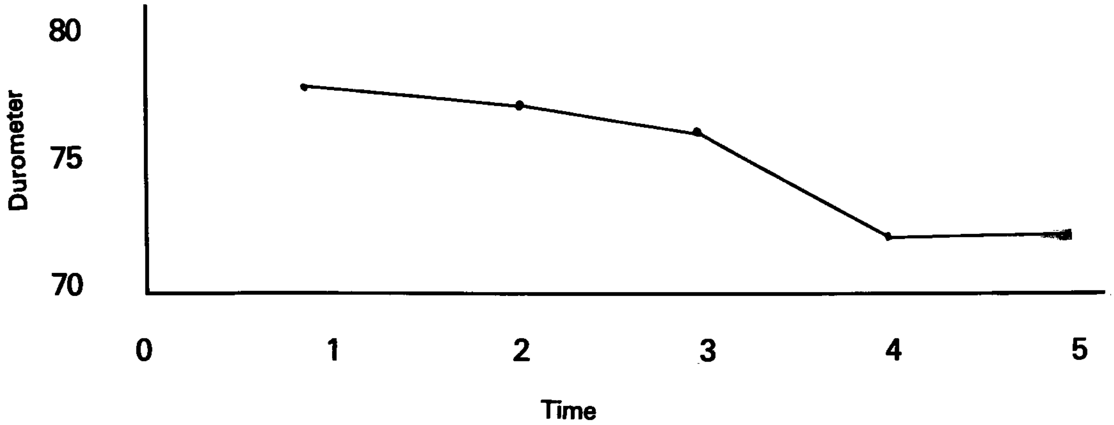


Figure 19. Interaction Plot of data, Time vs. Durometer, Plate 2.

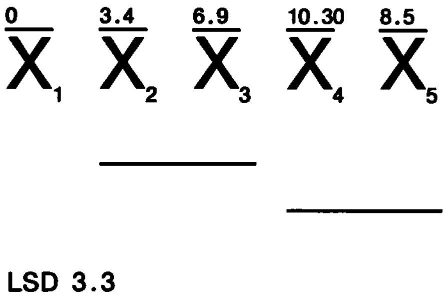


Figure 20. Multiple Range Test for Factor B Time, Plate 2. (The times with no significant difference are underlined.)

Analysis of Change in Plate 3 Hardness

The ANOVA Summary Table for Plate 3 (Table 4) shows that Factor A Solvent, Factor B Time, and the interaction between the two are all significant. A simple plot (Figure 21) of the data for Factor A Solvent reveals that this plate, like the others examined thus far, remains unchanged when subjected to water. Unlike the other plates, Plate 3 is not softened by soap compounds although it is softened by alcohol. Also this plate is not affected by solvent blends containing lactol spirits. The multiple range test for the Factor A Solvent (Figure 22) shows that Plate 3 is not significantly affected by water, 100% normal propyl alcohol, normal propyl lactol spirits, and normal propyl alcohol plus 10% acetate. Higher quantities of acetate have a significant effect on this plate. The multiple range test for the Factor B Time (Figure 23) and the simple plot of the data (Figure 24) both indicate that Plate 3 does not soften significantly when soaked in solvents over a period of eight hours although deterioration is evident after 24 hours. The interaction graph between the two factors (Figure 25) confirms that plate swelling is not significant when the plate is in contact with solvents for short periods of time but that softening increases with longer time periods.

Analysis of Change in Plate 4 Hardness

The ANOVA Summary Table for the experiment (Table 5) shows that Factor A Solvent and Factor B Time are significant for Plate 4, but that the interaction between the two is not significant (Figure 26). Although the manufacturers of this product recommend that this plate be used with normal propyl alcohol, the multiple range test (Figure 27) and the plotted data both indicate that, compared to water, the plate is softened significantly by normal propyl alcohol. The plotted data (Figure 28) and multiple range test (Figure 29) for Factor B Time show the plate softening significantly and continuously over time.

Source	Sum of Squares	df	Means Squares	F Ratio (Calculated)	F Ratio (Table)	Significant* Not Significant (N.S.)
Solvent	126.84999	9	14.09444	7.87401	2.1820	*
Time	221.29999	4	55.325000	30.90789	2.6060	*
Interaction	157.09999	36	4.36389	2.43793	1.6928	*
Total Error	89.49980	50	1.79000			

Table 4. ANOVA Summary Table for Plate 3

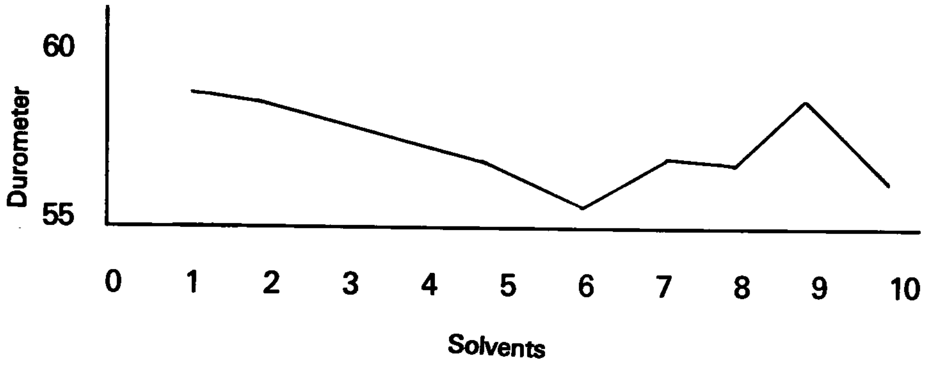
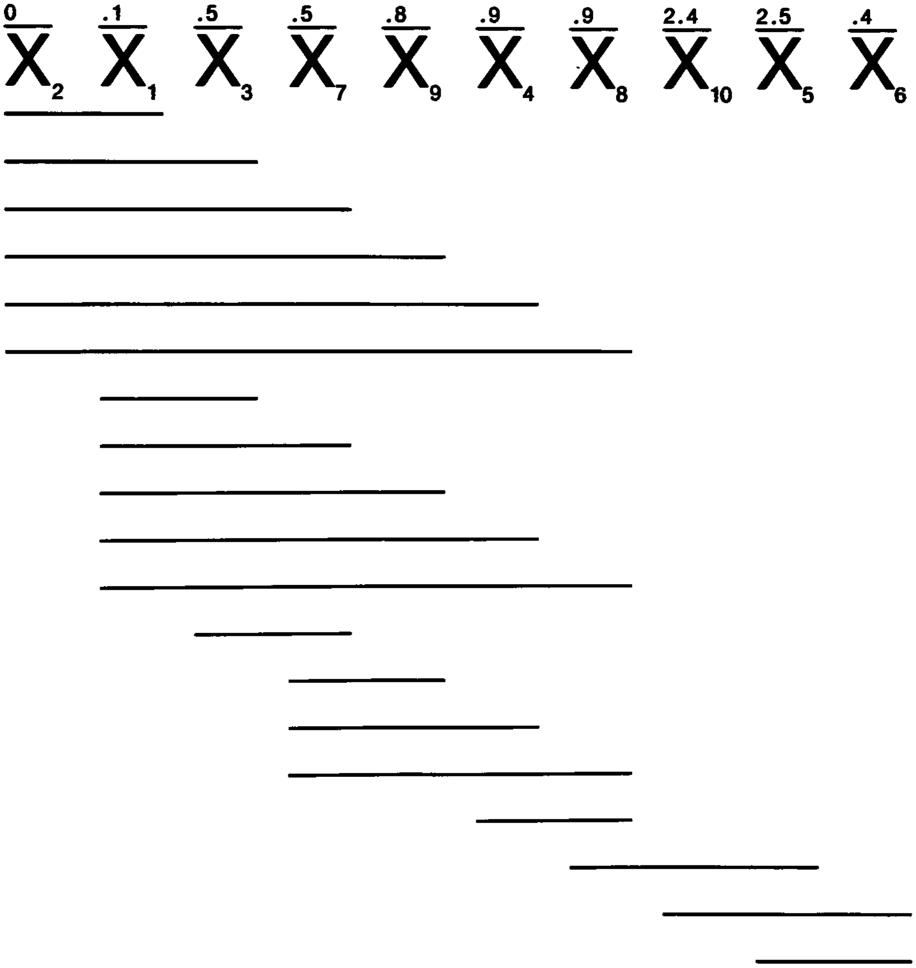


Figure 21. Plot of the data, Solvents vs. Durometer, Plate 3.



LSD 1.35

Figure 22. Multiple Range Test for Factor A Solvent, Plate 3. (The solvents with no significant difference are underlined.)

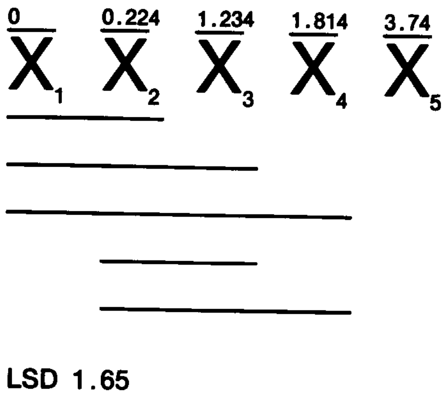


Figure 23. Multiple Range Test for Factor B Time, Plate 3. (The times with no significant difference are underlined.)

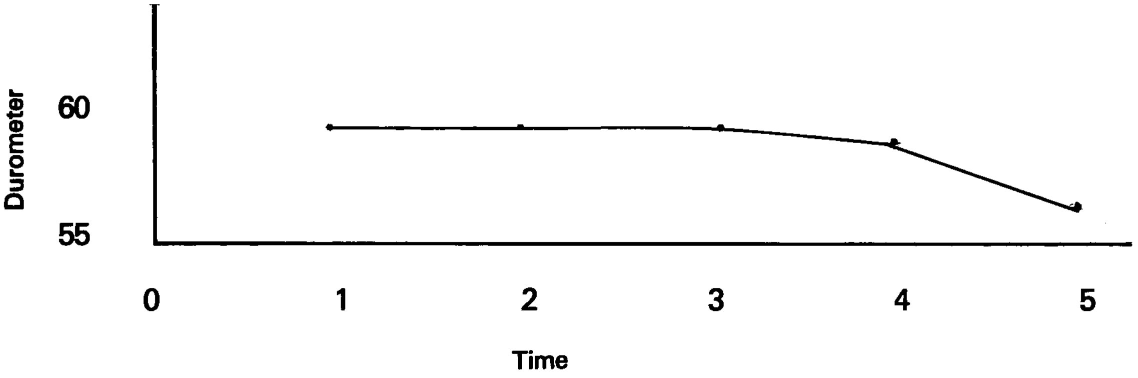


Figure 24. Plot of data, Time vs. Durometer, Plate 3.

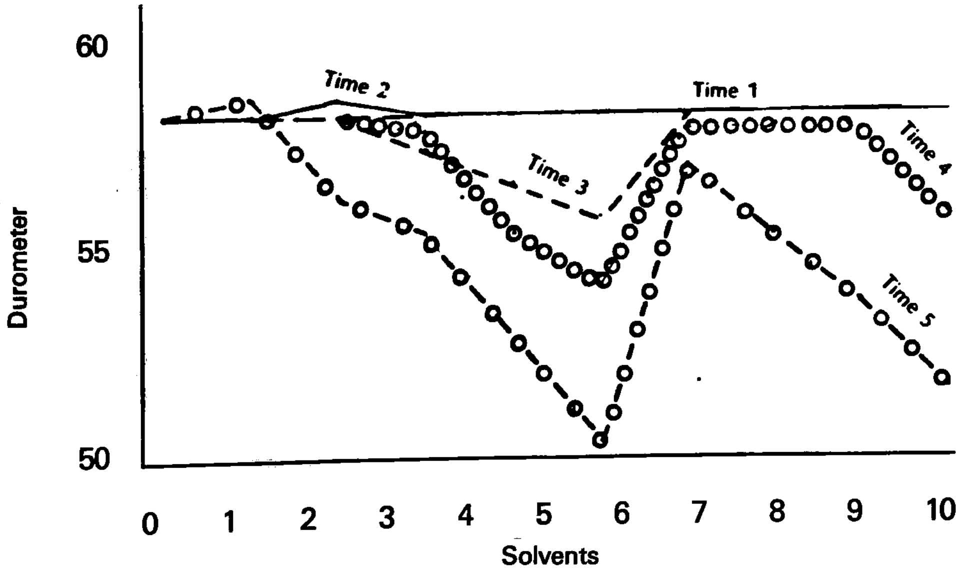


Figure 25. Plot of the data, Solvents vs. Durometer, Plate 3.

Source	Sum of Squares	df	Means Squares	F Ratio (Calculated)	F Ratio (Table)	Significant* Not Significant (N.S.)
Solvent	65.340991	9	72.60109	10.58326	2.08205	*
Time	1121.35986	4	280.33984	40.86950	2.56560	*
Interaction	332.03979	36	9.22333	1.34451	1.71925	N.S.
Total Error	342.9970	50	6.62333			

Table 5. ANOVA Summary Table for Plate 4

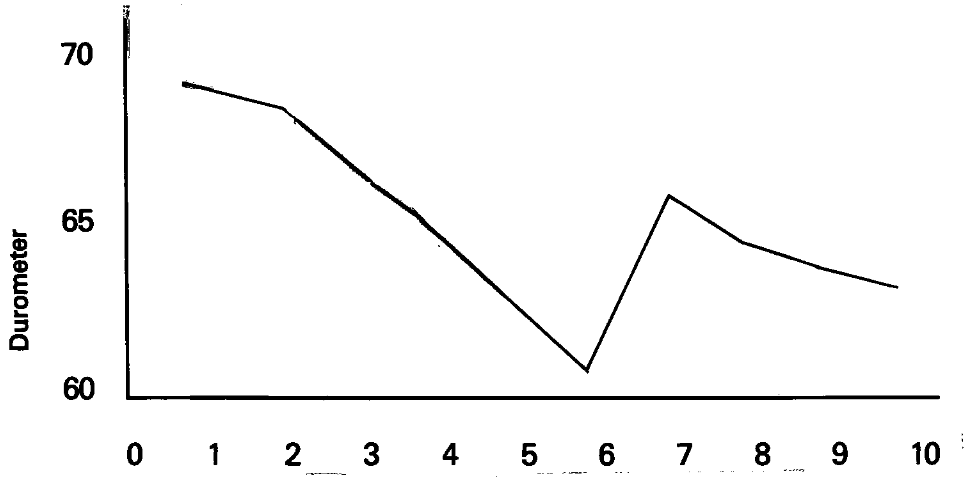


Figure 26. Plot of the data, Solvents vs. Durometer, Plate 4.

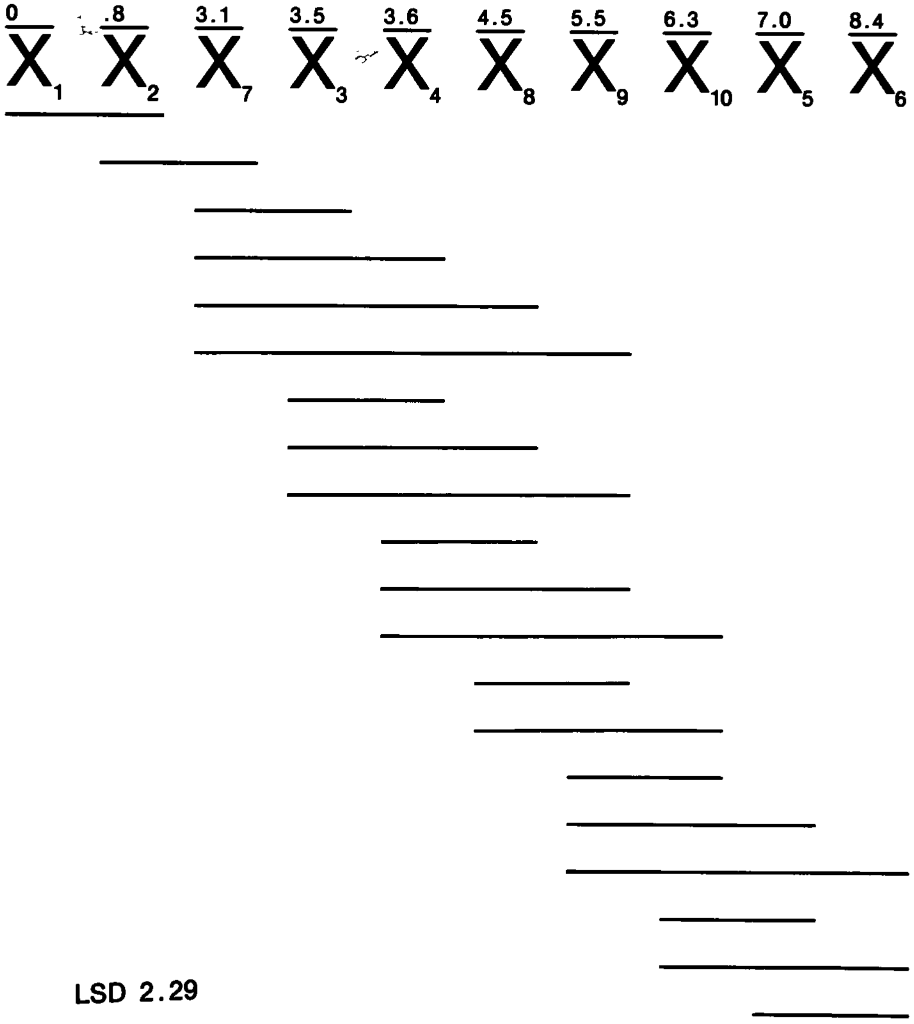


Figure 27. Multiple Range Test for Factor A Solvent, Plate 4. (The solvents with no significant difference are underlined.)

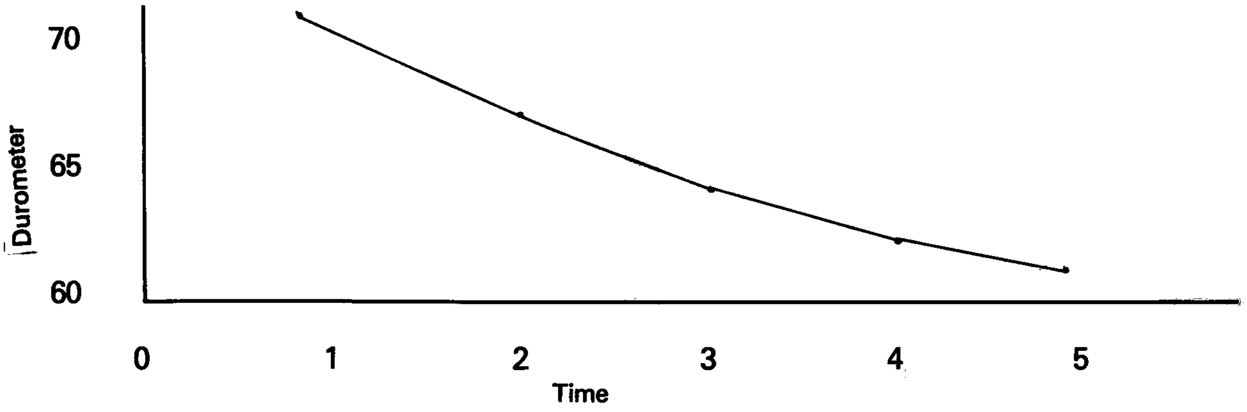


Figure 28. Plot of the data, Time vs. Durometer, Plate 4.

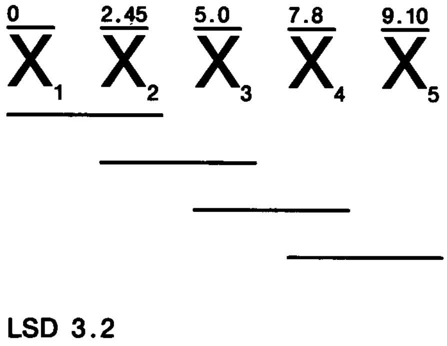


Figure 29. Multiple Range Test for Factor B. Time, Plate 4. (The times with no significant difference are underlined.)

Analysis of Change in Plate 5 Hardness

The ANOVA Summary Table for the experiment (Table 6) shows that Factor A Solvent, Factor B Time, and the interaction between the two are all significant for Plate 5. (Figure 30). The multiple range test (Figure 31) indicates that all of the solvents except water and the mixture of water and soap soften the plate significantly. However, this experiment cannot be considered a fair test of the plate because according to the plotted data (Figure 33) and the multiple range test (Figure 32) the plate softens so quickly with time that it is difficult to determine which solvents had a significant effect. This phonomenon is due to the fact that solvents compatible with this plate were not used in the experiment.

Analysis of Change in Plate 6 Hardness

The ANOVA Summary Table for the experiment (Table 7) shows that for Plate 6, Factor A Solvent, Factor B Time, and the interaction between the two are all significant. A simple plot (Figure 34) of all levels of Factor A Solvent in this experiment confirm that there is very little effect on the hardness of this plate caused by water, alcohol, soap, and solvents containing small quantities of lactol spirits and normal propyl acetate. The multiple range test for Factor B Time (Figure 35) indicates that the plate became significantly softer, when measured at Time 2, compared to Time 1. The plate then remained stable for four more hours before further softening occurred (Figures 36, 37).

Source	Sum of Squares	df	Means Squares	F Ratio (Calculated)	F Ratio (Table)	Significant* Not Significant (N.S.)
Solvent	305.23999	9	33.91554	24.22539	1.76545	*
Time	521.53979	4	130.38495	93.13211	2.06959	*
Interaction	150.85999	36	4.19055	2.99325	1.53975	*
Total Error	69.99999	50	1.40000			

Table 6. ANOVA Summary Table for Plate 5.

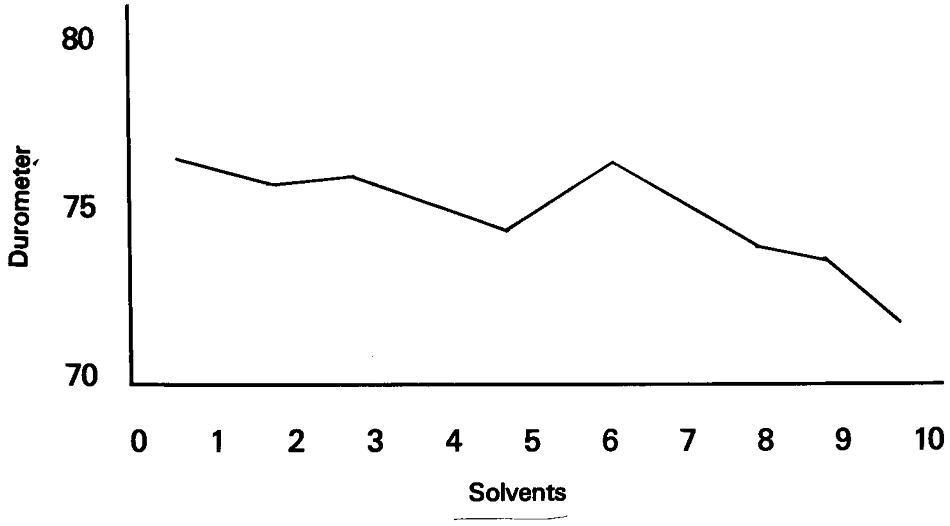
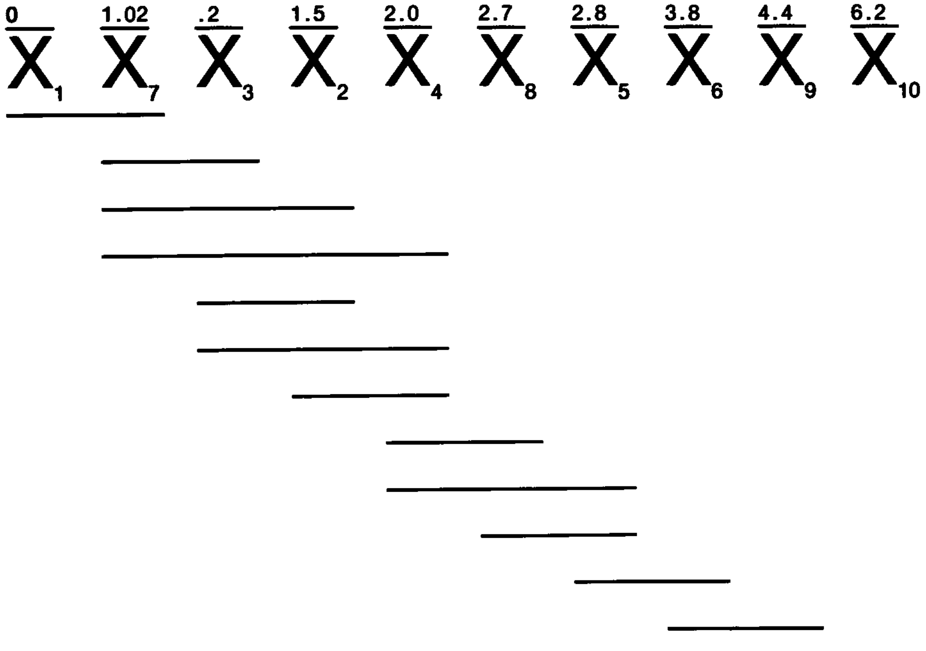


Figure 30. Plot of the data, Solvents vs. Durometer, Plate 5.



LSD 1.036

Figure 31. Multiple Range Test for Factor A Solvent, Plate 5. (The solvents with no significant difference are underlined.)

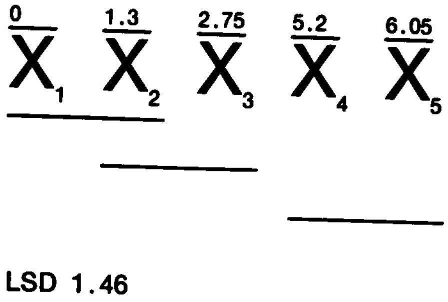


Figure 32. Multiple Range Test for Factor B Time, Plate 5. (The times with no significant difference are underlined.)

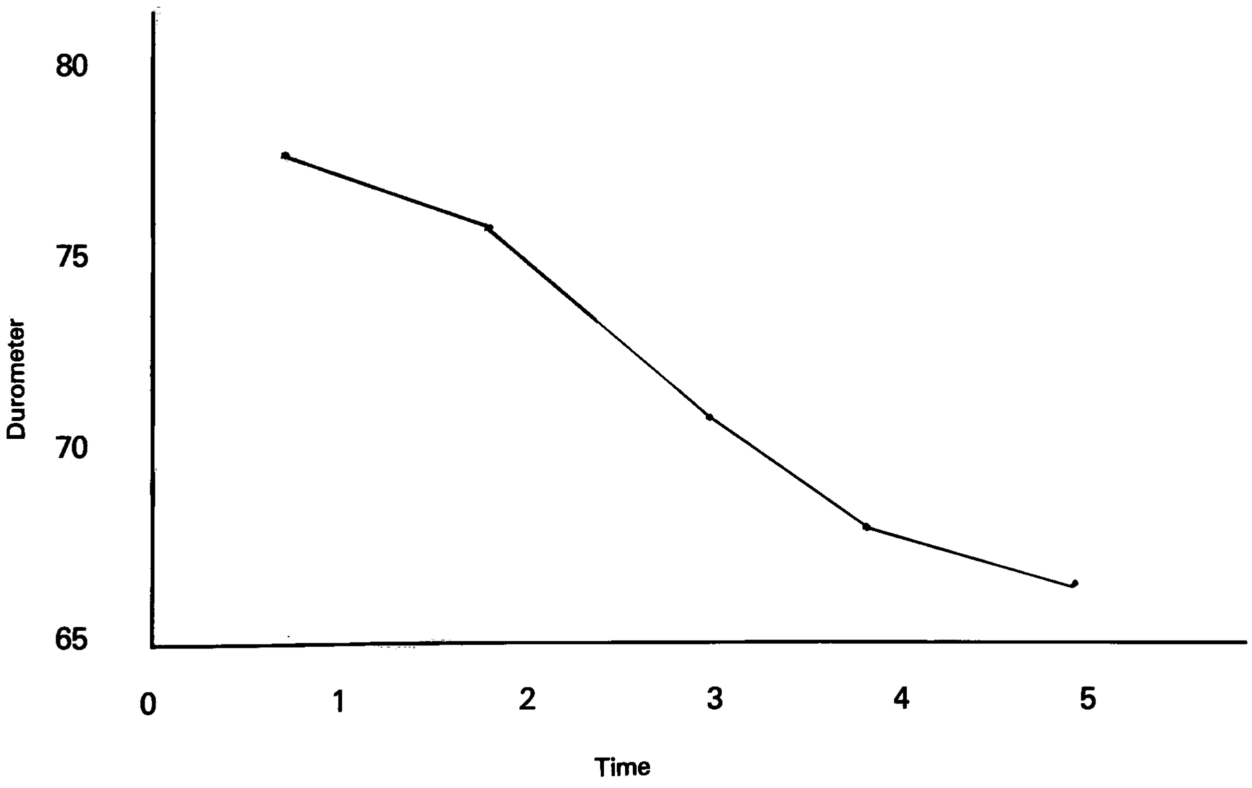


Figure 33. Plot of the data, Time vs. Solvent, Plate 5.

Source	Sum of Squares	df	Means Squares	F Ratio (Calculated)	F Ratio (Table)	Significant* Not Significant (N.S.)
Solvent	245.60990	9	27.28890	40.72970	1.73800	*
Time	159.56000	4	39.89000	59.53731	1.82380	*
Interaction	91.03999	36	2.52889	3.77446	1.39520	*
Total Error	33.50000	50	.67000			

Table 7. ANOVA Summary Table for Plate 6.

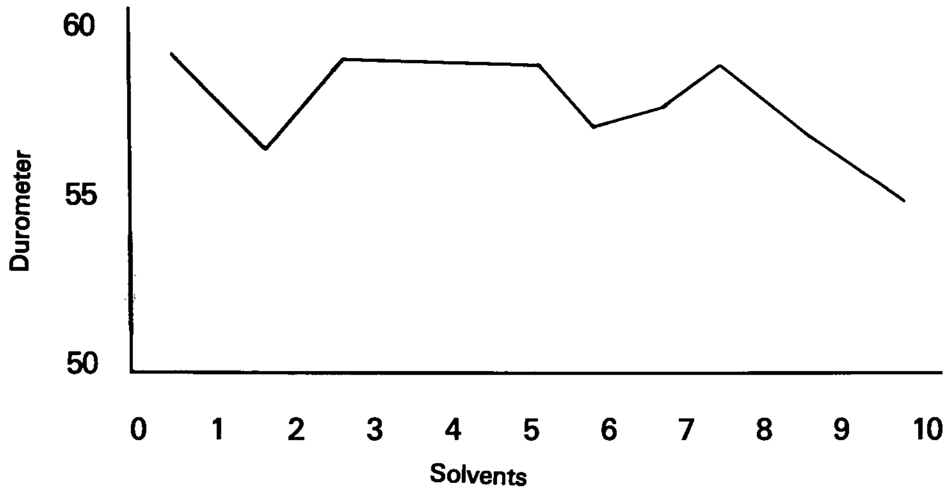
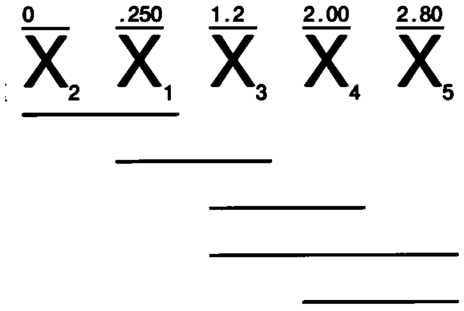


Figure 34. Plot of the data, Solvents vs. Durometer, Plate 6.



LSD 1.014

Figure 35. Multiple Range Test for Factor B Time, Plate 6. (The times with no significant difference are underlined.)

Analysis of Change in Plate 7 Hardness

The ANOVA Summary Table for the experiment (Table 8) shows that for Plate 7, Factor A Solvent, Factor B Time, and the interaction between the two are all significant (Figure 38, 39, 40). The plotted data indicates the plate is not affected by water and normal propyl alcohol but does soften significantly when immersed into solutions containing large quantities of acetate.

Source	Sum of Squares	df	Means Squares	F Ratio (Calculated)	F Ratio (Table)	Significant* Not Significant (N.S.)
Solvent	86.89000	9	9.654444	7.04704	2.16735	*
Time	165.6400	4	41.40999	30.22628	2.64780	*
Interaction	107.15999	36	2.97667	2.17275	1.86905	*
Total Error	68.49997	50	1.37000			

Table 8. ANOVA Summary Table for Plate 7.

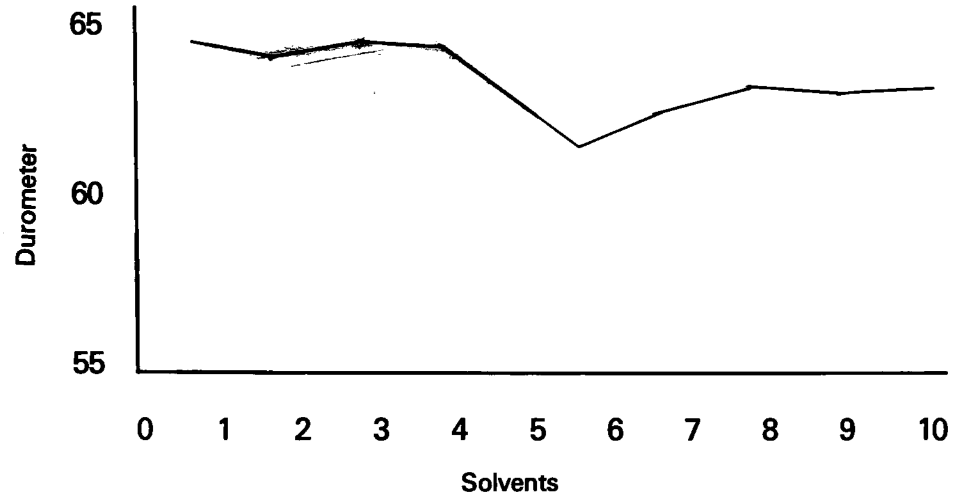


Figure 38. Plot of the data, Solvents vs. Durometer, Plate 7.

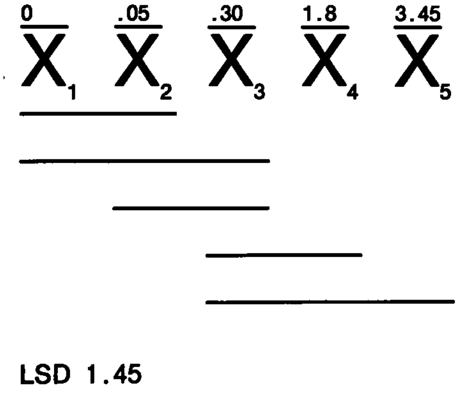
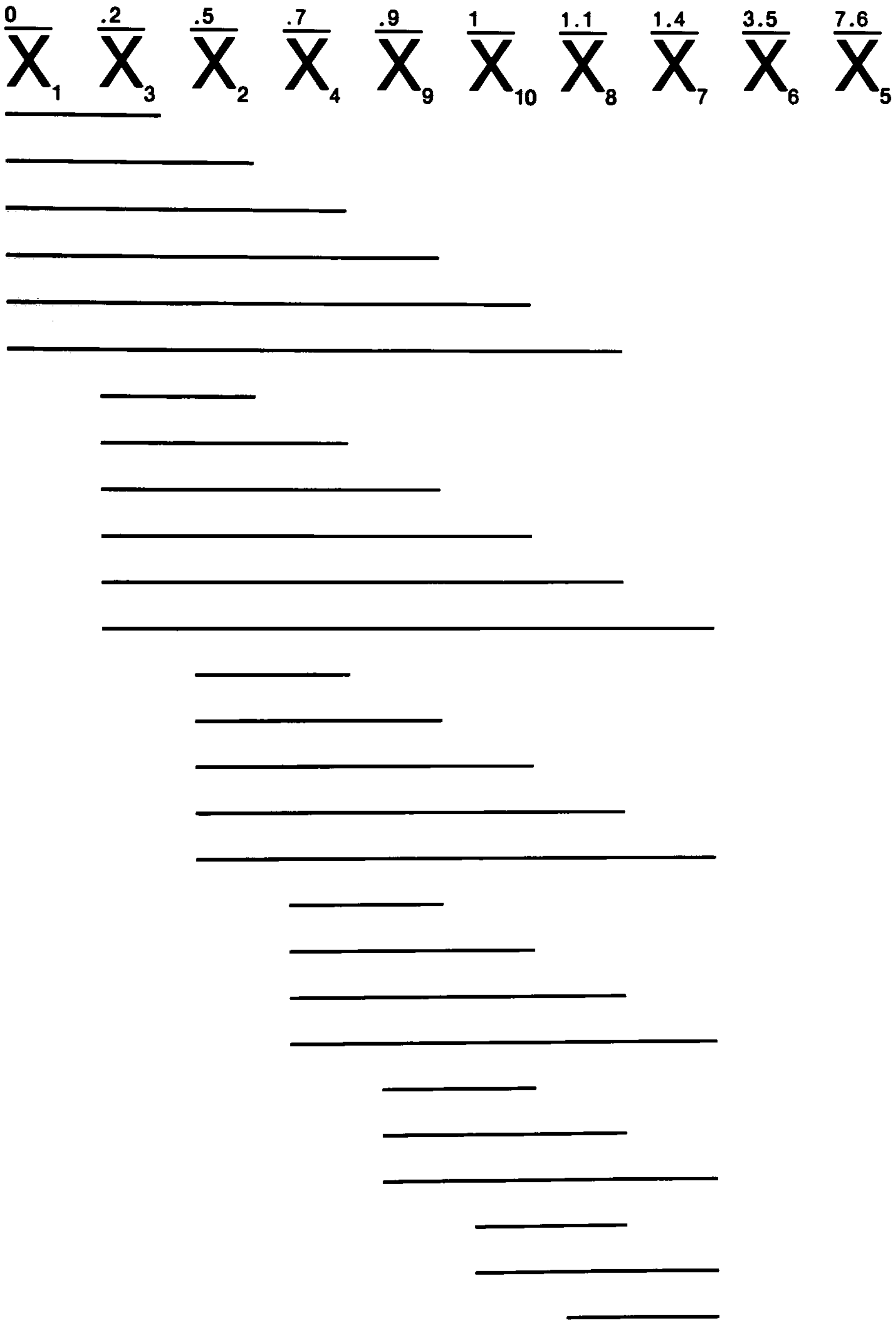


Figure 39. Multiple Range Test for Factor B Time, Plate 7. (The times with no significant difference are underlined.)



LSD 1.203

Figure 40. Multiple Range Test for Factor A Solvent, Plate 7. (The solvents with no significant difference are underlined.)

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Analysis of weight change data after 24 hours of treatment indicates a significant effect due to plates as well as solvent. Statistical analysis indicates that plate 4 gains a significantly greater amount of weight due to solvent exposure than the other plates tested. Water is shown to produce no change in plate weight gain after 24 hours of exposure. A statistically similar effect is indicated by the addition of soap to water, normal propyl alcohol, and the mixture of 5% lactol spirits and 10% acetate with the appropriate amount of normal propyl alcohol. Addition of larger amounts of these co-solvents to normal propyl alcohol produces a significantly greater weight change. The trend indicated is increased change in plate weight with increased substitution of the selected co-solvents.

The results of the experiment pertaining to Plate 1 are consistent with what may be expected of a photopolymer plate of this chemical composition. Plate 1 had some noticable changes after 24 hours. With solvent 2 it was cool to the touch. Solvent 3 and 4 turned the surface white. Solvent 5 caused the plate to curl. Solvent 6 created curling and also turned white.

Plate 2 can be used with water, 100% normal propyl alcohol, a mixture of normal propyl alcohol and 5% lactol.

Plate 3 is not softened by anti-foam compounds, but is softened by alcohol. Higher quantities of acetate have a detrimental effect on this plate. Plate deterioation is also evident after 24 hours soaking. It curled, started to turn white and also delaminated.

Plate 4 is not recommended to be used with solvents containing normal propyl alcohol, this affects the plate by marked softening.

Plate 5 softened so quickly with the solvents of this experiment that it is difficult to determine which solvents had a significant effect. This of course is due to the fact that solvents compatible with this plate were not used in this experiment.

Plate 6 had a reverse affect during the first time periods, caused by water, alcohol, anti-foam agents, and solvents containing small quantities of lactol spirits and normal propyl acetate. It softened a small amount, then became significantly harder, at Time 2 and then resumed its softening pattern.

Plate 7 was not affected significantly by water and 100% normal propyl alcohol, but did swell significantly when immersed in solutions containing increasing amounts of acetate.

Finally, Plates of similar polymer composition performed in a like manner. Plate 1 performed similar to natural rubber, Plate 3 similar to Buna N, and all photopolymer plates poorly in acetates.

However, it is possible to use acetates with these plates over short periods of time on small press runs. The crystaline photopolymer gained considerable weight when exposed to any other solvent except water and normal propyl alcohol.

Further work might include the correlation of these experiments with field experience to see if the results are at all consistent.

With the increasing use of flexography in the newspaper industry, it is recommended that further studies be made to note what changes have occured in the plates and solvents to allow for the differences in the printing on newsprint by flexography.

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GLOSSARY

Acetate. A family of solvents also known as esters; example normal propyl acetate. One of, or the family of, cellulose acetate films.

Acrylic. A general chemical term for a particular family of thermoplastic resins based on acrylic acid and its derivatives.

Actinic Rays. Those rays of light which cause the most intense chemical change to take place in plastic films, lacquer, photographic emulsions, etc.

Activate. To put into a state of motion or increased chemical activity.

Absorption. A concentration of a substance at a surface or interface resulting from the attractions of molecules of the two substances, e.g., the condensation of adhesion of gases, liquids or dissolved substances on the surface of solids.

Addition Photopolymerization Process. Monomers plus monomers plus light, plus monomers plus monomers, etc.

Alcohol. A group of organic solvents widely used in flexographic inks.

Aliphatic Hydrocarbons. Solvents obtained by fractionation of crude petroleum oil. Examples are lactol-lactol spirits, textile spirits, VMP Naphtha, gasoline, kerosene. Frequently used as part of the sovlent mixture in Co-solvent and polyamide type flexo inks, in conjunction with Buna-N type plates and rollers. Tend to swell natural and butyl rubber.

Ambient Temperature. A term used to denote the temperature of the surrounding air.

Amorphous. Devoid of definite form; having no definite crystalline structure.

ANOVA. (Analysis of Variance involves the concept: estimate the variance of all the data withour regard to cause; partitioning this total variance between (1) tested factor and (2) experimental error; compare these two variances by means of an F test.

Antifoaming Agent. An additive used in ink that prevents or eliminates foaming of a liquid or breaks foam already formed.

Aromatic Hydrocarbons. Petroleum solvents characterized by benzene or closed ring molecular configuration. Used only sparingly in flexographic inks.

A.S.T.M. American Society for Testing Materials.

Block Polymers. See Linear Polymers.

Buna-N. A synthetic rubber made from butadiene and acrylonitrile, used in the manufacture of flexo plates and rolls. Resistant to aliphatic hydrocarbons, alcohols, cellosolve, and water. Not resistant to aromatic hydrocarbons and esters (acetate), etc.

Cellosolve. Union Carbide Co. Trade name for ethylene glycol mono-ethyl either which is used as a retarding solvent in flexographic inks.

Copolymer. Polymer produced from a combination of two or more monomers. See Polymer.

Cross-linking. Attachment of two chains of polymer molecules by bridges composed of either an element, a group, or a compound which join certain carbon atoms together by primary chemical bonds. This can also be effected artifically either by subjecting the polymer to high-energy radiation. Examples are: (1) vulcanization of rubber with sulfer or organic peroxide.

Cure. The step in the manufacture of a rubber roller or plate in which it is subjected to temperature elevation under pressure for a length of time to vulcanize the elastomer until it reaches its optimum in elasticity and tensile strength. As applied to rubber rollers, the aging cycle required following vulcanization. To treat (with heat) to make infusible.

Double Bonds. (Unsaturation) of a chemical compound, the state in which not all available valence bonds are satisfied; in such compounds the extra bonds usually form double or triple bonds.

Durometer. A measure of rubber hardness usually made with Shore A Durometer Gauge.

Elasticity. The property of a substance which enables it to return to its original size or shape after being stretched or deformed.

Elastomer. Any rubber-like substance or polymer.

Ester. A group of solvents made by reacting an acid with an alcohol, e.g., ethyl acetate isopropyl acetate; acetate solvents.

Etch. To make an engraving by eating away the surface of a metal plate with acid.

Flash Point. The lowest temperature at which a substance can be ignited under standard test conditions.

Flexography. A method of direct rotary printing using resilient raised image printing plates, affixed to variable repeat plate cylinders, inked by a roll or doctor blade wiped engraved metal roll, carrying fluid or paste type inks to virtually any substrate.

Hickey. A piece of foreigh matter in paper; or similar defect. A burr or defect on the printing plate or engraving.

Homogenous. Of the same origin or structure.

Homogeneous. Of the same uniform composition or construction throughout.

Hydrocarbons. Materials composed entirely of carbon and hydrogen. General term for family of petroleum solvents.

Infrared Light. Refers to Infrared rays, the longer wave lengths below the red in the spectrum; used as a source of heat.

Ketones. A class of organic compounds; generally colorless volatile liquids, as acetone, methyl ethyl ketone, etc.

Light Reflection. The light, striking an object, which is turned back. The opposite of absorption.

Linear Polymers or Block Polymers. A recurring structure that is linked with other similar structures at both ends with a long chain consisting of hundreds or thousands of such units result.

Lithography. A method of printing from a plane surface (as a smooth stone or metal plate) on which the image to be printed is ink-receptive and the non-printing area ink repellent. Planography.

Matrix. A mold made from an engraving or type form from which a rubber plate is subsequently molded.

Melting Point. The temperature at which a solid substance begins to liquefy under standard conditions.

Methly Ethyl Ketone. (M.E.K.) A relatively fast-drying organic solvent of the ketone family. Highly flammable. Good solvent for nitrocellulose and vinyl lacquers. Small amounts will swell Buna-N plates, larger amounts will swell natural rubber. Boiling point 175 degrees Fahrenheit. Flash point 24 degrees Fahrenheit.

Mold. A female form used for the production of desired shapes. (Verb) To form a matrix or rubber plate. (Noun) See Matrix.

Monomer. A chemical combination of molecules corresponding to the individual units of a polymer. It is capable of being incorporated (polymerized) into polymers.

Naphtha. Alipathic hydrocarbon solvent derived from petroleum such as hexane, V M & P naphtha, etc. Characterized by low K.B. values. Will swell natural or butyl rubber, have slight effect on Buna-N or Neoprene.

Neoprene. A synthetic chlorinated butadiene rubber used in making flexo-rollers resistant to alcohols, cellosolve, water, aliphatic hydrocarbons and to a limited extent esters. (acetates). Not resistant to aromatic hydrocarbons.

Offset. THe transfer of an improper or incompletely dried ink from the face of the print to the back of the stock on top of it in the roll or pile. The accidental transfer of ink from the idler or other rolls in a press to the web.

Olefinic hydrocarbons. (olefin) straight chain in distinction to rings.

Organic. Refers to the compounds, in the field of chemistry, containing carbon.

Plattern or Pattern Plate. The engraving or combination of plates used for making the matrices from which rubber plates are made.

Photopolymer. A polymer or plastic that is made so that it is sensitive to and undergoes some kind of change on exposure to light. Such materials can be used for printing and lithography plates, for photographic prints and microfilm copying.

Pimples. Caused by excessive tooling or routing on the engraving. They show up on the finished prints as extra spots.

Plasticizers. Materials, usually liquid but sometimes solid, that impart flexibility to an ink or lqcquer.

Polymer. A compound formed by the linking of simple and identical molecules having functional groups that permit their combination to proceed to higher molecular weights under suitable conditions.

Polymerization. A chemical reaction in which the molecules of a monomer are linked together to form large molecules whose weight is a multiple of that of the original substamce.

Polyunsaturated ester. Ester is alcohol plus organic acid with carbon chain eith double bonds.

Scum. When the non-image areas of the plate loose their desensitization and begin to take ink.

Shoulder Angle. Angle of slant shoulder for the relief portion of a plate.

Softening Point. Temperatures at which plastic material will start to deform with no externally applied load.

Solidify. To make solid or firm; to harden; to become solid.

Solvent. The medium used to dissolve a substance.

Tack. The resistance of an ink between two surfaces which are being pulled apart.

Thermosetting. Term applied to synthetic resins which solidify or set on heating and cannot be remelted. The thermosetting property is usually associated with a crosslinking reaction of the constituents to form a three dimensional network of polymer molecules. This type includes phenolic resins, alkyds, aino resins, polyesters, j epoxies, polyurethanes, silicones.

Undercut. Engravings on which side-wall areas have been etched under the printing surface.

Vinyl. Informal generic term for any of the vinyl resins, or for film, or other products made from them.

Vinyl Plastics. Plastics based on resins made from vinyl monomers, except those specifically covered by other classifications such as acrylic and styrene plastics. Typical vinly plastics are polyvinyl chloride, polyvinyl acetate, polyvinly alcohol, and polyvinly butyral, and copolymers of vinyl monomers and unsaturated compounds.

Vitrify. The process of converting into glass or a glassy substance by heat and fusion.

Volatile. Easily passing from a liquid into a gaseous state. Subject to rapid evaporation. Having a high vapor-pressure at room temperature.

Vulcanization. Process of combining rubber with sulfur or other additives catalyzed by heat and pressure to improve useful properties of rubber such as strength, elasticity and abrasion resistance.

APPENDIX A

```
LEVELS OF FACTORS
  A            10
  B             7
  C             2

GRAND MEAN           16.50476


SOURCE OF                SUMS OF        DEGREES OF         MEAN
VARIATION                SQUARES         FREEDOM          SQUARES

A                   13282.83203              9        1475.87012
B                   17691.71875              6        2948.61963
AB                  10102.51953             54         187.08369
C                     562.20117              1         562.20117
AC                    457.87915              9          50.87546
BC                    636.60498              6         106.10083
ABC                  4298.37109             54          79.59946
TOTAL               47032.12109            139
```

Printout of Analysis of Variance pertaining to Table 1

```
ANALYSIS OF VARIANCE.....DURU1

LEVELS OF FACTORS
   A          10
   B           5
   C           2

GRAND MEAN              52.25999

SOURCE OF               SUMS OF          DEGREES OF        MEAN
VARIATION               SQUARES           FREEDOM         SQUARES

A                      483.83984             9           53.75998
B                      205.84000             4           51.45999
AB                     381.55981            36           10.59888
C                       27.03999             1           27.03999
AC                      90.75999             9           10.08444
BC                      16.75999             4            4.19000
ABC                     81.43999            36            2.26222
TOTAL                 1287.23877            99

COPY DURO1OUT TO LP(K)
   1 -    0.500 DURO1 03         A0010B0005C0002
   2 -    1.000  54.00 54.00 54.00 54.00 54.00 54.00 54.00 54.00 54.00 54.00
   3 -    2.000  54.00 54.00 54.00 54.00 54.00 50.00 54.00 54.00 54.00 54.00
   4 -    3.000  54.00 54.00 54.00 54.00 52.00 50.00 54.00 54.00 54.00 49.00
   5 -    4.000  54.00 54.00 54.00 54.00 51.00 47.00 54.00 54.00 52.00 50.00
   6 -    5.000  54.00 54.00 54.00 54.00 50.00 44.00 54.00 54.00 50.00 42.00
   7 -    6.000  54.00 54.00 54.00 54.00 54.00 54.00 54.00 54.00 54.00 54.00
   8 -    7.000  54.00 54.00 54.00 53.00 52.00 52.00 54.00 53.00 53.00 52.00
   9 -    8.000  54.00 54.00 54.00 53.00 52.00 52.00 52.00 53.00 52.00 46.00
  10 -    9.000  54.00 54.00 54.00 53.00 51.00 50.00 52.00 53.00 49.00 35.00
  11 -   10.000  54.00 54.00 53.00 53.00 49.00 46.00 52.00 52.00 43.00 33.00
```

Computer Printout of Analusis of Variance pertaining to Table 2, also durometer readings for plate 1.

```
ANALYSIS OF VARIANCE.....DURO2

LEVELS OF FACTORS
  A          10
  B           5
  C           2

GRAND MEAN              71.53000


SOURCE OF                   SUMS OF         DEGREES OF       MEAN
VARIATION                   SQUARES          FREEDOM        SQUARES

A                          2366.20996           9          262.91211
B                          1897.15991           4          474.28979
AB                          863.03979          36           23.97333
C                            86.48999           1           86.48999
AC                           93.81000           9           10.42333
BC                           64.95999           4           16.23999
ABC                         115.23999          36            3.20111
TOTAL                      5486.89844          99


COPY DURO2OUT TO LP(K)
     1 -      0.500 DURO2 03        A0010B0005C0002
     2 -      1.000  78.00 78.00 78.00 78.00 78.00 78.00 78.00 78.00 78.00 78.00
     3 -      2.000  78.00 76.00 78.00 78.00 78.00 73.00 75.00 76.00 72.00 70.00
     4 -      3.000  78.00 70.00 75.00 72.00 73.00 70.00 75.00 73.00 68.00 59.00
     5 -      4.000  78.00 70.00 76.00 72.00 69.00 65.00 73.00 71.00 65.00 54.00
     6 -      5.000  78.00 71.00 76.00 72.00 69.00 60.00 73.00 69.00 62.00 53.00
     7 -      6.000  78.00 78.00 78.00 78.00 78.00 78.00 78.00 78.00 78.00 78.00
     8 -      7.000  78.00 74.00 78.00 78.00 74.00 73.00 76.00 74.00 73.00 61.00
     9 -      8.000  78.00 74.00 78.00 76.00 72.00 70.00 73.00 70.00 63.00 55.00
    10 -      9.000  78.00 65.00 75.00 71.00 69.00 65.00 70.00 65.00 55.00 48.00
    11 -     10.000  78.00 62.00 73.00 70.00 66.00 63.00 67.00 62.00 54.00 46.00
```

Computer Printout of Analysis of Variance pertaining to Table 3, also durometer readings for plate 2.

```
ANALYSIS OF VARIANCE.....DURO3

LEVELS OF FACTORS
  A          10
  B           5
  C           2

GRAND MEAN                56.84999


SOURCE OF                            SUMS OF          DEGREES OF          MEAN
VARIATION                            SQUARES           FREEDOM           SQUARES

A                                   126.84999             9             14.09444
B                                   221.29999             4             55.32500
AB                                  157.09999            36              4.36389
C                                     9.61000             1              9.61000
AC                                   14.29000             9              1.58778
BC                                   39.73999             4              9.93500
ABC                                  25.85999            36               .71833
TOTAL                               594.74927            99
COPY DUR03001 TO LP(K)
   1 -      0.500 DURO3 03        A0010B0005C0002
   2 -      1.000   58.00 58.00 59.00 58.00 58.00 58.00 58.00 58.00 58.00 58.00
   3 -      2.000   58.00 58.00 58.00 58.00 58.00 58.00 58.00 58.00 58.00 58.00
   4 -      3.000   58.00 58.00 58.00 58.00 56.00 53.00 58.00 58.00 58.00 58.00
   5 -      4.000   58.00 58.00 58.00 58.00 55.00 52.00 58.00 58.00 58.00 55.00
   6 -      5.000   58.00 59.00 58.00 58.00 53.00 49.00 58.00 58.00 55.00 50.00
   7 -      6.000   58.00 58.00 58.00 58.00 58.00 58.00 58.00 58.00 58.00 58.00
   8 -      7.000   58.00 58.00 58.00 58.00 58.00 58.00 58.00 58.00 58.00 58.00
   9 -      8.000   58.00 58.00 58.00 58.00 56.00 57.00 58.00 58.00 58.00 58.00
  10 -      9.000   58.00 58.00 58.00 57.00 54.00 54.00 57.00 57.00 57.00 55.00
  11 -     10.000   58.00 58.00 53.00 51.00 50.00 48.00 55.00 51.00 52.00 49.00
```

Computer Printout of Analysis of Variance pertaining to Table 4, also durometer readings for plate 3.

```
ANALYSIS OF VARIANCE.....DUR04

LEVELS OF FACTORS
   A          10
   B           5
   C           2

GRAND MEAN            64.12999


SOURCE OF                    SUMS OF          DEGREES OF        MEAN
VARIATION                    SQUARES          FREEDOM           SQUARES

A                            653.40991           9              72.60109
B                           1121.35986           4             280.33984
AB                           332.03979          36               9.22333
C                            136.89000           1             136.89000
AC                            68.20999           9               7.57889
BC                            42.95999           4              10.74000
ABC                           94.43999          36               2.62333
TOTAL                       2449.30933          99

COPY DUR04OUT TO LP(K)
  1 -    0.500  DUR04 03      A0010B0005C0002
  2 -    1.000  69.00  69.00  69.00  69.00  69.00  69.00  69.00  69.00  69.00  69.00
  3 -    2.000  69.00  69.00  68.00  68.00  65.00  64.00  69.00  69.00  69.00  69.00
  4 -    3.000  69.00  69.00  66.00  63.00  65.00  62.00  68.00  67.00  66.00  65.00
  5 -    4.000  69.00  67.00  64.00  61.00  61.00  60.00  62.00  61.00  61.00  60.00
  6 -    5.000  69.00  69.00  63.00  59.00  59.00  55.00  63.00  59.00  59.00  55.00
  7 -    6.000  69.00  69.00  69.00  69.00  69.00  69.00  69.00  69.00  69.00  69.00
  8 -    7.000  69.00  67.00  65.00  65.00  63.00  63.00  65.00  65.00  65.00  65.00
  9 -    8.000  68.00  68.00  62.00  64.00  55.00  55.00  63.00  63.00  62.00  60.00
 10 -    9.000  68.00  66.00  62.00  63.00  53.00  52.00  63.00  59.00  57.00  55.00
 11 -   10.000  66.00  64.00  62.00  63.00  51.00  52.00  63.00  59.00  53.00  55.00
```

Computer Printout of Analysis of Variance pertaining to Table 5, also durometer readings for plate 4.

```
ANALYSIS OF VARIANCE.....DUROS

LEVELS OF FACTORS
   A         10
   B          5
   C          2

GRAND MEAN                 73.93999


SOURCE OF                        SUMS OF        DEGREES OF         MEAN
VARIATION                        SQUARES         FREEDOM          SQUARES
A                               305.23999            9           33.91554
B                               521.53979            4          130.38495
AB                              150.85999           36            4.19055
C                                 1.44000            1            1.44000
AC                               29.75999            9            3.30667
BC                                2.46000            4             .61500
ABC                              36.34000           36            1.00944
TOTAL                          1047.63916           99

COPY DUROSOUT TO LP(K)
     1 -      0.500  DUROS 03          A0010B0005C0002
     2 -      1.000  77.00 77.00 77.00 77.00 77.00 77.00 77.00 77.00 77.00 77.00
     3 -      2.000  77.00 77.00 77.00 76.00 75.00 75.00 77.00 76.00 75.00 74.00
     4 -      3.000  77.00 76.00 76.00 74.00 73.00 73.00 77.00 74.00 73.00 71.00
     5 -      4.000  77.00 74.00 73.00 72.00 71.00 68.00 75.00 72.00 71.00 64.00
     6 -      5.000  77.00 73.00 73.00 72.00 70.00 68.00 75.00 72.00 70.00 63.00
     7 -      6.000  77.00 77.00 77.00 77.00 77.00 77.00 77.00 77.00 77.00 77.00
     8 -      7.000  77.00 74.00 76.00 77.00 76.00 75.00 77.00 75.00 74.00 74.00
     9 -      8.000  76.00 74.00 76.00 76.00 76.00 74.00 75.00 74.00 70.00 70.00
    10 -      9.000  75.00 74.00 75.00 72.00 72.00 71.00 74.00 72.00 67.00 67.00
    11 -     10.000  75.00 74.00 73.00 72.00 70.00 69.00 71.00 69.00 67.00 66.00
```

Computer Printout of Analysis of Variance pertaining to Table 6, also durometer readings for plate 5.

```
ANALYSIS OF VARIANCE.....DURO61

LEVELS OF FACTORS
  A          10
  B           5
  C           2

GRAND MEAN              57.23000

SOURCE OF                      SUMS OF        DEGREES OF        MEAN
VARIATION                      SQUARES         FREEDOM        SQUARES
A                             245.60999           9          27.28999
B                             159.56000           4          39.89000
AB                             91.03999          36           2.52889
C                               7.29000           1           7.29000
AC                              7.61000           9            .84556
BC                              6.56000           4           1.64000
ABC                            12.04000          36            .33444
TOTAL                         529.70898          99

COPY DURO61OUT TO LP(K)
     1 -      0.500 DURO6103           A0010B0005C0002
     2 -      1.000  59.00  59.00  59.00  59.00  59.00  59.00  59.00  59.00  59.00  58.00
     3 -      2.000  59.00  57.00  59.00  59.00  59.00  58.00  59.00  59.00  59.00  55.00
     4 -      3.000  58.00  55.00  58.00  59.00  58.00  56.00  59.00  58.00  55.00  53.00
     5 -      4.000  58.00  55.00  58.00  58.00  57.00  54.00  56.00  56.00  54.00  50.00
     6 -      5.000  58.00  52.00  59.00  58.00  55.00  54.00  56.00  56.00  53.00  50.00
     7 -      6.000  59.00  59.00  59.00  59.00  59.00  59.00  59.00  59.00  59.00  59.00
     8 -      7.000  59.00  57.00  59.00  59.00  59.00  59.00  59.00  59.00  58.00  55.00
     9 -      8.000  59.00  57.00  59.00  59.00  59.00  57.00  59.00  56.00  55.00  53.00
    10 -      9.000  59.00  55.00  59.00  59.00  59.00  57.00  59.00  56.00  55.00  52.00
    11 -     10.000  59.00  55.00  59.00  57.00  57.00  55.00  58.00  55.00  53.00  51.00
```

Computer Printout of Analysis of Variance pertaining to Table 7. also durometer readings for plate 6.

```
ANALYSIS OF VARIANCE.....DURO7

LEVELS OF FACTORS
  A          10
  B           5
  C           2

GRAND MEAN                    62.90999


SOURCE OF                     SUMS OF        DEGREES OF        MEAN
VARIATION                     SQUARES         FREEDOM         SQUARES

A                             86.89000           9            9.65444
B                            165.64000           4           41.40999
AB                           107.15999          36            2.97667
C                             18.48999           1           18.48999
AC                             5.21000           9             .57889
BC                            17.35999           4            4.34000
ABC                           27.43999          36             .76222
TOTAL                        428.18970          99

COPY DURO7OUT TO LP(K)
   1 -     0.500 DURO7 03         A0010B0005C0002
   2 -     1.000  64.00 64.00 64.00 64.00 64.00 64.00 64.00 64.00 64.00 64.00
   3 -     2.000  64.00 64.00 64.00 64.00 64.00 64.00 64.00 64.00 64.00 64.00
   4 -     3.000  64.00 64.00 64.00 64.00 64.00 64.00 64.00 64.00 64.00 64.00
   5 -     4.000  64.00 64.00 64.00 64.00 62.00 59.00 64.00 64.00 64.00 64.00
   6 -     5.000  64.00 64.00 64.00 62.00 62.00 55.00 60.00 60.00 62.00 61.00
   7 -     6.000  64.00 64.00 64.00 64.00 64.00 64.00 64.00 64.00 64.00 64.00
   8 -     7.000  64.00 63.00 64.00 64.00 64.00 64.00 64.00 64.00 64.00 64.00
   9 -     8.000  64.00 63.00 64.00 64.00 64.00 59.00 64.00 64.00 64.00 64.00
  10 -     9.000  64.00 63.00 63.00 63.00 58.00 56.00 59.00 61.00 62.00 62.00
  11 -    10.000  64.00 62.00 63.00 60.00 58.00 56.00 59.00 60.00 59.00 59.00
```

Computer Printout of Analysis of Variance pertaining to Table 8, also durometer readings for plate 7.