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Effects of the Degree and Type of Sizing on the Dyeing of Paper

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EFFECTS OF THE DEGREE AND TYPE OF SIZING ON THE DYEING OF PAPER

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ABSTRACT

A study was made comparing papers dyed in a rosin/alum sized system to papers dyed in two alkaline sized systems. The alkaline sizes chosen were alkyl ketene dimer and alkenyl succinic anhydride. The dye types studied were acid, basic, anionic direct, and cationic direct. The degree of sizing was varied for each sizing type to see if the amount of sizing would effect dye retention. The papers dyed with anionic and cationic direct dyes and the basic dye were not significantly effected by sizing type or sizing degree. The direct dyes did give a lighter shade when the rosin size was used. The acid dye was the only dye type that was effected by sizing degree. For all three sizings, the color of the acid dye became darker with increased sizing. Unexpectedly, the acid dye was retained when alkyl ketene dimer was used as a sizing, even without the aid of a mordant.

Keywords: Dyes, Sizing Chemicals, Color

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INTRODUCTION

Serious consideration of alkaline sizing arose in the 1960's. Many advantages are claimed by neutral or alkaline sizing, over the standard acid system of rosin size and alum. These advantages include improved aging properties, reduced corrosion,[1] and an immediate lift in the brightness of the paper from the natural pulp color.[2] Sizing of this nature allows for the possibility of using alkaline pigments such as $CaCO_3$.[3] It is also claimed that increased strength of the paper results which allows for a decrease in refining needed, a good economic reason for using alkaline sizing.[4]

The change from acid to alkaline sizing alters many parameters of the papermaking process, one of which is the dyeing of paper. Dyes that perform well at a pH of three to five in the typically used sizing sytem of rosin and alum, may not yield the same color appearance at a pH of seven or eight which is present in an alkaline sizing system. The two relatively new alkaline sizing agents used today are alkyl ketene dimer and alkenyl succinic anhydride. The degree of sizing that is achieved with a particular sizing agent may also effect the color imparted to the paper.

The objective of the following study was to judge the effect of sizing degree and sizing type on the dyeing of paper. The study was carried out with acid, basic, and direct dye types and sizing agents of rosin, alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA).

BACKGROUND INFORMATION

Dyes

Most synthetic colorants are manufactured from derivatives of coal tar (benzene, anthracene, naphthalene, etc.). Dye intermediates, like toluidine or aniline, are transformed from these derivatives. The intermediates are then converted into specific dyes and pigments.[5] The three major categories of dyes that are important to the paper industry are acid, basic, and direct dyes. Chemical differences must exist to create color variations within each group. However, the dyes in a specific category will usually behave in similar manners.

Acid Dyes Acid dyes are usually sodium or potassium salts of color acids. They carry a weak anionic (negative) charge, and when dissolved in water are actually neutral or slightly alkaline.[5] Acid dyes give good brightness and fair light fastness, and are highly soluble. They possess no natural affinity for cellulose (bleached or unbleached), so a mordant must be used to bond them to the fiber. Because of their inability to bond directly to the fiber and their high solubility, acid dyes give considerable two-sideness to the sheet of paper. They have a high sensitivity to heat and if care is not taken they can be burned when the paper is dryed.[5] Since they have no affinity for cellulose, they give a very even shade to paper instead of dyeing some fibers more than others.

Since acid dyes have no affinity for cellulose a dyeing aid (mordant) must be used. Mordants work by chemically reacting to form a complex with the dye which in turn deposits itself in the middle lamella of the fibers.[6] Alum is the most common mordant used, which alone causes retention of the dye on the paper. However, in a rosin sized system, the rosin/alum complex will increase retention substantially, above that with just alum. An interesting point is that rosin size alone will give no retention of acid dye to the paper.[5]

When using acid dyes, the order of addition to the beater is very important. If alum is put in the beater before the dye, there is a possibility of causing a precipitation of the dye and alum before fixaton can occur on the fiber. The pH at the time of acid dye addition should be neutral or slightly alkaline. Therefore, the order to the beater for acid dyes should be fiber, dye, rosin, alum; or fiber, rosin, dye, alum.[7]

Basic Dyes Basic dyes are salts of color bases, in most cases hydrocholorides or oxalates. They are cationic in nature and are particularily sensitive to free alkali, which tends to precipitate the free color base.[8] Basic dyes impart excellent brightness and intense color value to paper.[7] They are relatively low in cost and quite soluble in water and acid media. Basic dyes only offer poor to fair light stability.[5] They tend to give a graniting effect, which means selective dying of a few individual fibers, which appear much deeper in shade than the remaining fibers.[9] Since they are cationic, they are substantive to acidic materials, such as lignin groups,[5] in which they bind by ionic forces.[10] Therefore, basic dyes have an affinity for unbleached and groundwood fibers. For light and medium shades of color, with these types of pulp, no mordant is required. Basic dyes have no affinity for pure cellulose, so they offer very little affinity for bleached pulps and need a mordant for retention in this case.[5]

When dyeing with basic dyes it is best to dye under neutral to acid conditions and stay away from alkali, therefore, a use of alum is desirable.[11] The order of addition to the beater with acid dyes should either be fiber, dye, rosin, alum; or fiber, rosin, alum, and dye.[7]

Direct Dyes Direct dyes are the most common class of dyes used in papermaking.[1] They are sodium salts of dye acids. Chemically they are similar to acid dyes except they have a high affinity for cellulose. Many explanations for the substantive nature (attaching directly without the aid of a mordant) of direct dyes exist: Substantivity could be due largely to their low solubility. Aqueous solutions are often very colloidal instead of true solutions.[5] Chemical combinations may take place due to a stronger affinity of color to cellulose than to the liquid (water) in which the dye is kept. Cellulose may act to absorb dyes from their solutions.[6] Most directs have long straight molecules and are similar to cellulose, in this way. Therefore, it is possible for the fiber and dye to be held together by atomic interaction. It is probable that the hydroxyl groups of cellulose are involved in the interaction, since acetylation of the cellulose results in a loss of affinity for direct dyes. These hydroxyl groups may be part of hydrogen bonds with the dyes. The direct dyes are believed to move into cavities in the cellulose structure and become attached by two or more hydrogen bonds.[12] Direct dyes are known to form multimolecular structures within the fiber and in some cases even microcrystallites may form.[10]

Direct dyes give superior lightfastness, but generally give a duller shade and less tinctorial value than basic and acid dyes. As was the case with basic dyes, directs tend to dye some fibers more than others, especially in mixed furnishes, which gives an appearance termed as graniting, to the sheet.[5] Directs offer superior fastness to bleeding when wet.[7] Bleedfastness and affinity can be improved even more with the addition of a cationic fixing agent or size and alum. When alum is used, directs can loose some of their brightness and fastness to light.[8] The pH when dyeing with directs should be neutral to alkaline. If kept alkaline, however, there may be a loss of color in the white water. Addition of alum can be helpful in clearing this up.[7]

There is a relatively new class of direct dyes called "cationic directs". Since they are new, not much has been written about them in the literature. These dyes behave like direct dyes but are cationic in nature rather than anionic. They have excellent affinity for cellulose, and it is claimed that they perform equally well in both acid and alkaline systems.[1]

Hunter Color Measurement When light comes in contact with an object, such as paper, it is absorbed, transmitted, and reflected. The observed color of the object is a subtractive property that is based on the absorbed part of the light into the object, in the visible wavelength region (400 - 700 Mu). There are several terms used to describe color. Hue or dominant wavelength characterize whether the color is blue, green, red, etc. Saturation, chroma, or purity give an account of the extent to which the color has departed from a neutral gray, or a measure of the amount of white light that is diluting the color. Brightness, brilliance and value render a measurement of the total amount of light that is reflected back to the eye.[13]

The Hunter L,a,b system uses multiple filter colorimetry to measure color. These color values (L, a, b) are measured for each sample, which roughly correlate with visual judgments of color appearance. This method does not cover color effects due to fluorescence, illuminant changes, and surface characteristics of luster, gloss, and texture. Therefore, a complete description of the samples color appearance is not provided by this method.[14]

The values of L, a, b were defined by Hunter in 1958. "L" gives a measurement of the lightness of the specimen (varying from 100 - perfect white to 0 - perfect black). "a" provides a measurement of redness when it is positive, gray when zero, and greeness when it is negative. "b" gives a measurement of yellowness when positive, gray when zero, and blueness when negative. This can be visualized in the following diagram.[14]

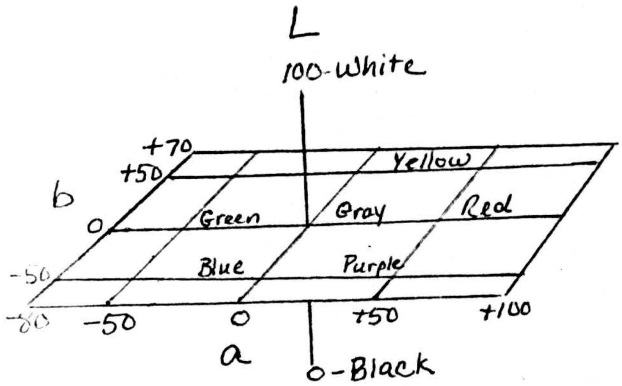


Figure 1: Relationship of Colors in L, a, b Color Space

SIZING

The term sizing, basically means the rate of adsorption of a liquid into paper. It is necessary for most types of paper to have some degree of sizing, since cellulose is hydrophilic, or water loving, and therefore, has no water holdout capabilities. Problems such as feathering or curl are caused by a lack of sizing.

The penetration of a fluid into paper happens in several ways; by open spaces in the paper structure, by fiber to fiber contact, by capillary action, and other methods of sorption/desorption. The properties of paper that effect its degree of sizing are the hydrophobicity of the fibers, the pores in the sheet, the surface of the paper, and the sheet structure.[15] The more highly sized a sheet of paper is, the more hydrophobic it is, and therefore the lower the rate of liquid penetration.

In order to decrease the wettability of the fiber surfaces, hydrophobic (water hating) groups must be attached to the cellulose with a sizing agent. The sizing provides the fiber surfaces with a low surface energy coating, so that high energy aqueous liquids will form high contact angles at the liquid/paper interface. A contact angle is measured from the paper surface to the drop of liquid as follows:

0 = Contact Angle

the lower the contact angle is, the more wetting and spreading the liquid drop will do at the paper surface.[17]

To accomplish sizing, the size must be retained on the cellulose fiber, distributed evenly over the fiber surface, and then attached firmly to the cellulose with the hydrophobic groups directed out.[16] Most sizing agents consist of amphipathic molecules, molecules that have both polar and non-polar ends. The polar end is attracted to cellulose and the non-polar end will remain out. This non-polar end is hydrophobic and therefore resists water.[17]

Measurement of the Degree of Sizing There are several methods for measureing the degree of sizing of paper. These many procedures differ widely and give results that disagree with each other.

One category of procedures measures the penetration of aqueous fluids through paper. This can be done by using conductivity to measure the penetration of water, but this type of test is very sensative to sheet formation. Measurement of the penetration of fluids can also be carried out by using reflectance. This type of test measures the change in reflectance with time, as an aqueous fluid permeates paper. Included in this group of sizing measurement is the Hercules Size Test.[15]

Another category of methods for measuring sizing uses the relationship between the surface of the sheet of paper and the sizing of the entire sheet. The cobb test is included in this category. In this test method a hydrostatic head of water is placed on the paper surface for a certain length of time. The amount of water sorbed by the paper is measured by weight. A weakness of this test is that is is not sensative to paper with a large degree of sizing (hard sized). The cobb test is one of the most widely used methods of size testing.[15]

Contact angle can also be used to correlate the surface sizing with that of the entire sheet. The mesurement of the angle between the paper surface and that of a drop of liquid is difficult to do. The test is mainly used to help understand how a given agent affects the hydrophobicity of paper.[15]

A third category for determining the degree of sizing uses paper properties that relate to sizing. Curl tests or ink feathering are examples of properties that can be measured to correlate to sizing degree.

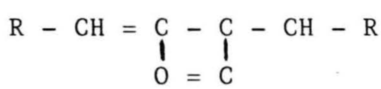
For this study the cobb size test was used. It was chosen because it is a widely used test and for its ease of use. Since dyed papers were to be tested, a method such as the Hercules Size Test, which measures sizing optically, could not be used because it could be effected by the different shades of color of the paper samples. The cobb size test is not dependant on optical properties.

Acid Sizing (Rosin/Alum) The normally used sizing agent in the paper industry is rosin in conjunction with alum. Rosin reacts with alum to form a sizing precipitate. The formation of these particles is achieved in the wet end of the papermaking process, where retention and distribution of the size on the pulp occurs[16] due to electrostatic attractions and the desire of the hydrophobic precipitate to get away from the water of the pulp slurry.[17] A majority of the rosin sizing process occurs prior to sheet formation, however some rearangement and polymerization will happen during paper drying. The weakest part of the rosin and alum system is the bond of the particles to the cellulose.[16] Typical addition levels for rosing sizing are from 2 - 15 pounds per ton of paper, depending on the degree of sizing desired. Approximately 20 to 40 pounds alum per ton are added to the sizing to give a pH of 4.0 to 4.5.[18]

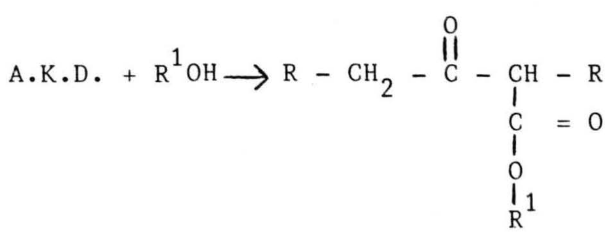
Alkaline Sizing Cellulose reactive sizes are used to size paper with neutral to alkaline sizing conditions. Excellent sizing is often achieved at a theoretical minimum addition level (0.05 to 0.15%) of this type of sizing agent. Rosin size requires about ten times as much to achieve the same sizing degree.[16]

Cellulose reactive sizes generally take longer to complete the sizing mechanism than rosin does. Retention of the size emulsion occurs in the wet end by electrostatic forces. The sizing is redistributed over the fiber surface during pressing and drying.[16] At the elevated temperatures of the dryers, the sizing agent actually melts and spreads over the fiber surface.[19] During drying the size is bound to the cellulose with a strong covalent bond.[16]

<u>Alkyl Ketene Dimers</u> The first cellulose reactive sizing agent introduced was the alkyl ketene dimer (AKD), in 1952. It wasn't until 1960 that it began to be recognized as a viable commercial process.[18] The alkyl ketene dimers (AKD) were first manufactured by Hercules and were called Aquapels. These sizing agents are made from fatty acids and consist of two hydrocarbon chains attached by a four membered lactone ring.[17] The structure of an alkyl ketene dimer (AKD) is as follows:



The lactone ring reacts with hydroxyl groups to form a stable ester linkage, (this is what occurs with cellulose).[20]

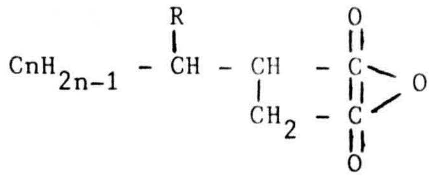


Hydrolysis is always a problem with cellulose reactive sizes and therefore conditions must favor reaction with cellulose instead of with water. When Aquapel is added to a pulp slurry, 60 to 70% will react with cellulose rather than with water,[17] and the hydrolysis product formed in the side reaction with water does not significantly detract from sizing.[16] Alkyl ketene dimers have a low melting point of 40 - 50 C which provides for excellent spreading and distribution during the elevated temperature in drying. A hydrophobic monolayer results making this a very efficient sizing.[17]

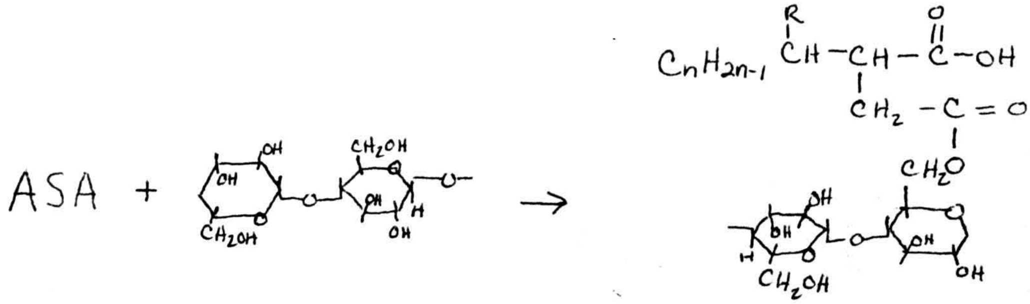
To use Aquapel, aqueous emulsions are made with a cationic starch. The cationic starch functions as an emulsifying agent, a retention aid for the emulsified particles, and can also serve as a retention aid for fillers. Hercules manufactures another Ketene Dimer, which is easier to use, called Hercon. Hercon is a cellulose reactive sizing emulsion that is strongly cationic and self-retaining on the fiber. Additional cationic starch is not required for size retention.[21] For paper sizing with alkyl ketene dimers, approximately 0.05 - 0.15% (1 - 3 pounds per ton paper) is required. For bleached pulps more sizing is needed and it may require 0.10 - 0.30% sizing (2 - 6 pounds per ton).[22] Hercon should be kept as cool as possible without freezing when it is stored to ensure the highest efficiency.[21]

Alkenyl Succinic Anhydride Another cellulose reactive size is alkenyl succinic anhydride (ASA). ASA is a liquid derived from petroleum, which is easily emulsified at low temperatures.[16] It hydrolyzes easily, producing a liquid that interfears with sizing.[17] Therefore, the emulsion must be used quickly so that the ASA reacts with cellulose before it all hydrolyzes.

One common alkenyl succinic anhydride (ASA) is Fibran 68 produced by National Starch and Chemical Corporation. A dicarboxylic acid anhydride with a long hydrophobic side chain is the formula for ASA:



When combined with cellulose, ASA reacts through its acid anhydride groups with the hydroxyl groups on the cellulose fiber as follows:



This forms a stable chemical linkage between the sizing agent and cellulose, giving and end result of a series of hydrophobic side chains chemically attached to the fibers.[3]

To use alkenyl succinic anhydride as a sizing, a preliminary emulsion is made with the sizing agent and a nonionic surfactant (often ASA comes in this preliminary emulsion form). This emulsion is then emulsified with a cationic starch and water. The ASA/Starch emulsion should be used immediately since hydrolysis is taking place. Alum is needed to retain the ASA/Starch emulsion on the fiber. From 2 - 8 pounds per ton ASA should be added to the slurry, with a ratio of two pounds cationic starch to one pound ASA.[3] One percent Alum is commonly used for retention.

EXPERIMENTAL PLAN

Dyeing in an Alkaline System

A bleached pulp furnish of 50/50 hardwood/softwood was used. Since basic dyes are not substantive to bleached pulp they should fade away in the alkaline systems without the use of alum as a mordant. Acid dyes should fade away also, since they are not substantive to cellulose at all. Both cationic and anionic direct dyes should affix themselves to the fibers without the presence of alum. The unanswered question, was how well would the dyed papers compare from acid to alkaline sizing and how would the degree of sizing in both sizing types effect the color of the dyed sheets?

Important Details

Order of addition to the furnish was important in this study. It seemed reasonable enough to assume, that since both direct dyes and alkaline sizing agents react with cellulose hydroxide groups, if the dye was added first, more color would be obtained. Inversely, if the size emulsion was added first to the furnish, a higher degree of sizing would result, with a lower value of color. In view of this, in all cases the dye was added first to the furnish.

The dyes used came from all three groups; acid, basic, and direct. The acid and basic dyes were not expected to perform well in alkaline systems, so one dye from each of the two groups was used. The direct dyes, both anionic and cationic, were assumed to work well in an alkaline system, so two anionic and two cationic direct dyes were used. Each dye within a category of dyes is chemically different from the others of that group, in order to produce varying shades. Therefore, it is quite possible that differences among dyes of the same category could occur. However, since it was impracticle to examine every dye existing, it was assumed that most of the dyes behave similarly to others belonging to the same category.

PROCEDURE

Water and Pulp Needs

Kalamazoo water can vary drastically from day to day. For this reason, water was stored in three 55 gallon barrels to be used throughout the experimental analysis. The water line was cleared for one half an hour before filling the tanks, which were then allowed to stand for a day before conductivity and pH were tested. As the barrels emptied they were refilled in the same manner. The conductivity was checked to make sure there wasn't a drastic change in the water used.

Pulp was refined in accordance with TAPPI Procedure 200 os-70. The softwood used was Royonier Georgianier J-FA, kraft, and the hardwood was Weyerhaeuser kraft from Washington. 50/50 hardwood/softwood combinations were refined together in the Valley beater to freenesses of approximately 370 CSF. The pulp was stored in a large barrel at 40^{0}F. Throughout the experimentation as pulp was used, new batches were refined following the same procedure. The newly refined pulp was blended with the remaining stock to ensure a somewhat standard furnish. By blending the old with freshly refined pulp any changes that occured in the furnish, such as hardwood/softwood ratio or refining degree, would be lessened and therefore reduce variations in the stock used in the study.

Preliminary Trials

Preliminary trials were carried out with each sizing type in an attempt to get three distinct sizing levels of approximately the same degree for each type of sizing. The trials were conducted without using dye.

Final Trial Procedure

Rosin/Alum Since rosin size developes in the wet end of the paper machine, sizing was carried out on each handsheet separately.

Step 1: Pulp and standard water were added to the proportionator with five pounds dye per ton of pulp (O.D.). The slurry was allowed to dye for 15 minutes. Approximately eight gallons of standard water were added to the recycle tank of the noble and wood headbox in preparation for sheetmaking.

Step 2: An aliquot of pulp was taken and placed in a beaker and sized with rosin for eight minutes. The rosin used was Hercules' Pexol 277 fortified pale paste size, which had been diluted to 3% solids.

Step 3: After the pulp slurry was sized for eight minutes, alum was added to achieve a pH of 4.5. The alum was allowed to react for five minutes before a noble and wood handsheet was made. The sheet was weighed and the aliquot amount adjusted to achieve a sheet of 2.5 grams. The procedure was repeated to make ten handsheets. The recycle was used and therefore the first four sheets made were discarded to ensure that the white water was in equilibrium. The last six sheets were saved.

Alkyl Ketene Dimer Alkaline sizing agents develop in the dryer. Therefore, it was not necessary to size each sheet separately.

Step 1: Pulp and standard water were added to the proportionator with five pounds dye per ton of oven dry pulp. The slurry was allowed to dry for 15 minutes.

Step 2: Hercon (Alkyl Ketene Dimer) was added to the proportionator and allowed to mix for 15 minutes.

Step 3: Standard water was added to the recycle tank and handsheets were made in the same manner as with the rosin/alum system (first four discarded; next 6 saved).

<u>Alkenyl Succunic Anhydride</u> The ASA/starch emulsion makeup consists of 2% starch, 1% ASA, and 97% water.

Step 1: Starch and water were cooked in a double boiler at 190°F for one half hour. The starch was then allowed to cool and water was added to bring the system to the correct solids level (to compensate for evaporation losses).

Step 2: Pulp and standard water were added to the proportionator and dyed with five pounds dye per ton of pulp.

Step 3: One percent alum was added to the pulp slurry for a retention aid for the ASA.

Step 4: Using a laboratory mixer, ASA is added to the starch solution. The starch solution must be mixing when the ASA is added. The solutions are emulsified for five minutes and then the correct quantity of the emulsion was added to the proportionator.

Step 5: Handsheets were made in the same manner as before.

For each set of handsheets a whitewater sample was taken for visual evaluation and to check the pH. The sets were all dryed in an oven at 105°C for one half hour to ensure adequate drying for alkaline sizing development. The rosin/alum sheets were also dryed to provide identical treatment for the control sheets.

The following is a list of all the dyes used in the experimentation. All of the dyes were acquired from Sandoz, Incorporated.

anionic direct	:	Cartasol Blue 4GF
anionic direct	:	Cartasol Red 2GF
cationic direct	:	Cartasol Turquoise K-RL
cationic direct	:	Cartasol Red K-2B
acid	:	Cartacid Scarlet MOO
basic	:	Bismark Brown R

Rosin was used at 40, 60 and 80 pounds per ton in conjunction with all six dyes. Alkyl Ketene Dimer was used at four, five, and six pounds per ton also with all six dyes. Due to lack of time, ASA was used at four and six pounds per ton in conjunction with all the dyes except the anionic and cationic direct blue dyes.

Each handsheet was tested for color using the Hunter L, a, b method on both the wire and felt sides. Of the six handsheets, the first, third, and fifth were tested for cobb size on the wire side. The felt side was tested on sheet number two, four, and six. Cobb size was used for the size test since it is an easy method, it is widely used, and colored sheets will not effect the test. The Hercules Size test was considered but this method works on optical properties which could change with color.

DISCUSSION OF DATA

A comparison of the quantity of sizing used and the level of sizing achieved, shows a high degree of variability (Figure 2). For this reason, any further comparisons will be based on the size addition level.

Acid Dye

The acid dye seems to be the most effected by sizing degree. This may be observed in Figure 3, a graph of the parameters L, a, and b versus the sizing addition level. The plotted values are those for the wire side of the paper. (Note: for definitions of the values of "L", "a", and "b", refer to the discussion on the Hunter Color Method on page five.)

It should first be noted that ASA is much more white than the rosin and AKD sized sheets. Rosin sizing allows the acid dye to impart a redder color, while the ASA sized sheet is duller and closer to gray. There is very little yellowness in any of the acid dyed trials; the AKD sized paper being the least yellow.

In all three sizing conditions, the color becomes less light and more red when sizing is increased. ASA shows the least change with increased sizing for these two parameters "L" and "a", for which the slopes are -0.9 and +1.7 respectively. In contrast with this, the slope for "L" when sized with AKD is -3.4, and that for "a" is 2.6. In both cases, rosin is more like paper sized with AKD.

The degree of two sidedness may be observed in Table I where it can be seen from these values that the largest difference in wire side and felt side occurs in the sheets sized with AKD. The differences in the values for "L" and "a" tend, in all cases, to increase with increased sizing. The rosin

Figure 2

Addition Level Versus Cobb Size (Wire Side)

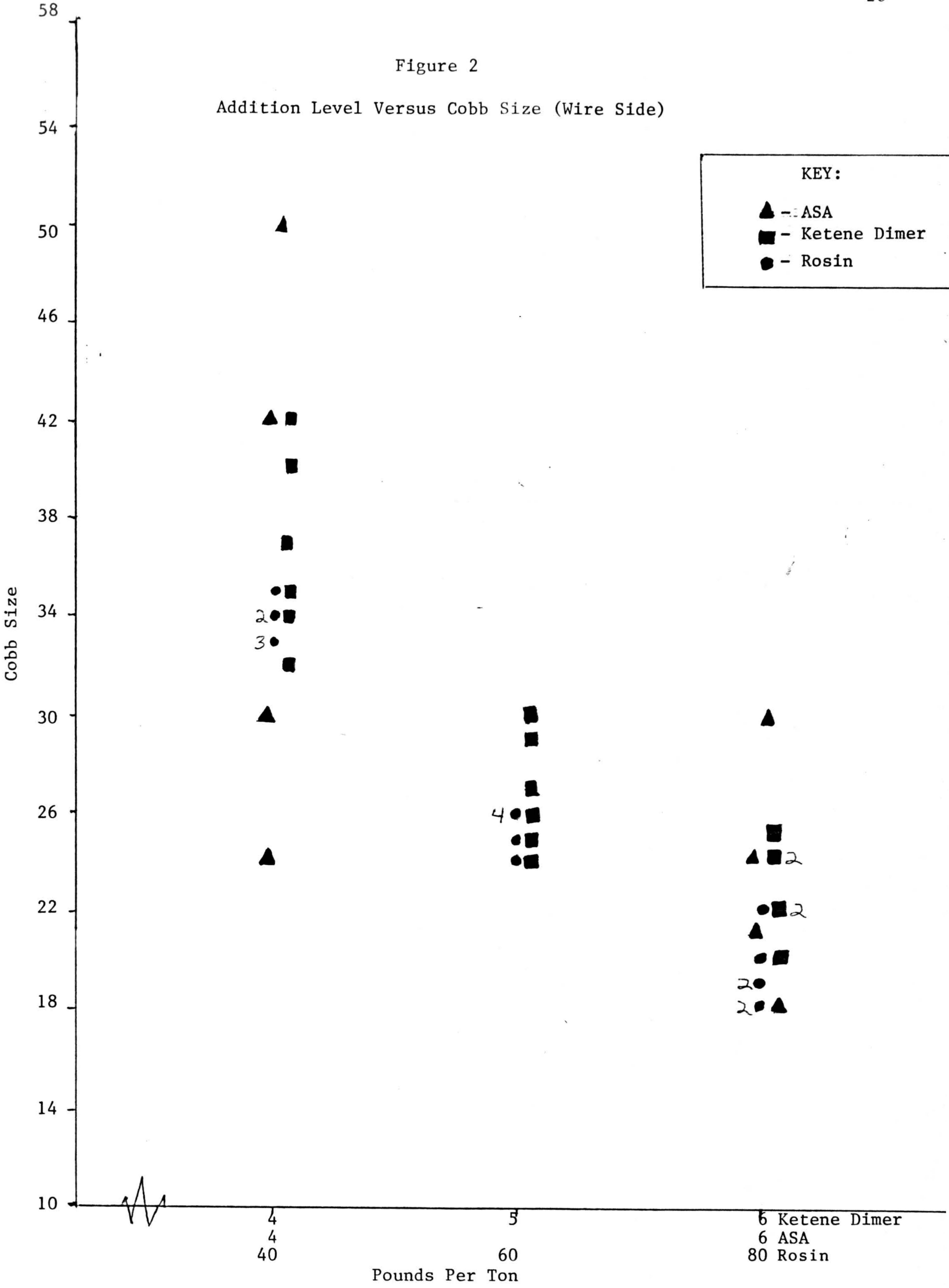
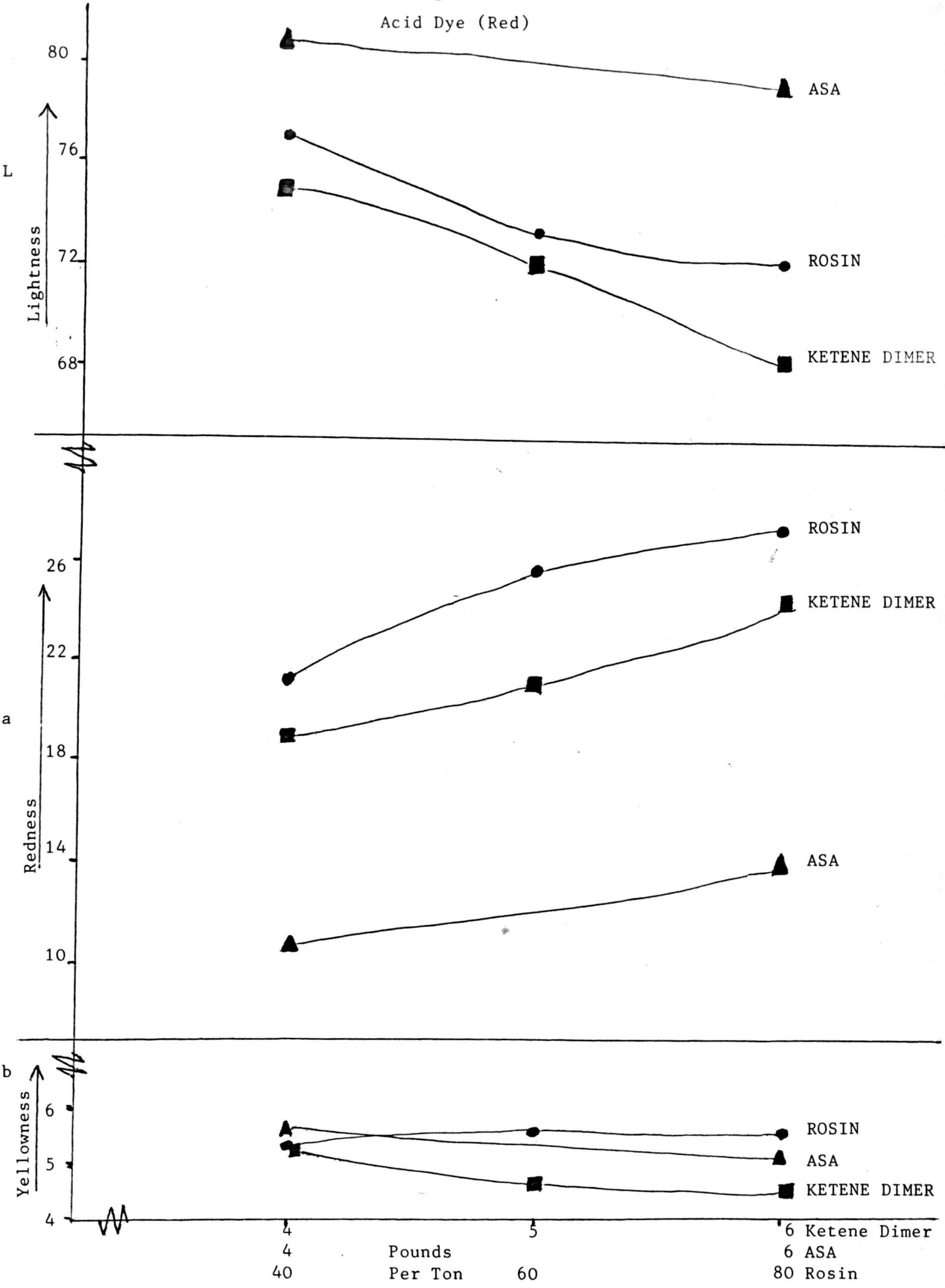


Figure 3

Acid Dye (Red)



	ROSIN			AKD			ASA	
	40#	60#	80#	4#	5#	6#	4#	6#
L	+0.34	-0.09	-0.47	-1.98	-2.26	-2.76	+0.06	+0.35
a	-0.52	+0.34	+0.53	+2.21	+2.87	+3.53	-0.38	-0.67
b	+0.38	+0.35	+0.30	+1.40	+1.13	+1.23	+0.40	+0.39

Degree of Two Sidedness - Acid Dye (Wire Side - Felt Side)

TABLE I

sized system shows an odd occurance in that at its low sizing level the wire side is more light and the felt side is more red; this changes as sizing is increased, to the wire side being less light and the felt side being less red. For AKD sized sheets the felt side is lighter and wire side redder. Just the opposite occurs with the ASA, since the wire side is lighter and felt side redder.

Acid dye is probably most effect by sizing degree because it has no ability to bond to the fiber itself. The rosin/alum complex was stated earlier to be more effective as a mordant than alum alone. Therefore, as the amount of rosin increases the rosin/alum complex will increase, giving an explanation for increased rosin size causing an increase in color. The alum also may cause the dye to fade slightly since the rosin sized system is the most red, but is lighter than the AKD system.

Since only one percent alum was used to retain the ASA size on the furnish, it was not enough to cause a retention of the acid dye. This explains the small amount of color visible in the ASA sized papers.

It is unknown why the AKD system retained the acid dye. The literature says a mordant is needed, therefore something in the AKD emulsion must be acting as a dye retention aid. It does give the highest degree of two sidedness, with the wire side having the most color. Therefore, the fines must be dyed more than the longer fibers.

Basic Dye

The basic dye did not behave as the literature said it should. Basic dyes are not supposed to bond to bleached furnishes without the aid of a mordant. However, in all three sizing systems there is no significant differences in retention of dye.

Problems were encountered with this dye, in variations of color within the same sheet. The paper seemed to be extremely sensitive to conditioning because the color variations cleared when the paper was evenly conditioned. The dye also showed a low level of light sensitivity as was expected.

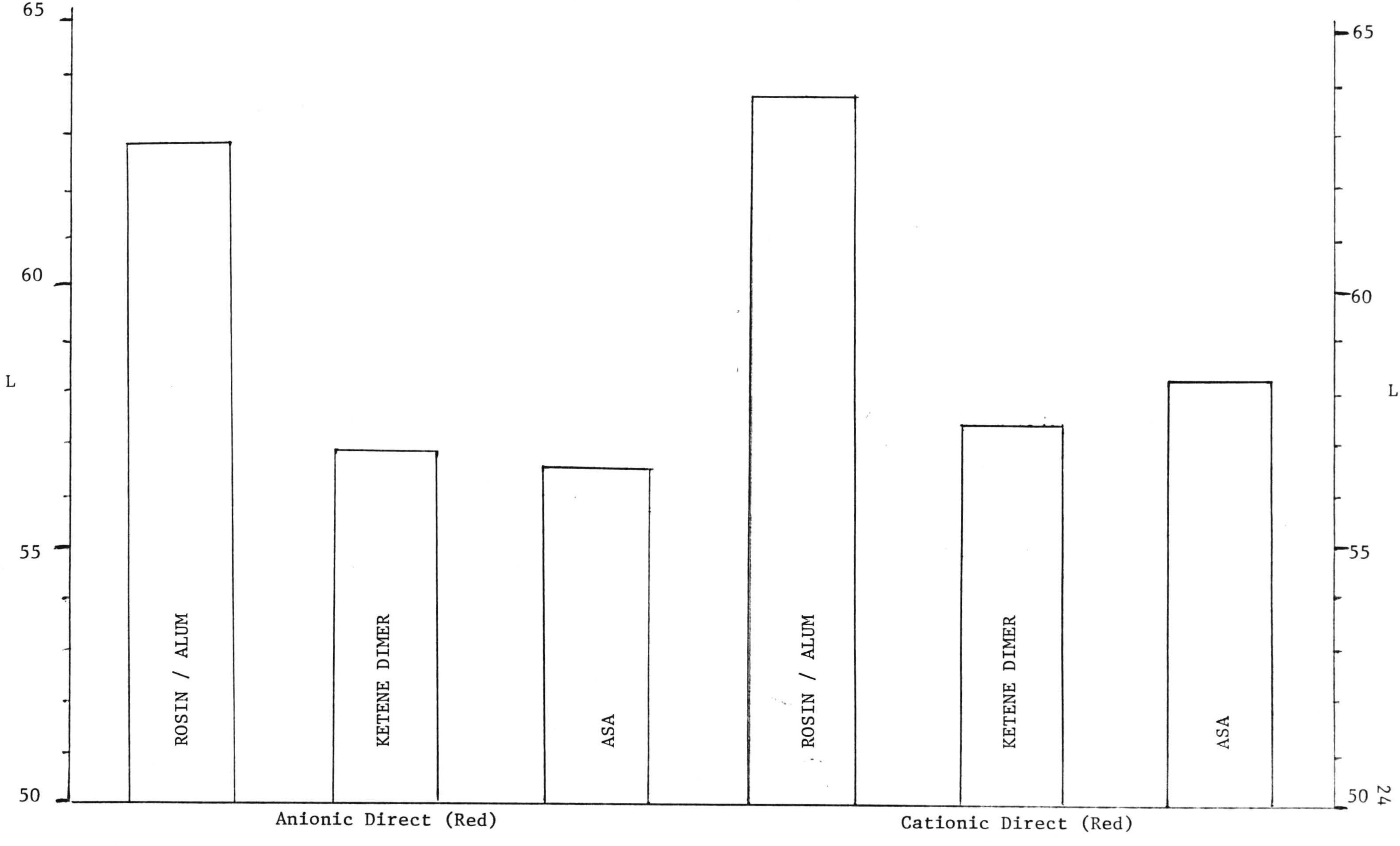
Direct Dyes: Anionic and Cationic

In all cases for the anionic and cationic direct dyes, the rosin/alum sizing system imparted a significantly higher value for "L" than that of AKD and ASA sized systems. This may be viewed in Figure 4 which is a graph of the average "L" values of a sizing type, measured on the wire side of the sheet, for the red dyes of both anionic direct and cationic direct dye types. This tends to show that alum causes the color to fade and be diluted by white light. It is stated in the literature that alum causes a loss in brightness with direct dyes. Upon visual inspection, however, the rosin/alum sized sheets appear much more bright and brilliant than those sized with AKD and ASA.

The color tends to change slightly with different sizing types for both anionic and cationic direct dyes. The cationic directs are possibly less receptive to changes, since there is no substantial changes for cationic direct blue in the values of "a" and "b". The cationic direct red dye does

Figure 4

Lightness Versus Sizing Type



tend to become more yellow with the alkaline sizing agents, but it is a slight change.

The same is true for anionic direct dyes. There is only a slight change from anionic direct blue sized with rosin and AKD. It tends to be greener with AKD. Anionic direct red is approximately the same for AKD and rosin sizings, it becomes more red with ASA sizing.

All of the changes, aside from rosin/alum giving high "L" values to the color of paper, are insignificant upon visual comparison, showing that both anionic and cationic directs behave equally well in alkaline and acid sizing conditions and at varying degrees of sizing.

CONCLUSIONS

The acid dye that was studied was the only dye type significantly effected by sizing degree, probably due to its inability to bond to the cellulose. In the rosin sized sheets, as the rosin/alum complex was increased acid dye retention also increased. It is unknown why the papers sized with AKD also retained the acid dye, and why retention was increased with increased sizing. The AKD sized sheets also gave the most difference in color from wire side to felt side with the acid dye. The wire side has the most color, showing that the fines are dyed more than the long fibers.

The basic dye that was studied did not behave according to the literature. With all three sizing systems the dye gave approximately the same degree of retention. It is unknown why this dye was retained without the aid of a mordant in the ASA and AKD sizing systems.

The anionic and cationic direct dyes worked equally well in both the acid and alkaline sizing systems. When sized with rosin, the dyed papers tended to be lighter than those sized with the alkaline sizing agents. This is probably caused by the alum fading the dye. There are slight changes in color appearance when comparing the different sizing methods, however a significant difference in color is not apparent.

RECOMMENDATIONS

Since the changes in dye appearance are not positively from sizing type, but possibly from pH change, further study should be carried out changing only the pH of the system. Further studies should be carried out with basic dyes, to see if more would behave in the manner that the dye in this study did or according to the literature. An analysis of the AKD system should be made to see what is acting as a mordant for retention of the acid dye in this sizing system.

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to Sandoz Colors and Chemicals for donating dyes, to Hercules Incorporated for donating sizing chemicals and pulp, and to James River Corporation of Parchment, Michigan for allowing me to use their colorimeter.

REFERENCES

1. Hoffmann, G. C., "Technology, Paper Quality Changes Impact Wet End, Surface Coloring," Pulp & Paper, 56 (April 1982): p. 98-100.

2. "Neutral/Alkaline Sizing Rules in Scottish Mills," PPI (Aug. 1977): p. 45-47.

3. National Starch & Chemical Corporation, Technical Service Bulletin, "Fibran 68 for Internal Sizing of Paper."

4. "Role of ASA in Alkaline papermaking," TAPPI Papermakers Conference, (Atlanta) Proc. 45-50 (April 5-8, 1982).

5. Schwalbe, H. C., Papermaking and Paperboard Making, McGraw-Hill Book Company, New York, (1970) p. 77-101.

6. Erfurt, J., Dyeing of Paper Pulp, (translation), D. Van Nostrand Company, New York, (1901).

7. "Dyestuff Data for Papermakers," American Cyanamid Company, Calco Chemical Division, (1952).

8. "Dyeing of Paper," E. I. duPont de Nemours & Company, Incorporated, Wilmington, Deleware.

9. "Colourful Paper: More Than Just the Mixing of Dyes & Pigments," Pulp & Paper of Canada, (June 1970): p. 77-79.

10. Kuehni, R. G., Computer Colorant Formulation, Lexington Books, Toronto (1975).

11. Dyes for Paper, National Aniline and Chemical Company Incorporated, New York.

12. Allen, R. L. M., Colour Chemistry, Appleton-Century-Crofts, New York, (1971).

13. Kline, James E, Class notes, Fall 1981.

14. Hunter, R. S., "Color of Paper and Paperboard by Hunter L, a, b Colorimetry, Tappi Standard Proposed New suggested Method T524," Tappi, 55 (July 1972): p. 1121-24.

15. Guess, J. M., "The Measurement of Sizing of Paper," Tappi, 64 (January 1981): p. 35-39.

16. Dumas, D. H., "An Overview of Cellulose Reactive Sizes," Tappi, 64 (Jan. 1981): p. 43-46.

17. Davison, R. W., "The Sizing of Paper," Tappi, 58 (March 1975): p. 48-56.

REFERENCES

(Cont.)

18. Watkins, S. H., "New Trends & Developments in Sizing of Paper," Paper Trade Journal, (Sept. 1973): p. 28-29.

19. Abstract Bulletin of Institute of Paper Chemistry, 52 (Nov. 1981) Abstract No. 4923.

20. Weisgerber, C. A.; Hanford, C. B., "Alkaline Sizing with Aquapel," Tappi, 43 (Dec. 1960): p. 178A.

21. Hercules Incorporated, Product Data Sheet, "Hercon 40 Reactive Size," Number 7232-5.

22. Davis, J. W.; Roberson, W. H.; Weisgerber, C. A., "A New Sizing Agent for Paper - Alkyl Ketene Dimers," Tappi, 39 (Jan. 1956): p. 21-23.

APPENDIX

SIZING DEGREES - (WIRE/FELT)

	Rosin			AKD			ASA	
	40#	60#	80#	4#	5#	6#	4#	6#
Red A.D.	33/41	26/34	19/24	35/45	25/37	22/31	50/52	30/33
Blue A.D.	34/39	26/33	18/24	40/51	29/40	20/32	-----	-----
Red C.D.	34/38	25/34	18/25	34/45	27/33	24/30	42/47	24/30
Blue C.D.	33/38	26/35	20/35	32/43	26/32	24/31	-----	-----
Red Acid	35/39	24/33	22/25	42/50	30/39	25/35	30/32	21/24
Brown Basic	33/39	26/34	19/26	37/41	24/30	22/30	24/29	18/26

HUNTER COLOR L, a, b, VALUES

Acid Dye (Red)

	40# Rosin				60# Rosin				80# Rosin			
	Wire		Felt		Wire		Felt		Wire		Felt	
	X	S	X	S	X	S	X	S	X	S	X	S
L	77.00	0.65	76.66	0.64	73.45	0.76	73.54	0.81	72.22	0.89	72.69	0.64
a	21.41	1.04	21.93	0.91	25.79	1.09	25.45	1.24	27.25	1.43	26.72	1.16
b	5.40	0.14	5.02	0.13	5.64	0.24	5.29	0.35	5.76	0.29	5.46	0.26

	4# Hercon				5# Hercon				6# Hercon			
	Wire		Felt		Wire		Felt		Wire		Felt	
	X	S	X	S	X	S	X	S	X	S	X	S
L	75.00	0.67	76.98	0.28	71.92	0.33	74.18	0.31	68.21	0.76	70.97	0.31
a	18.98	0.68	16.77	0.30	21.36	0.43	18.49	0.25	24.27	0.64	20.74	0.16
b	5.37	0.16	3.97	0.13	4.64	0.13	3.51	0.08	4.53	0.15	3.30	0.07

	4# ASA				6# ASA			
	Wire		Felt		Wire		Felt	
	X	S	X	S	X	S	X	S
L	80.86	0.21	80.80	0.19	79.05	0.32	78.70	0.06
a	10.69	0.49	11.07	0.59	14.03	0.38	14.70	0.23
b	5.70	0.20	5.30	0.29	5.25	0.11	4.86	0.19

HUNTER COLOR L, a, b, VALUES

Basic Brown Dye

	40# Rosin				60# Rosin				80# Rosin			
	Wire		Felt		Wire		Felt		Wire		Felt	
	X	S	X	S	X	S	X	S	X	S	X	S
L	71.15	0.37	70.59	0.25	70.77	0.27	70.33	0.30	68.92	0.40	68.17	0.43
a	14.89	0.22	15.04	0.21	15.16	0.18	15.52	0.36	15.41	0.28	16.05	0.31
b	19.25	0.42	20.01	0.33	18.68	0.19	19.93	0.52	17.91	0.35	18.86	0.48

	4# Hercon				5# Hercon				6# Hercon			
	Wire		Felt		Wire		Felt		Wire		Felt	
	X	S	X	S	X	S	X	S	X	S	X	S
L	70.34	0.29	70.07	0.36	69.54	0.41	69.27	0.38	67.99	0.38	67.85	0.63
a	15.14	0.08	15.37	0.27	15.23	0.16	15.51	0.28	15.59	0.19	15.99	0.37
b	21.35	0.36	22.04	0.36	21.78	0.13	22.38	0.31	21.43	0.34	21.92	0.64

	4# ASA				6# ASA			
	Wire		Felt		Wire		Felt	
	X	S	X	S	X	S	X	S
L	65.52	0.27	65.61	0.42	65.68	0.19	66.01	0.63
a	15.04	0.11	15.03	0.27	14.97	0.10	14.84	0.20
b	21.72	0.16	22.25	0.10	21.29	0.48	21.98	0.47

HUNTER COLOR L, a, b, VALUES

Anionic Direct (Red Dye)

	40# Rosin				60# Rosin				80# Rosin			
	Wire		Felt		Wire		Felt		Wire		Felt	
	X	S	X	S	X	S	X	S	X	S	X	S
L	62.45	0.34	63.65	0.26	63.34	0.42	62.73	0.52	62.63	0.26	61.86	0.41
a	39.68	0.41	38.36	0.17	38.77	0.44	39.68	0.54	39.79	0.24	40.94	0.45
b	10.67	0.09	10.66	0.19	10.15	0.20	10.49	0.16	10.36	0.15	10.68	0.05

	4# Hercon				5# Hercon				6# Hercon			
	Wire		Felt		Wire		Felt		Wire		Felt	
	X	S	X	S	X	S	X	S	X	S	X	S
L	56.59	0.39	56.86	0.30	57.18	0.46	57.77	0.40	56.80	0.31	58.04	0.50
a	39.50	0.28	39.08	0.43	37.48	0.14	36.77	0.27	37.78	0.29	36.79	0.32
b	10.50	0.16	9.83	0.12	10.44	0.17	9.50	0.18	10.53	0.13	9.48	0.13

	4# ASA				6# ASA			
	Wire		Felt		Wire		Felt	
	X	S	X	S	X	S	X	S
L	56.75	0.46	56.78	0.20	56.42	0.38	57.77	0.19
a	42.57	0.23	42.19	0.29	42.26	0.24	40.36	0.22
b	10.84	0.10	10.60	0.07	10.99	0.07	10.16	0.11

HUNTER COLOR L, a, b, VALUES

Anionic Direct Blue

	40# Rosin				60# Rosin				80# Rosin			
	Wire		Felt		Wire		Felt		Wire		Felt	
	X	S	X	S	X	S	X	S	X	S	X	S
L	66.80	0.12	65.48	0.14	64.35	0.18	63.17	0.29	64.18	0.35	62.94	0.22
a	-7.44	0.08	-8.00	0.11	-7.34	0.12	-7.96	0.09	-7.67	0.07	-8.36	0.09
b	-15.80	0.20	-16.75	0.21	-17.39	0.22	-18.18	0.19	-17.07	0.19	-17.83	0.13

	4# Hercon				5# Hercon				6# Hercon			
	Wire		Felt		Wire		Felt		Wire		Felt	
	X	S	X	S	X	S	X	S	X	S	X	S
L	61.85	0.81	62.58	0.63	61.29	0.48	63.06	0.44	60.36	0.47	61.91	0.40
a	-9.60	0.18	-9.45	0.14	-9.15	0.07	-8.88	0.07	-8.70	0.05	-8.40	0.13
b	-13.02	0.38	-13.78	0.11	-14.20	0.21	-13.82	0.08	-14.43	0.14	-13.82	0.10

HUNTER COLORIMETRY (AVERAGES)

Cationic Direct Red Dye

	40# Rosin				60# Rosin				80# Rosin			
	Wire		Felt		Wire		Felt		Wire		Felt	
	X	S	X	S	X	S	X	S	X	S	X	S
L	63.03	0.23	61.92	0.20	63.48	0.15	62.40	0.23	64.68	0.21	63.65	0.15
a	33.83	0.20	35.38	0.21	33.84	0.30	35.30	0.41	33.29	0.20	34.63	0.30
b	1.09	0.18	1.40	0.14	0.73	0.05	0.99	0.10	0.63	0.11	0.86	0.07

	4# Hercon				5# Hercon				6# Hercon			
	Wire		Felt		Wire		Felt		Wire		Felt	
	X	S	X	S	X	S	X	S	X	S	X	S
L	58.01	0.33	57.80	0.18	56.78	0.17	56.30	0.37	57.47	0.26	56.95	0.33
a	35.26	0.28	35.91	0.24	34.84	0.24	35.67	0.34	35.34	0.10	35.96	0.34
b	2.72	0.12	2.78	0.13	2.62	0.10	2.81	0.10	3.30	0.26	3.12	0.21

	4# ASA				6# ASA			
	Wire		Felt		Wire		Felt	
	X	S	X	S	X	S	X	S
L	58.27	0.19	57.40	0.24	58.17	0.24	57.52	0.34
a	36.10	0.15	36.92	0.23	36.92	0.26	37.74	0.24
b	3.04	0.14	3.12	0.11	3.10	0.05	3.21	0.04

HUNTER COLORIMETRY (AVERAGES)

Cationic Direct Blue Dye

	40# Rosin				60# Rosin				80# Rosin			
	Wire		Felt		Wire		Felt		Wire		Felt	
	X	S	X	S	X	S	X	S	X	S	X	S
L	76.57	0.15	76.55	0.16	76.95	0.19	76.91	0.10	77.00	0.12	76.99	0.20
a	-17.18	0.05	-17.02	0.16	-16.84	0.08	-16.68	0.09	-17.01	0.10	-16.77	0.14
b	-14.84	0.41	-14.95	0.36	-15.38	0.33	-15.39	0.22	-14.50	0.25	-14.56	0.16

	4# Hercon				5# Hercon				6# Hercon			
	Wire		Felt		Wire		Felt		Wire		Felt	
	X	S	X	S	X	S	X	S	X	S	X	S
L	73.83	0.18	73.59	0.28	73.50	0.16	73.29	0.18	73.13	0.20	73.07	0.16
a	-17.75	0.11	-17.79	0.09	-17.96	0.09	-17.96	0.08	-18.12	0.09	-18.04	0.13
b	-14.63	0.20	-14.76	0.20	-15.36	0.11	-15.40	0.13	-16.00	0.06	-16.08	0.10

Acid Dye

Wire Felt

40# Rosin

Wire Felt

60# Rosin

Wire Felt

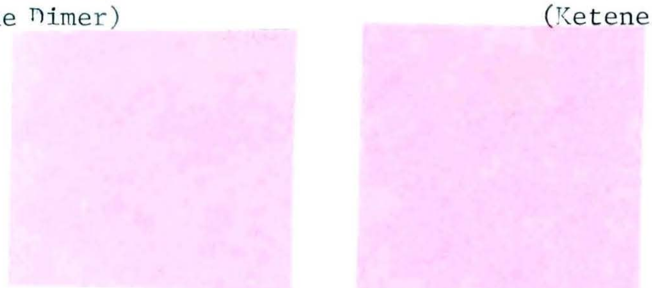
80# Rosin

Wire Felt

4# Hercon
(Ketene Dimer)

Wire Felt

5# Hercon
(Ketene Dimer)



Wire Felt

6# Hercon

Wire Felt

4# ASA

Wire Felt

6# ASA

Wire Felt
40# Rosin

Wire Felt
60# Rosin

Wire Rosin
80# Rosin

Wire Felt
4# Ketene Dimer

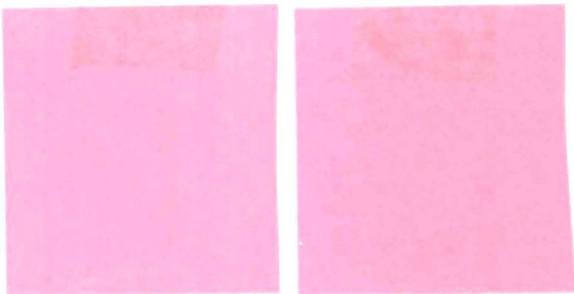
Wire Felt
5# Ketene Dimer

Wire Felt
6# Ketene Dimer

Wire Felt
4# ASA

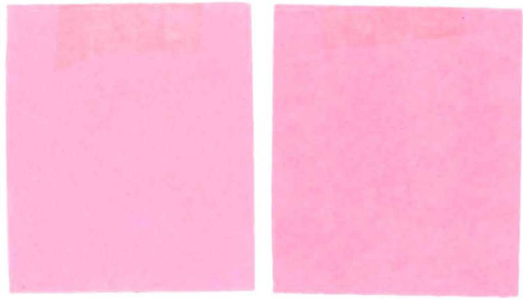
Wire Felt
6# ASA

Anionic Direct Dye



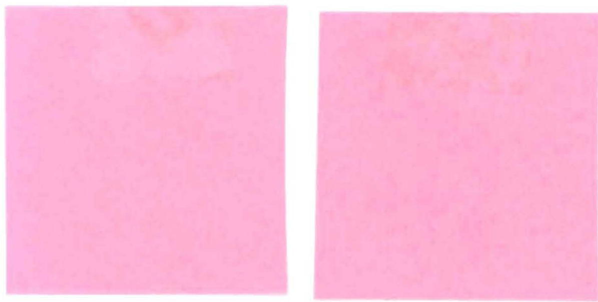
Wire Felt

40# Rosin



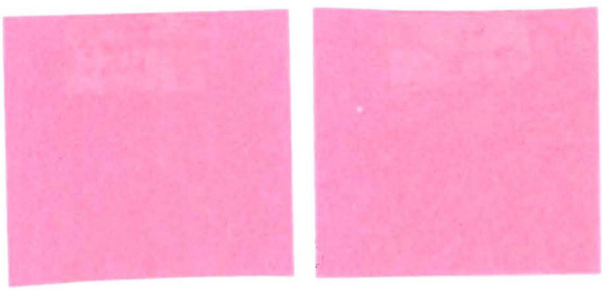
Wire Felt

60# Rosin



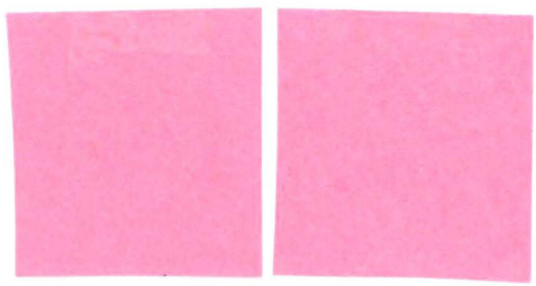
Wire Felt

80# Rosin



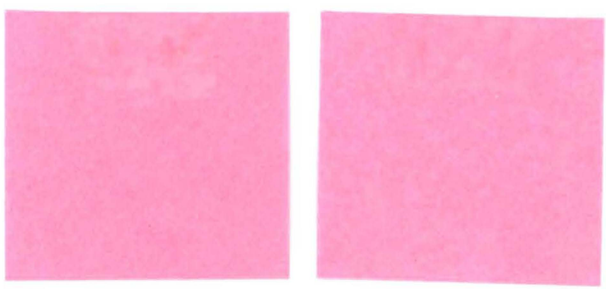
Wire Felt

4# Ketene Dimer



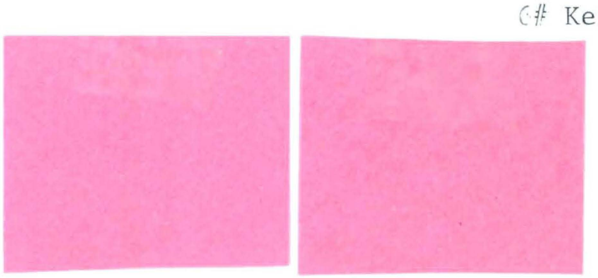
Wire Felt

5# Ketene Dimer



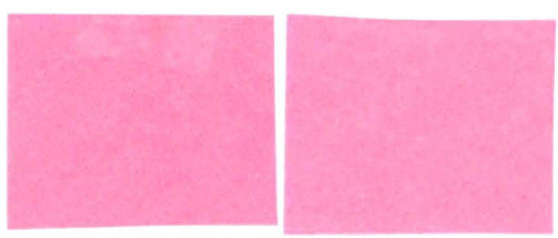
Wire Felt

6# Ketene Dimer



Wire Felt

4# ASA

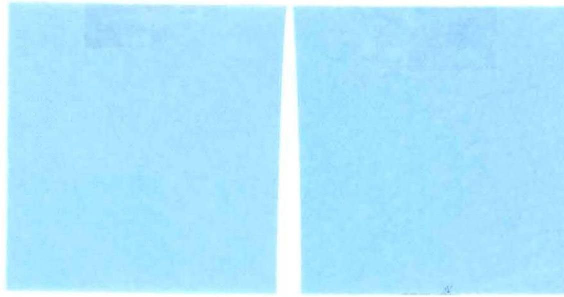


Wire Felt

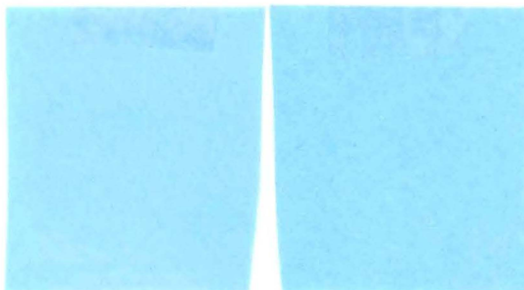
6# ASA

Anionic Direct Dye

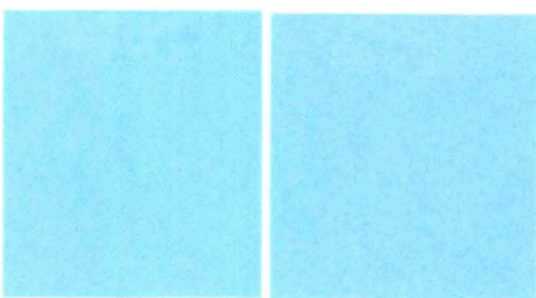
Wire Felt
40# Rosin



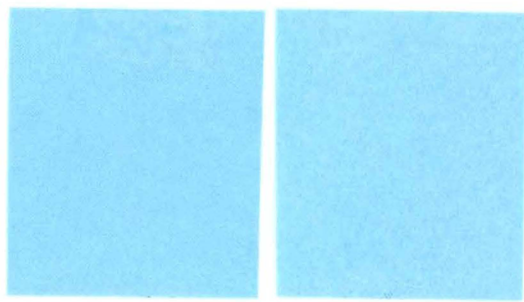
Wire Felt
60# Rosin



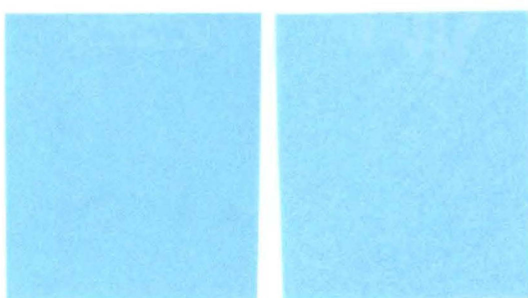
Wire Felt
80# Rosin



Wire Felt
4# Ketene Dimer



Wire Felt
5# Ketene Dimer



Wire Felt
6# Ketene Dimer

Cationic Direct Dye

Wire Felt

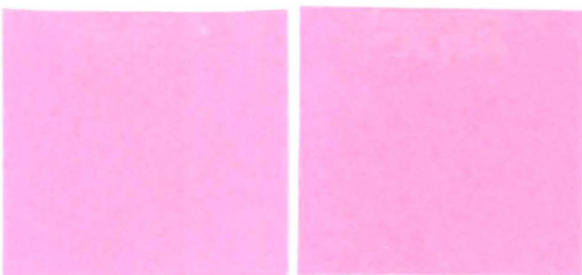
40# Rosin

Wire Felt

60# Rosin

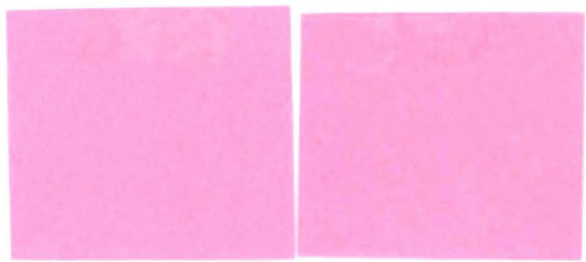
Wire Felt

80# Rosin



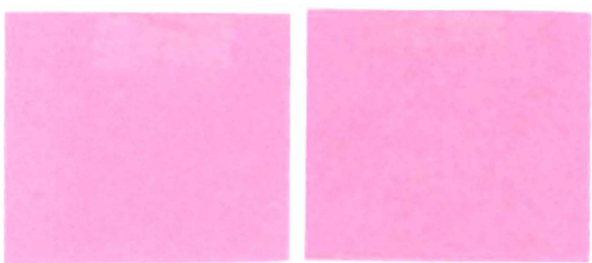
Wire Felt

4# Ketene Dimer



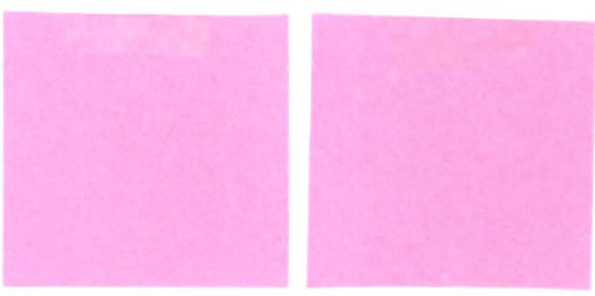
Wire Felt

5# Ketene Dimer

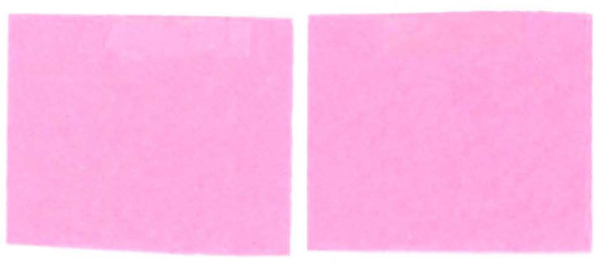


Wire Felt

6# Ketene Dimer



Wire 4# ASA Felt



Wire 6# ASA Felt

Cationic Direct Dye

Wire Felt

40# Rosin

Wire Felt

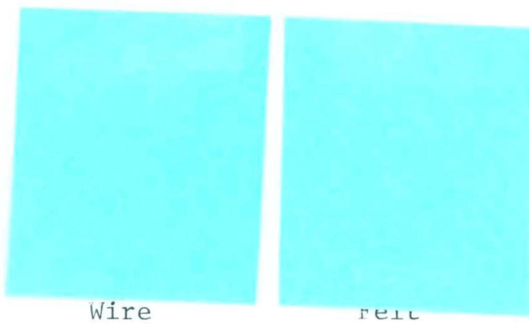
60# Rosin

Wire Felt

80# Rosin

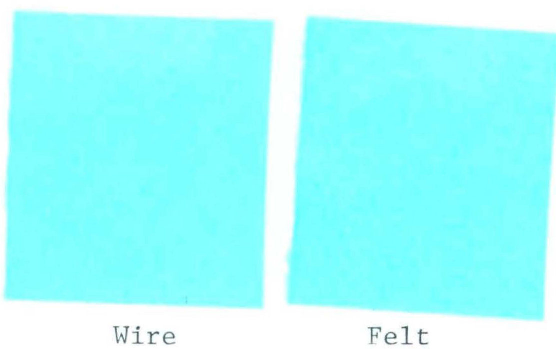
Wire Felt

4# Ketene Dimer



Wire Felt

5# Ketene Dimer



Wire Felt

6# Ketene Dimer