

Jan. 10, 1956

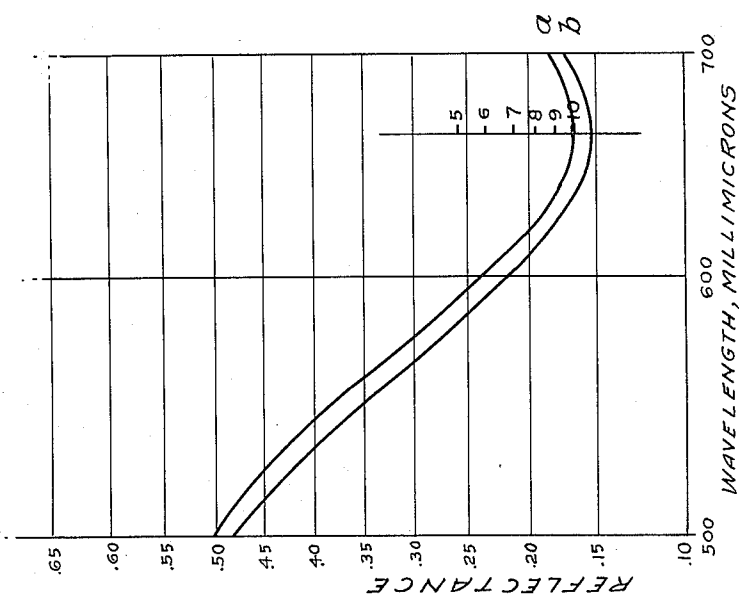
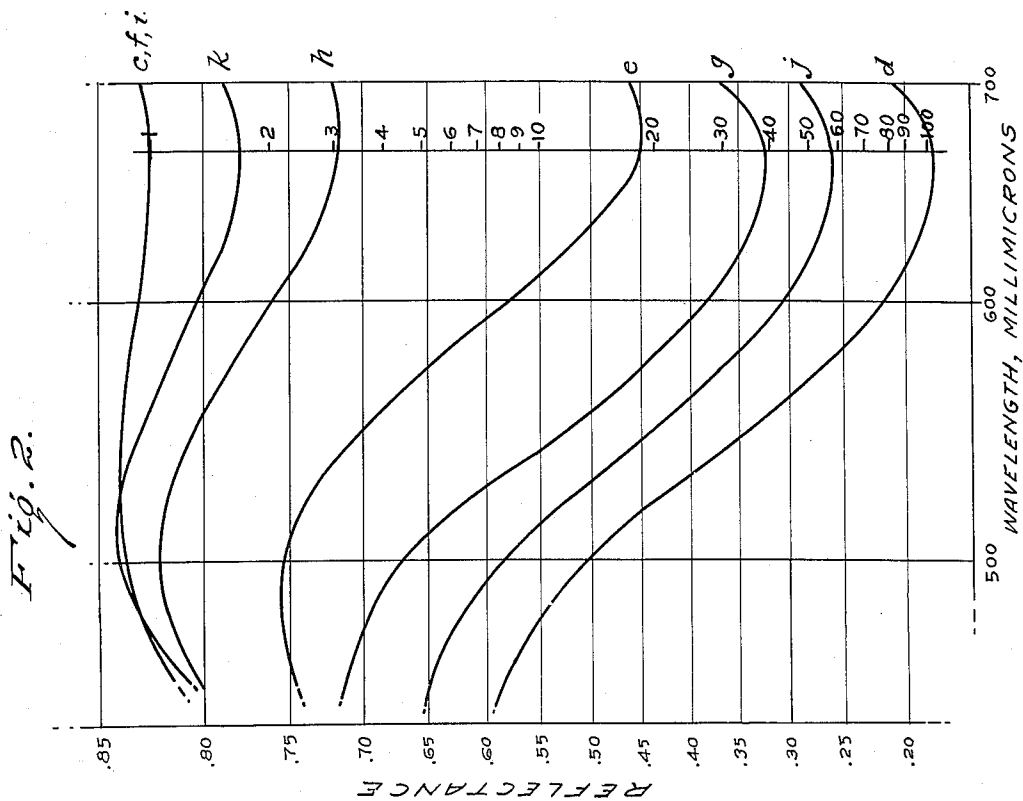
M. C. HUTCHINS

2,730,446

COLOR IMPROVEMENT OF UNSIZED POROUS PAPER

Filed March 15, 1952

8 Sheets-Sheet 1



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Jan. 10, 1956

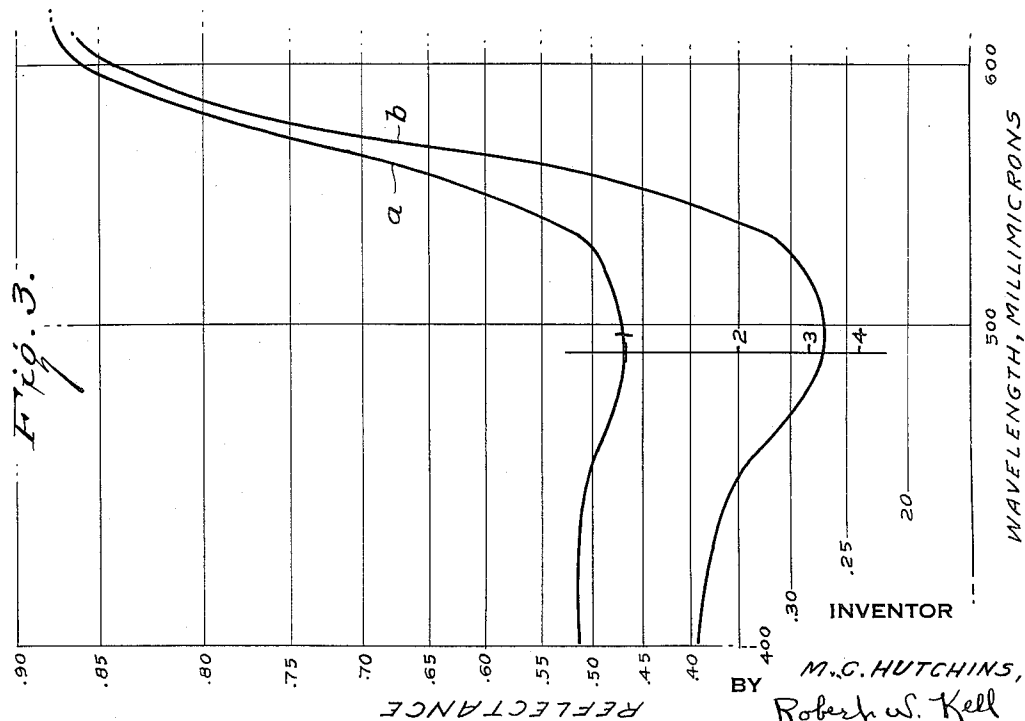
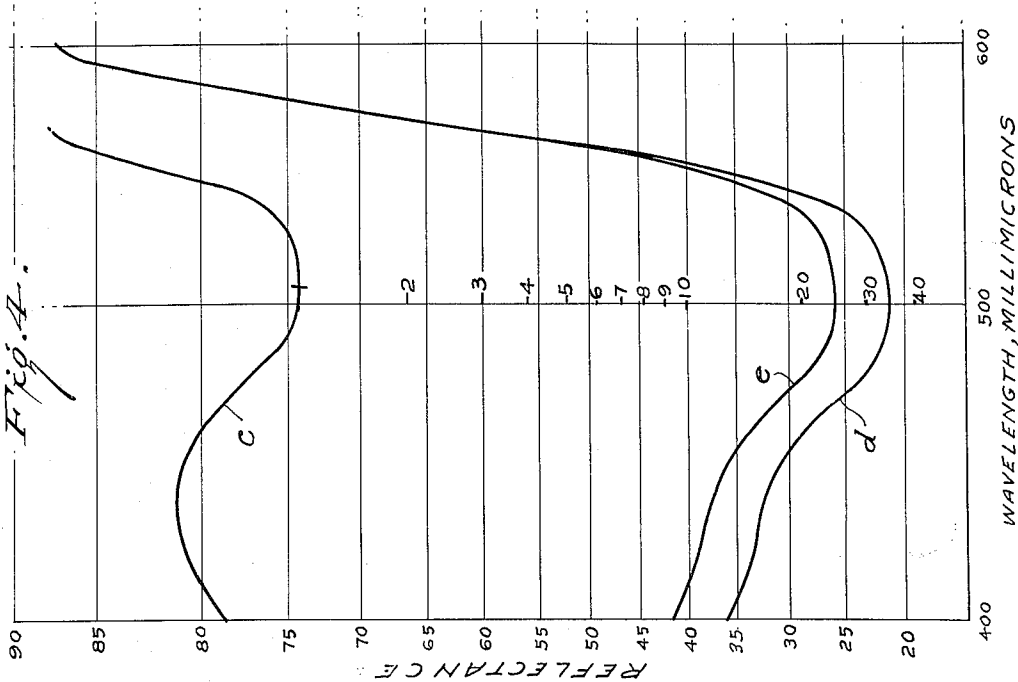
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COLOR IMPROVEMENT OF UNSIZED POROUS PAPER

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8 Sheets-Sheet 2



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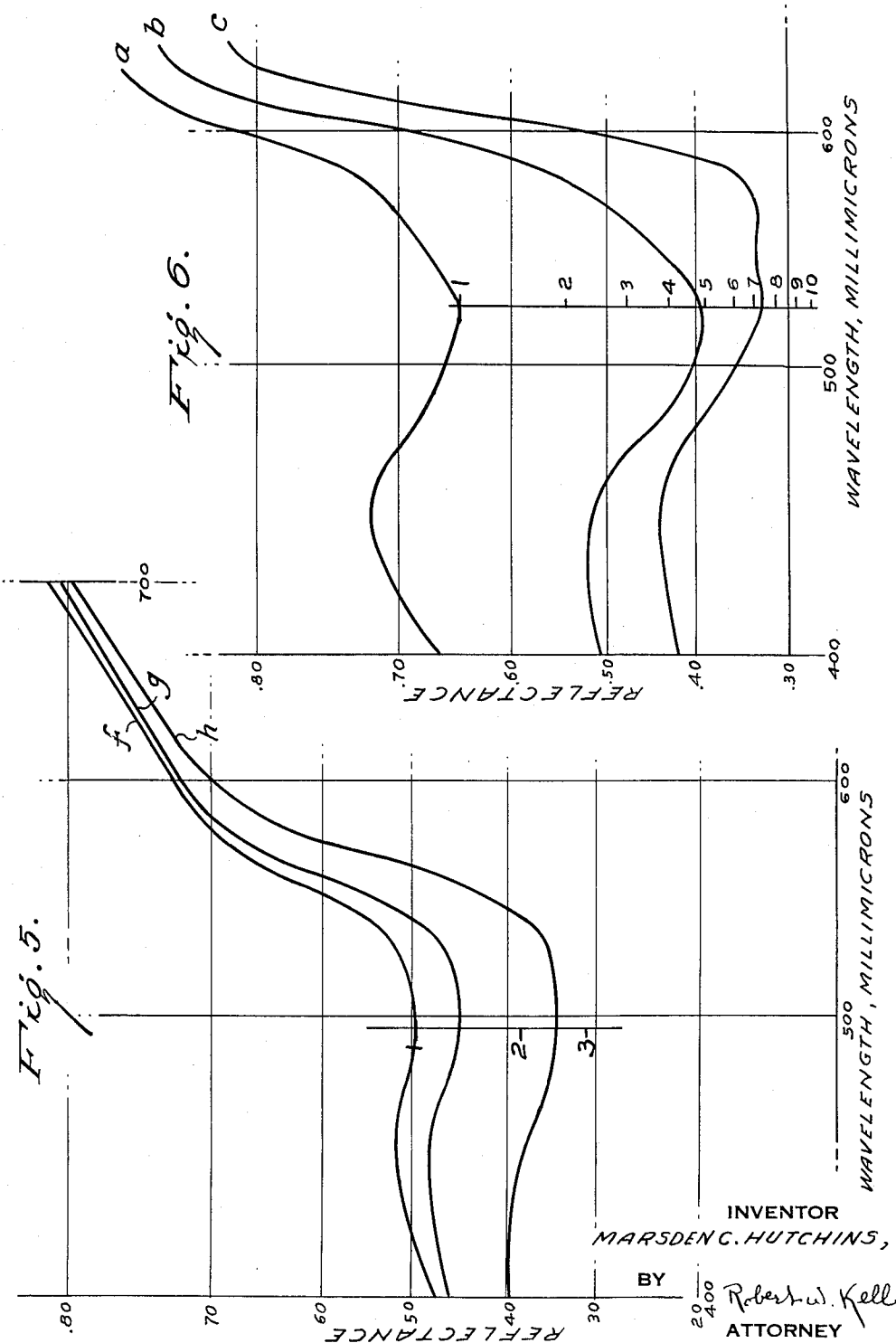
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8 Sheets-Sheet 3



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COLOR IMPROVEMENT OF UNSIZED POROUS PAPER

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8 Sheets-Sheet 4

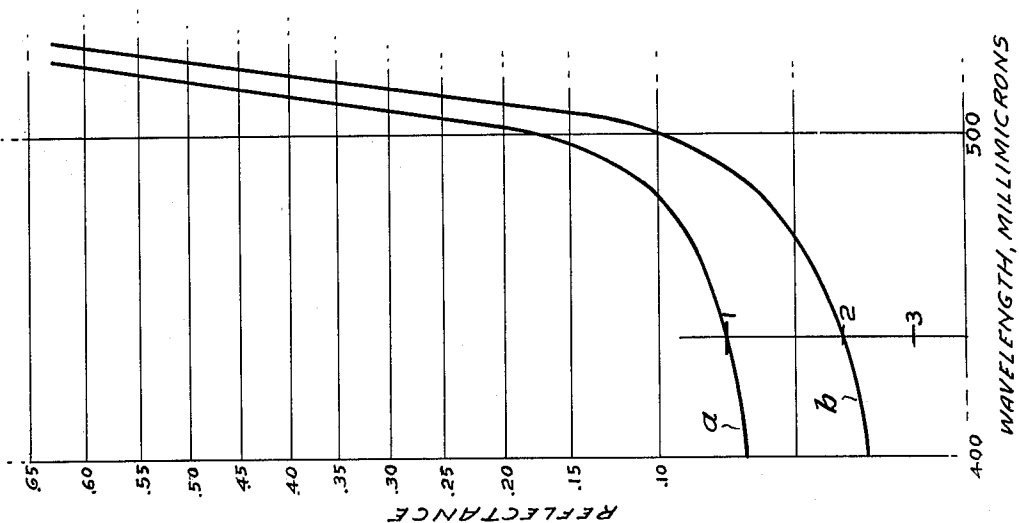
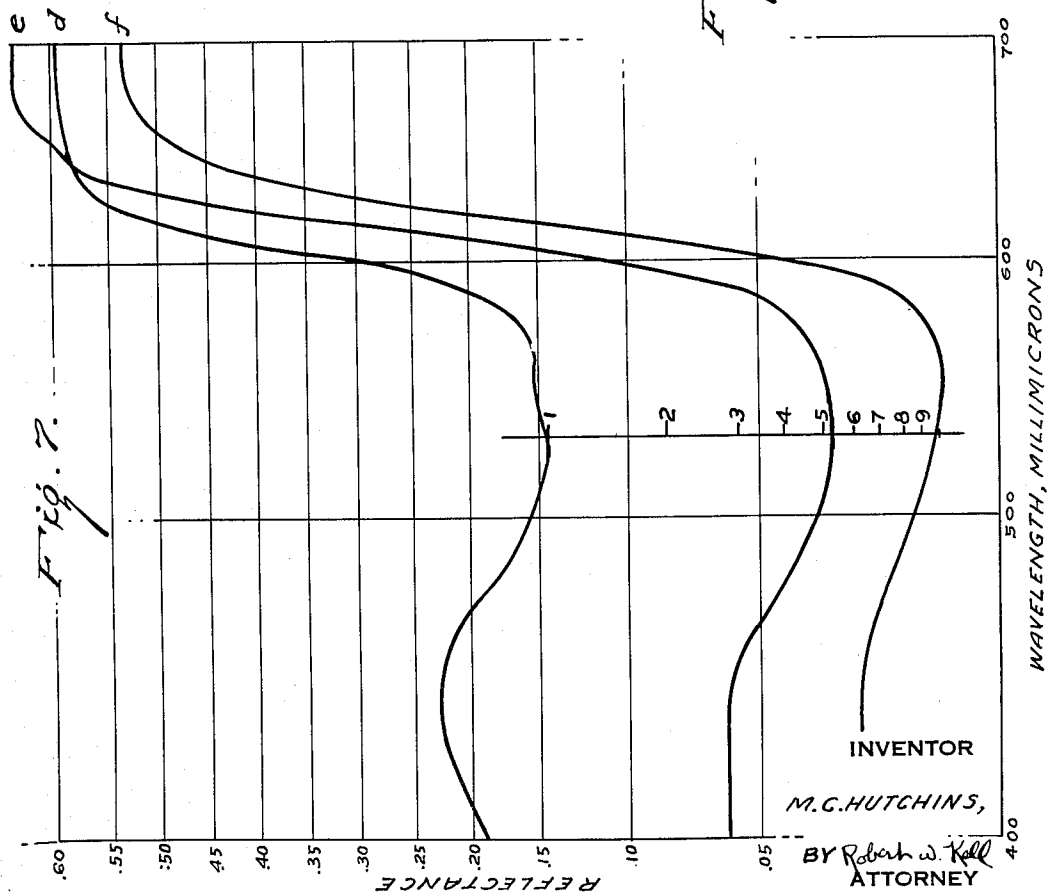


Fig. 9.



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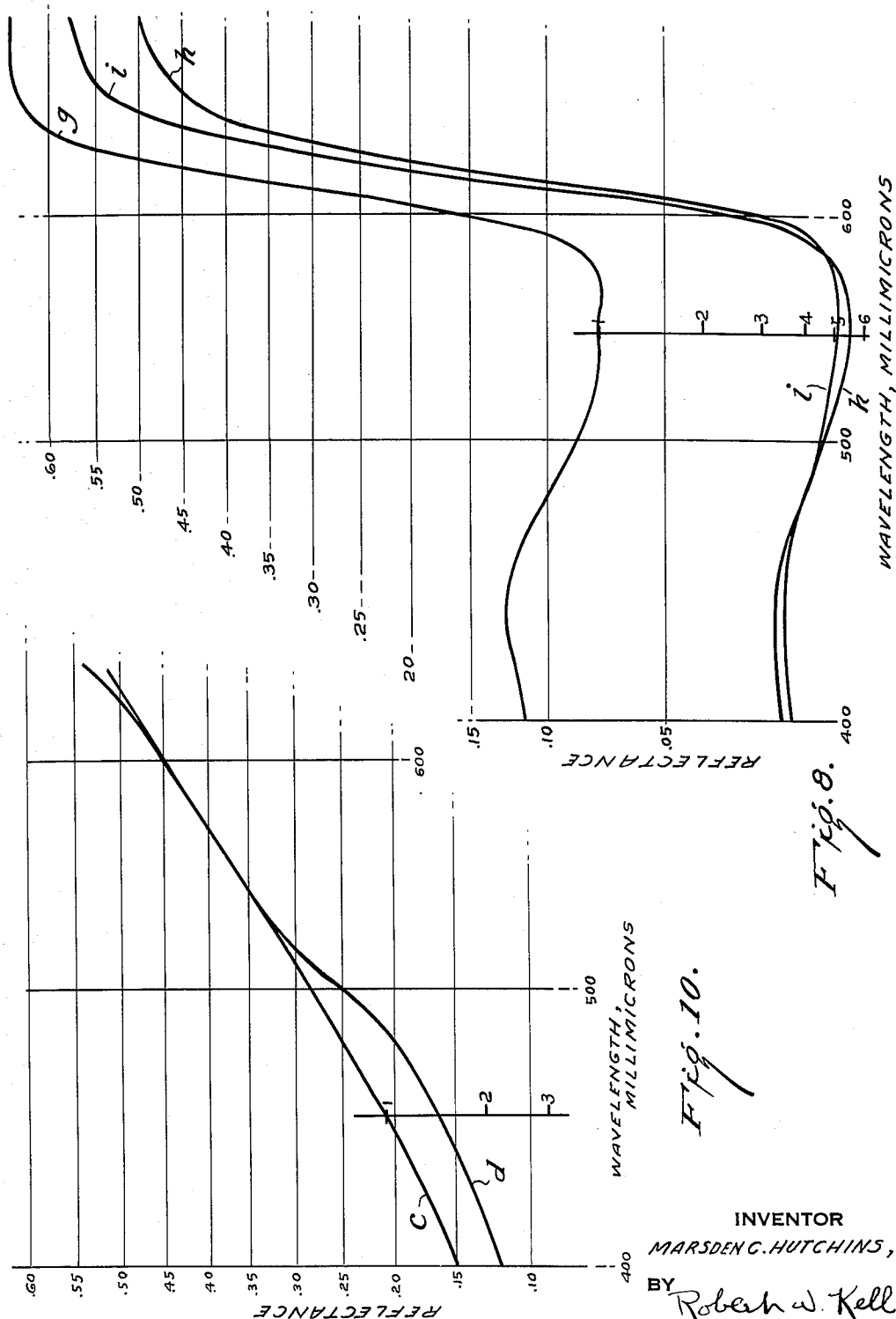
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COLOR IMPROVEMENT OF UNSIZED POROUS PAPER

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8 Sheets-Sheet 5



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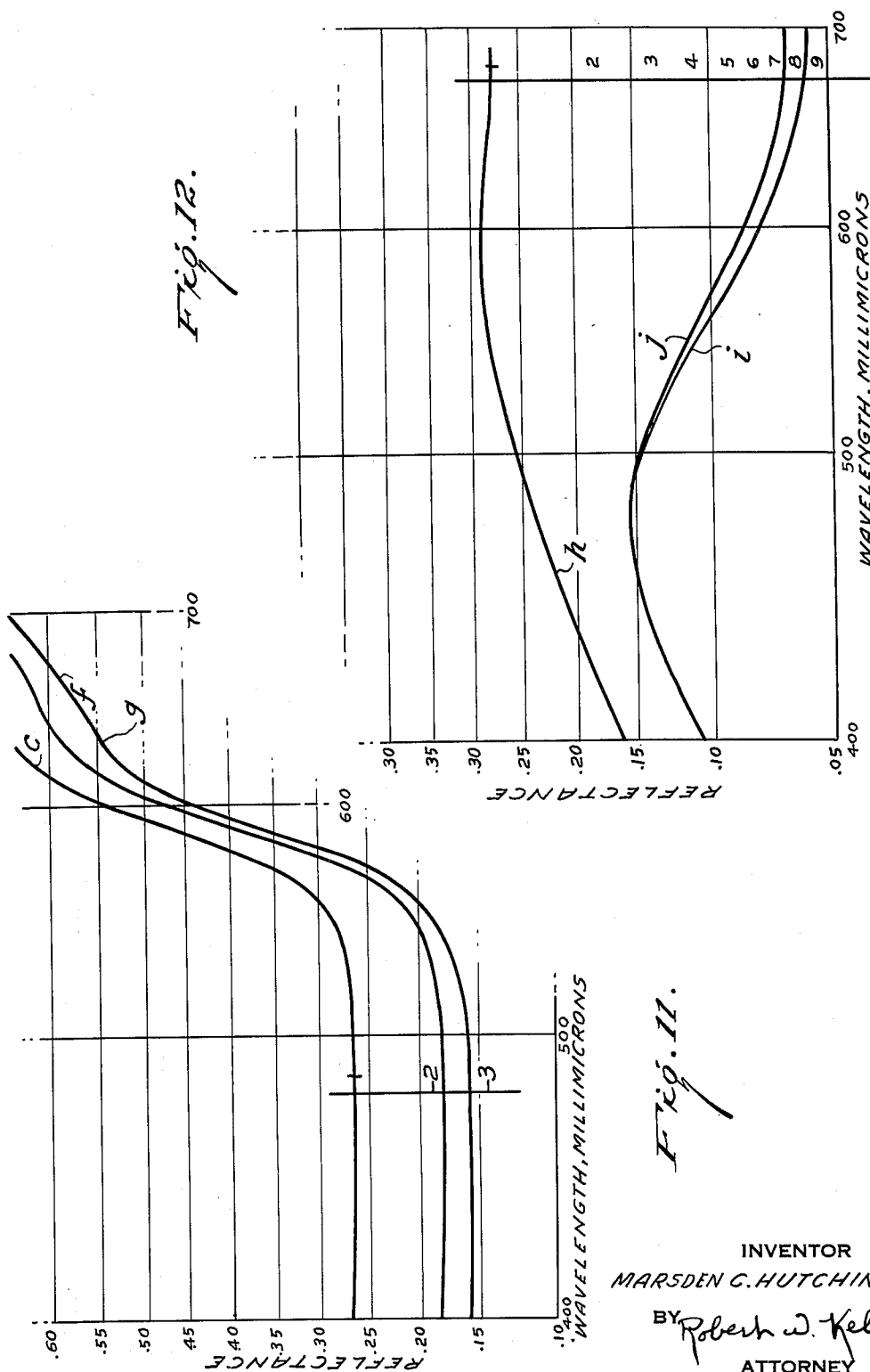
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COLOR IMPROVEMENT OF UNSIZED POROUS PAPER

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8 Sheets-Sheet 7

Fig. 13.

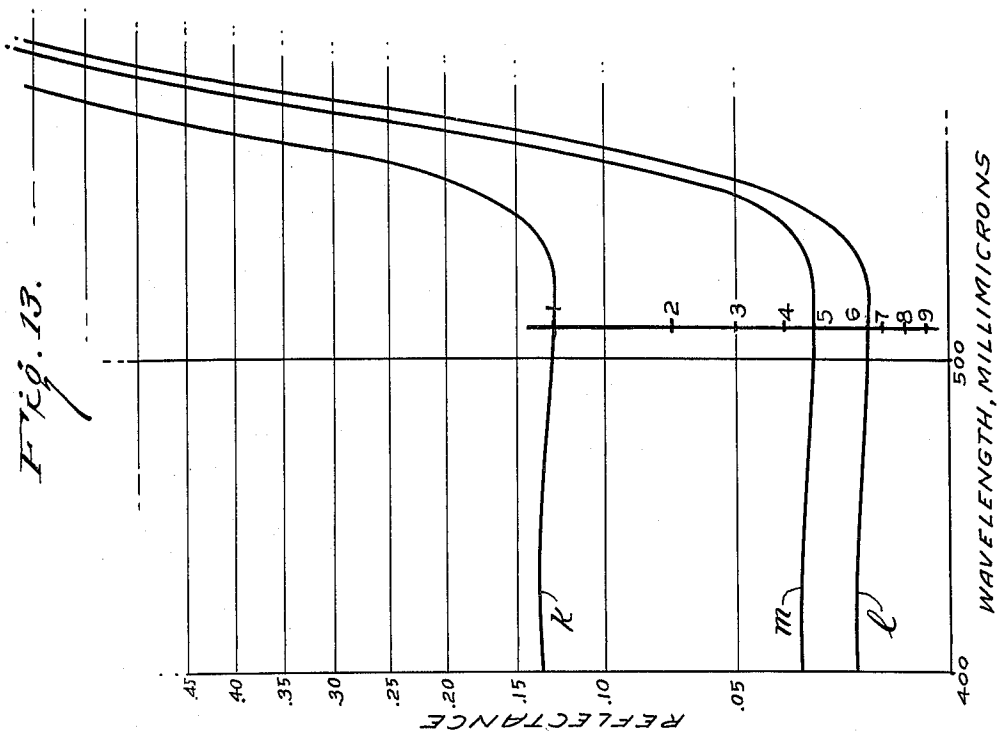
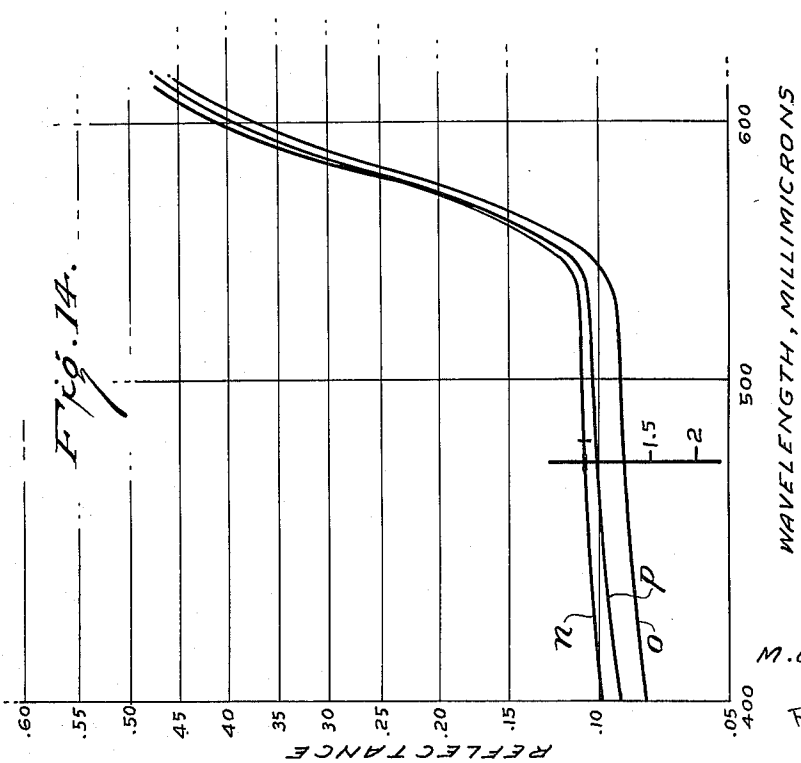


Fig. 14.



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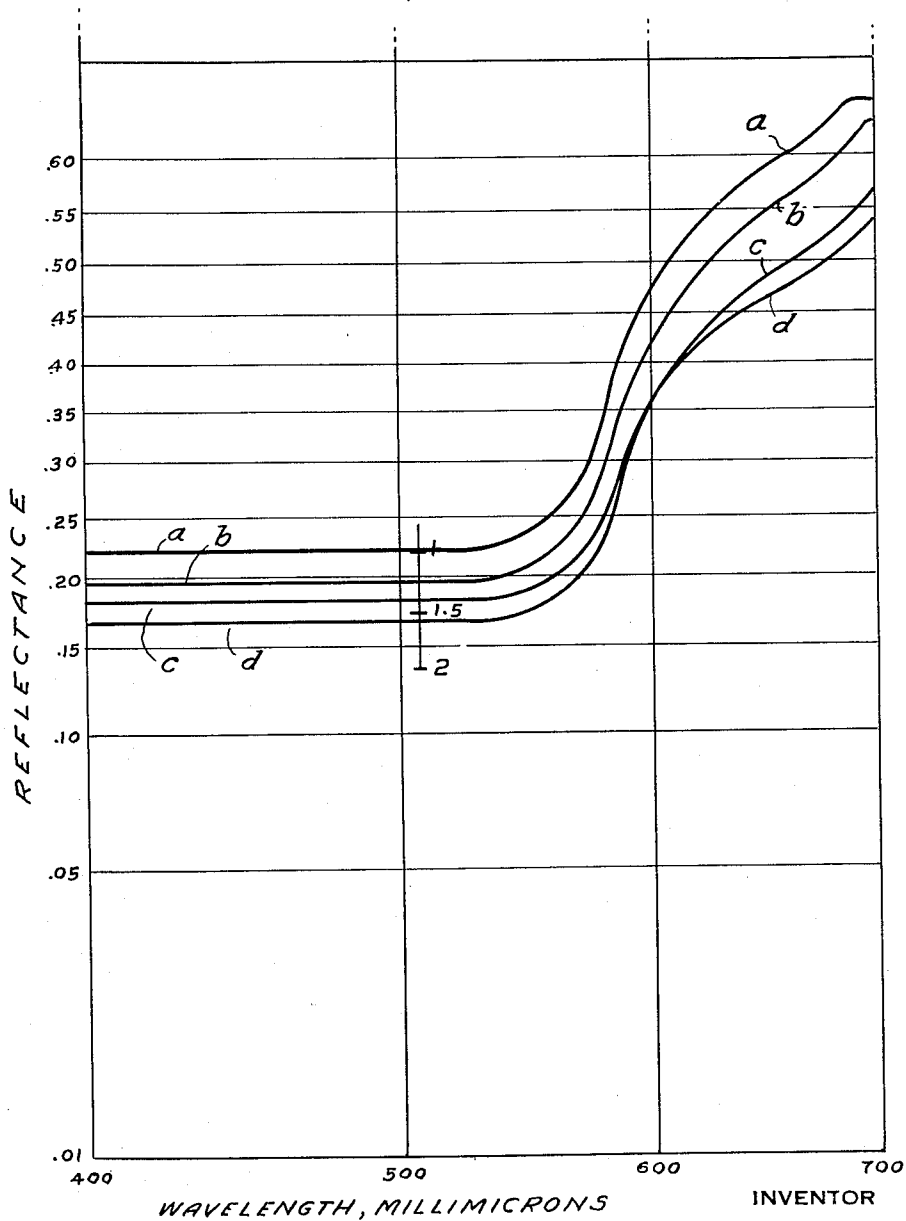
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COLOR IMPROVEMENT OF UNSIZED POROUS PAPER

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8 Sheets-Sheet 8

Fig. 15.



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2,730,446

COLOR IMPROVEMENT OF UNSIZED POROUS PAPER

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corporation of Maine

Application March 15, 1952, Serial No. 276,854

12 Claims. (Cl. 92—21)

This invention relates to an improvement in the color-retention of absorbent paper stock. I accomplish this increase in the color value of paper by the addition of one or more cationic resins to the paper-making fibers.

The importance of color to the paper industry is not always evident to the casual observer; actually, however, very few papers are made without coloring matter of some kind. This is self-evident in heavily colored papers, or with pronounced shades, but it is equally true of white papers, because very few are the natural color of the fibers.

The colors used in paper may be divided into two general groups: pigments, which are insoluble materials, and dyes, which are employed in solution. Each of these groups may be sub-divided into others according to certain characteristics.

Pigments include all colors which are not strictly soluble in water and which are held in the paper by mechanical means. They may be divided into groups as earth pigments, colored metallic salts, carbon blacks, vat colors, and lakes, such as those prepared from basic dyes and phosphotungstic or phosphomolybdic acids. All pigments may be used in the present invention. Pigments are usually very fast to light, but dull in shade; their reactions toward acids and alkalis vary with the individual substances. The majority are not bleached by hypochlorite and must be avoided if bleachable waste stock is desired. They add weight to the sheet, but if used in considerable quantities they tend to weaken it, as do other fillers.

Pigments should be added to the beater as early in the cycle as possible in order to assure good dispersion. Their retention is increased by alum and by increased hydration of the fibers as beating proceeds. This makes it difficult to control the results obtained. The backwaters from heavily pigmented papers are always colored, and the colors in the paper bleed somewhat when in contact with the water.

The pigments, and especially the earth colors, have more and more been replaced in the paper mill by dyes, which although more expensive, have fewer of the disadvantages mentioned above.

The most satisfactory dyes for coloring paper fibers have been direct dyes which may be used on fibers in neutral or alkaline condition without the aid of mordants, such as rosin size and alum. Direct dyes if added under the right conditions, will not bleed from the fiber. As a class, the direct colors have less tinctorial power than basic or acid colors, but most of those which are used in paper are faster to light and other deteriorating influences.

Basic colors are salts of organic bases which contain the color-bearing group. These color bases are precipitated in an alkaline medium and are often used in coloring paper where great tinctorial power and pure and brilliant shades are required. These dyes, however, are fugitive to light, and cannot be used where permanence is of importance.

Acid colors are of three groups: (1) nitro compounds;

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(2) azo compounds that contain the sulfonic acid group; and (3) sulfonated basic colors. Acid colors can be mixed with each other to produce compound shades. They generally have less tinctorial power than basic colors, but dye more evenly and are faster to light. They vary considerably in their reaction to acidity and the stock on the wire must be maintained at the optimum pH in order to obtain the highest retention of color. It is a disadvantage of acid dyes that paper colored with them bleeds freely in water or alcohol, and like pigments, the acid dyes have never been suitable for unsized paper, as they have little affinity for fibers. Rosin sizing has always been considered essential for good results, especially for deep shades and fixation is better if the color is added and is mixed before the sizing is added.

I have now discovered that the insoluble pigments and acid dyes of the class discussed above may be used to color unsized paper if approximately 1/8%—10% of a cationic urea-formaldehyde or melamine-formaldehyde resin is added to the pulp suspension. Surprisingly enough, the cationic resin not only eliminates all necessity for sizing agents, but actually increases the color strength by many hundred percent and decreases the tendency to bleed; thus, the main disadvantages inherent in pigments and acid dyes, that is, low tinctorial power and tendency to bleed, have largely been eliminated with no compromise in their highly desirable properties, such as fastness to light.

The phenomenal increase in color value is the primary advantage of the present invention and this unusual feature of my development was entirely unexpected. I am not able, even at this time, to postulate any mechanism or reaction that would satisfactorily account for an improvement of 1000 or 5000 per cent in the color value of paper containing such a small amount of a cationic resin. Such increases in color strength will be repeatedly demonstrated in the examples that follow.

It is a further advantage of the present invention that "two-sidedness" has been reduced. "Two-sidedness" is a term used to describe a color difference in the two surfaces of a paper sheet. This effect may be caused by an uneven distribution of the fine cellulose particles which are strongly colored and the larger paper fibers which contain less color. Under ordinary conditions, when pigments are used for coloring they may tend to concentrate on the felt side of the paper in the absence of any cationic resin.

It is a further advantage of the present invention that it may be used with any type of pulp, that is, unbleached sulfite, groundwood, soda pulps, natural semi-bleached and bleached krafts. The cationic urea-formaldehyde or melamine-formaldehyde resin may be added in the beater, stock chest, or head box, but the best results are obtained by adding it directly to the beater. Although any order of addition will give an improvement in color-retention, the greatest improvement is obtained by adding the cationic resin before the color is added, then thoroughly mixing with the fiber. The addition of the resin before the color also improves the dyeing levelness.

A further advantage of the present invention is that unsized paper may be dyed to give a colored product that is both soft and absorbent.

In general, the consistency of the stock has very little effect if kept within the normal paper-making ranges. Increasing the temperature will usually improve the color-retention.

A description of cationic resins suitable for use in the present invention and their method of preparation is given in United States Patents No. 2,345,543 and 2,554,475.

It was disclosed above that the amount of the cationic resin may be varied from as little as 1/8% to as much as

10% with good results. The optimum amount varies widely with the individual resin as well as the color concentration. The type of pulp and pulp freeness also influences the amount of resin needed to obtain maximum retention. Amounts of cationic resin in excess of the optimum amount are less effective in increasing the color value, and I have found—much to my surprise—that too large an excess of cationic resin actually acts to reduce the color value of pigmented paper. It will be appreciated, therefore, that although the optimum amount is within the range from ¼ % to 5%, it is possible to obtain a very slight improvement with less than ¼ %. Furthermore, 7.5% or even 10% of a cationic resin may be added with improved results over the control. The use of such large quantities is not, however, economically desirable. The practical operating range may be determined by consulting the examples and Tables I through V.

All the drawings are reproductions of spectrophotometric curves obtained on a Calco modified General Electric recording spectrophotometer having a variable ratio drive which produces curves of a shape that is invariant with concentration. (See U. S. Patent No. 2,218,357.) The percentage improvement in color value may be read directly from these curves, using a log scale. Such a spectrophotometer plots a curve which is proportional to log

$$\frac{1-b}{b}$$

in which equation *b* is the reflectance. The percent change in color concentration, therefore, may be determined from these curves using a log scale of suitable dimensions which in effect transforms the log into its antilog. A log scale has been interposed in the drawings at the predominate wave length for convenience in relating the curve displacement to color value. Figures 1 and 2 illustrate the improvements in color value summarized in Table I. Figures 3, 4, and 5 show the improvements summarized in Table II. Figures 6, 7, and 8 are reproductions of certain spectrophotometric curves identified in Table III. Figures 9 through 14, inclusive, illustrate differences obtained with various dyes on alpha an kraft pulps and refer to the data of Table IV. Figure 15 is a reproduction of the spectrophotometric curves of Table V.

Since conditions of the paper-making slurry will vary widely, depending on the machine, the following examples were all carried out on the same scale according to standard laboratory procedure to obtain strictly comparable results. In all the examples and tables, the amount of dye refers to real dye, that is, the amount of dye which has tinctorial value, and the amount of resin is based on 100% solids.

EXAMPLE 1

Sixteen grams of an alpha pulp having a freeness of 640 ml. on a two-gram sample as determined by the Schopper-Reigler freeness tester, was added to a one-liter beaker and diluted to 4% consistency with water. The temperature of the pulp suspension was about 80° F. To this slurry was added 80 mg. of an acid dye (C. I. 1054) and the pulp was stirred for 10 minutes. The pH was adjusted to 5 and the stirring continued for 10 minutes longer before diluting to 0.5% consistency. One-fourth of this suspension (100 ml.) was made into a circular sheet having a surface area of about 48 square inches. A sheet of 9" x 9" standard blotting paper was placed over the formed sheet which was then couched off the wire by rolling a bronze couch roll back and forth over the blotting paper. Another 9" x 9" blotter was placed on the wire side of the sheet and the formed sheet between the blotters was then placed between wool felts and pressed in a hydraulic press for two minutes at about 600 pounds total pressure. The sheet was dried on a drum dryer for about seven minutes at 250° F. before removal of the blotters. This sheet was used as a control.

A set of sheets was dyed in the same manner, except

that after the pulp was diluted to 0.5% consistency and about five minutes before the sheet was formed, a cationic resin was added. The color value of the paper dyed in the presence of the cationic resin was greatly improved over the control. The effect of two different resins when used with alpha pulp or bleached sulfite pulp, and varying concentrations of dye, is summarized in Table I. The spectrophotometric curves are reproduced in Figures 1 and 2. The results obtained when an acid dye having C. I. 161 is used with alpha or kraft pulp is summarized in Table II. The spectrophotometric curves are reproduced in Figures 3, 4, and 5.

Table I

	Pulp	Acid Dye, C. I. 1054		Resin			pH	Color Value, Pct.
		Amt. (mg.)	Per-cent	Type	Amt. (mg.)	Pct.		
(a)....	Alpha.....	80	½		none		5	100
(b)....	do.....	80	½	M. F.	480	3	5	111
(c)....	Bleached Sulfite.....	80	½		none		5	100
(d)....	do.....	80	½	M. F.	480	3	5	10,300
(e)....	do.....	80	½	U. F.	480	3	5	1,850
(f)....	do.....	160	1		none		5	100
(g)....	do.....	160	1	M. F.	480	3	5	3,800
(h)....	do.....	160	1	U. F.	480	3	5	315
(i)....	do.....	320	2		none		5	100
(j)....	do.....	320	2	M. F.	480	3	5	5,700
(k)....	do.....	320	2	U. F.	480	3	5	170

Table II

	Pulp	Acid Dye, C. I. 161		Resin			pH	Color Value, Pct.
		Amt. (mg.)	Per-cent	Type	Amt. (mg.)	Pct.		
(a)....	Alpha.....	80	½		none		5	100
(b)....	do.....	80	½	M. F.	480	3	5	330
(c)....	do.....	80	½		none		6.8	100
(d)....	do.....	80	½	U. F.	480	3	6.8	3,400
(e)....	do.....	80	½	M. F.	480	3	6.8	2,450
(f)....	Kraft.....	80	½		none		6.8	100
(g)....	do.....	80	½	U. F.	480	3	6.8	135
(h)....	do.....	80	½	M. F.	480	3	6.8	260

EXAMPLE 2

Sixteen grams of an alpha pulp having a freeness of 665 ml. on a two-gram sample as determined by the Schopper-Reigler freeness tester, was added to a one-liter beaker and diluted to 4% consistency with water. The temperature of the pulp suspension was about 80° F. To this slurry was added 160 mg. of a pigment paste (C. I. 189) equal to 32 mg. of real pigment. The pH was adjusted to 5 and stirring continued for 10 minutes longer before diluting to 0.5% consistency. One-fourth of this suspension (100 ml.) was made into a circular sheet having a surface area of about 48 square inches. A sheet of 9" x 9" standard blotting paper was placed over the formed sheet which was then couched off the wire by rolling a bronze couch roll back and forth over the blotting paper. Another 9" x 9" blotter was placed on the wire side of the sheet and the formed sheet, between the blotters, was then placed between wool felts and pressed in a hydraulic press for two minutes at about 600 pounds total pressure. The sheet was dried on a drum dryer for about seven minutes at 250° F. before removal of the blotters. This sheet was used as a control.

A set of sheets was colored in the same manner, except that after the pulp was diluted to 0.5% consistency, a cationic resin was added to the suspension and stirred for five minutes before forming the sheet. The color value of the paper dyed by this procedure was greatly improved over the control. The effect of two different resins when used with bleached sulfite pulp and varying concentrations of pigments, is summarized in Table III. The spectrophotometric curves are repro-

duced in Figures 6, 7, and 8. Table IV summarizes the results obtained with various dyes on alpha and kraft pulps. The spectrophotometric curves are reproduced in Figures 9 through 14, inclusive. Table V summarizes the results obtained when the pigment having C. I. 1276 was used to color a bleached sulfite pulp of 610 ml. on a two-gram sample as measured by a Schopper-Reigler freeness tester, and the temperature is kept at 145° F. during the dyeing and resin-addition steps. The spectrophotometric curves are reproduced in Figure 15.

Table III

	Pulp	Pigment, C. I. 189		Resin			pH	Color value, Pct.
		Amt. (mg.)	Percent	Type	Amt. (mg.)	Pct.		
(a)....	Alpha....	32	0.20	-----	none	-----	5	100
(b)....	do.....	32	0.20	M. F.	480	3	5	490
(c)....	do.....	32	0.20	U. F.	480	3	5	720
(d)....	do.....	160	1.00	-----	none	-----	5	100
(e)....	do.....	160	1.00	M. F.	480	3	5	550
(f)....	do.....	160	1.00	U. F.	480	3	5	970
(g)....	do.....	320	2.00	-----	none	-----	5	100
(h)....	do.....	320	2.00	M. F.	480	3	5	480
(i)....	do.....	320	2.00	U. F.	480	3	5	530

Table IV

	Pulp	Pigment			Resin			pH	Color Value, Pct.
		C. I.	Amt. (mg.)	Pct.	Type	Amt. (mg.)	Pct.		
(a)...	Alpha...	Lead	800	5	-----	none	-----	6.8	100
(b)....	do.....	Chrom.	800	5	U. F.	480	3	6.8	200
(c)...	Kraft...	Lead	800	5	-----	none	-----	6.8	100
(d)....	do.....	Chrom.	800	5	U. F.	480	3	6.8	140
(e)...	Alpha...	1276	800	5	-----	none	-----	6.8	100
(f)....	do.....	1276	800	5	M. F.	480	3	6.8	180
(g)....	do.....	1276	800	5	U. F.	480	3	6.8	216
(h)...	Kraft...	1288	800	5	-----	none	-----	6.8	100
(i)....	do.....	1288	800	5	M. F.	480	3	6.8	800
(j)....	do.....	1288	800	5	U. F.	480	3	6.8	720
(k)...	Alpha...	Moly. Lead Chr.	800	5	-----	none	-----	6.8	100
(l)....	do.....	do.....	800	5	M. F.	480	3	6.8	470
(m)....	do.....	do.....	800	5	U. F.	480	3	6.8	640
(n)...	Kraft...	do.....	800	5	-----	none	-----	6.8	100
(o)....	do.....	do.....	800	5	M. F.	480	3	6.8	128
(p)....	do.....	do.....	800	5	U. F.	480	3	6.8	167

Table V

	Pulp	Pigment			Resin			pH	Color Value, Pct.
		C. I.	Amt. (mg.)	Pct.	Type	Amt. (mg.)	Pct.		
(a)...	Bleached Sulfite.	1276	160	1	-----	none	-----	6.8	100
(b)....	do.....	1276	160	1	U. F.	40	0.25	6.8	121
(c)....	do.....	1276	160	1	U. F.	80	0.50	6.8	156
(d)....	do.....	1276	160	1	U. F.	400	2.50	6.8	136
(e)....	do.....	1276	160	1	U. F.	800	5.00	6.8	136

I claim:

1. In the manufacture of colored paper, a method of improving the color-retention, which comprises mixing with the pulp suspension a pigment and a cationic resin, prior to forming the sheet; the amount of said cationic resin being not less than 1/8 % and not more than 10 % of the pulp solids.

2. In the manufacture of colored paper, a method of improving the color-retention, which comprises mixing with the pulp suspension an acid dye and a cationic resin, prior to forming the sheet; the amount of said cationic resin being not less than 1/8 % and not more than 10 % of the pulp solids.

3. In the manufacture of colored paper, a method of improving the color-retention, which comprises mixing with the pulp suspension a pigment and a cationic urea-formaldehyde resin, prior to forming the sheet; the amount of said resin being not less than 1/4 % and not more than 5 % of the pulp solids.

4. In the manufacture of colored paper, a method of improving the color-retention, which comprises mixing with the pulp suspension an acid dye and a cationic urea-formaldehyde resin, prior to forming the sheet; the amount of said resin being not less than 1/4 % and not more than 5 % of the pulp solids.

5. In the manufacture of colored paper, a method of improving the color-retention, which comprises mixing with the pulp suspension a pigment and a cationic melamine-formaldehyde resin, prior to forming the sheet; the amount of said resin being not less than 1/4 % and not more than 5 % of the pulp solids.

6. In the manufacture of colored paper, a method of improving the color-retention, which comprises mixing with the pulp suspension an acid dye and a cationic melamine-formaldehyde resin, prior to forming the sheet; the amount of said resin being not less than 1/4 % and not more than 5 % of the pulp solids.

7. A paper sheet manufactured by the process of claim 1.

8. A sheet of paper prepared by the process of claim 2.

9. A sheet of paper manufactured by the process of claim 3.

10. A sheet of paper manufactured by the process of claim 4.

11. A sheet of paper manufactured by the process of claim 5.

12. A sheet of paper manufactured by the process of claim 6.

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