DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS

George K. Burgess, Director

TECHNOLOGIC PAPERS OF THE BUREAU OF STANDARDS, No. 323

[Part of Vol. 20]

USE OF GLUE IN COATED PAPER

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Bureau of Standards

August 18, 1926

PRICE 15 CENTS

\$1.25 PER VOLUME ON SUBSCRIPTION

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Washington, D. C.

WASHINGTON
GOVERNMENT PRINTING OFFICE
1926

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By George K. Hamill, V. H. Gottschalk, and George W. Bicking

On account of the interest among manufacturers of coated papers in alternative adhesives for use in their industry, this investigation was made to gather data and information on the use of glue for coating paper and the relation of such paper to present-day printing practice. Various factors advanced as inhibiting the use of glue, such as price, lack of waterproofness, and variations in quality, were tested by laboratory studies and by semicommercial runs in the experimental paper mill of the bureau. Commercial scale runs were made at a paper-coating plant. Printing tests were obtained on papers coated with different grades of glue and with casein for comparison. Eight different glues were used with clay, satin white, and blanc fixe as the coating minerals. The major conclusions of the investigation are that the amount of glue required in coating mixtures varies with the grade of the glue chosen and with the better-grade glues may be less than that of casein. Little change from present equipment and operating technic is required by using glue. The choice of various types of glues offers a considerable latitude within which local conditions may be met. Uniformity in glue for coating purposes may be attained by drawing specifications to meet local and product requirements. The use of ordinary glue-bound coated papers presents no new difficulties in printing except in those lithographic and, possibly, offset processes where a high degree of water resistance is required. The need for an extraordinary degree of waterproofness in coated paper for ordinary printing work is questionable.

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I. INTRODUCTION

1. DESCRIPTION OF COATED PAPERS

The demand for papers possessing surface qualities not obtainable through the ordinary paper manufacturing and finishing processes has led to the development of the so-called coated papers. These papers are characterized by having surfaces of material other than that composing the main body of the sheet. These surfaces are composed of mineral matter bound together and to the body of the sheet by a suitable adhesive, generally casein, glue, or starch, or a mixture of these.

Special surfaced papers are divided into three major classes: (a) Those for high-grade printing, engraving, and lithographic purposes (some photographic papers, such as barytes papers, are of this class); (b) glazed or high-finished papers, as used in box making; and (c) specialty papers, such as cover stock, imitation leather, etc.

The work of the present investigation has been confined to the first kind of paper mentioned, and this is the type ordinarily referred

to by the general term "coated paper." Such paper is used chiefly for magazine, book, and catalogue printing and illustrating, where a smooth, continuous, and semiabsorbent surface is required to permit the use of fine screen half tones and for lithographic and offset work.

In order to produce this even, continuous surface, there is applied to the comparatively rough surface of the paper to be coated, referred to as "coating," "body," or "raw stock," a layer of mineral matter and adhesive with possible additions of waxes, soaps, or similar materials, plus coloring matter if desired, the whole being suspended in water and referred to as the "coating mixture" or "color mix." This color mix is applied to the coating stock by various types of coating machines, all of which rely on brushes moving across the coated surface to unite the coating with the paper stock, and to make the coat smooth and even.

After the coating operation the coated paper is dried in festoons, and, if desired, is calendered in order to impart a high glossy finish.

2. PURPOSE OF INVESTIGATION

Prior to the introduction of the use of casein as an adhesive, glue had been commonly used as the sizing or binding agent in the manufacture of coated papers. While this use of glue has persisted in certain phases of the industry, as in the manufacture of glazed papers, imitation metal foils, and other specialties, casein has largely taken the place of glue in preparing the types of coated paper used for printing and lithographic processes.

Considerable interest has been shown by manufacturers of coated paper in the development of alternative adhesives for use in their industry. This investigation was undertaken by the Bureau of Standards in cooperation with the National Association of Glue Manufacturers because the interest just referred to indicated the advisability of gathering data and information on the use of glue for coating paper.

Among the reasons that have been advanced as militating against the use of glue for this purpose have been its lack of waterproofness and reputed variations in acidity, grease content, odor, and color. The economy of using glue has been questioned and, furthermore, opinions as to the printing qualities of glue-bound coated paper have been conflicting.

This investigation has included observations of several factors which materially influence the important questions of price and waterproofness, such as quality of materials entering into the product and lack of coordination between the manufacturers of coated paper, the manufacturers of inks, and the consumers using both paper and inks. Consideration has also been given to the printing qualities of glue-bound coated paper, to the need of specifications for coaters'

glue, and to a minor extent to the possibility of increasing the water resistance of glue-bound coated paper.

II. MATERIALS USED IN THE MANUFACTURE OF COATED PAPER

1. PAPER

Depending on the product requirements and on the sale price, the stock used for coating may vary through the range of fibers from ground wood to 100 per cent rag. Chemical wood fiber is favored for medium-priced work. Regardless of the kind used, the stock should be selected with considerable care, for, though the heavier-weight coatings have excellent covering power, it is impossible to hide the too flagrant defects of a poor body even by the use of the best grade of coating. The coating stock should have a good formation, as a "wild" sheet tends to cause mottling during the calendering operations, with subsequent trouble in printing due to uneven ink absorption. Similar difficulties may be caused by the presence of hard spots, as from uneven sizing, specks of dirt, metal, or shives (small particles of wood). The degree of sizing of coating stock is varied to meet local coating conditions and the product requirements; for instance, in book paper, soft (or slack) sized stock is generally used, whereas for litho paper the stock is generally hard sized. Limits are placed on sizing variations by the tendency of too hard sizing to cause poor binding of the coating to the stock and of too soft sizing to absorb too much adhesive from the coating mixture, either extreme causing difficulties in the finishing operations or in subsequent printing processes. The color of the stock coated should be as good as possible, for the color of the finished sheet is influenced markedly by that of the body. With white papers the color of the stock should be as close to that of the finished sheet as is obtainable. Under these conditions variations in the weight, uneven coating, brush marks, or similar faults arising from operating difficulties are less prominent than with an off-color stock.

2. COATING MATERIALS

(a) MINERALS.—Among the white pigments which form the base of most coatings are clay (foreign and domestic), satin white, blanc fixe, and barytes. Clay alone is used as the mineral in a large proportion of all coated papers on account of its lower cost and is combined with satin white, blanc fixe, or both in most other papers.

The choice of mineral matter, as well as the adhesive and special materials used, affects the character of the finished paper very largely. Under parallel conditions a smoother coat and a higher finish may be obtained with satin white than with any other material commonly used. Blanc fixe coatings, while very smooth, do not take as high a

gloss as those made with satin white and are often used for matte and semidull effects. Blanc fixe and barytes are also largely employed in the manufacture of special sensitized and photographic papers. The use of clay gives coatings of relatively poor finish and color which may be improved by mixture with other minerals and coating materials.

Clays used for coating purposes are of higher quality than those ordinarily used as paper fillers, the coating grades being whiter and finer grained, with less grit. For these reasons imported clays are favored by the coating trade. The size of the clay particles has a marked effect on the amount of adhesive required to produce satisfactory binding of the coat to the body stock, on the consistency of the coating mixture, and on the degree of suspension obtained in the coating mixture. In general, the finer-grained clays remain suspended longer, require larger amounts of adhesive, and form thicker coating mixtures than the coarser ones. Clays of fine particle size will take a higher gloss on calendering than the coarser types, but this advantage is offset to some extent by the larger proportions of adhesives required. Such clays are less sticky than the coarser types and therefore offer less resistance to the brushing operation of the coating process, with consequent freedom from brush marks in the finished coat. The particle size of different samples may be compared by measuring the relative bulks of equal weights of material permitted to settle from water suspensions.

Satin white is used largely in the manufacture of better-grade coated papers, especially those to be finished with high gloss. It is the product of the interaction of slaked lime and aluminum sulphate. Depending on the concentration of alkali during the formation, one of the following reactions¹ take place:

¹ The chemistry and manufacture of satin white, by A. Cobenzl, *Chemiker-Zeitung*, Sept. 7, 1920, pp. 661-662.

The above equations are commonly offered as explaining the frequently observed occurrence that samples of different lots of satin white, whose analyses indicate identical chemical compositions, possess very different physical properties. The best satin white is a pure white lustrous pulp (generally containing about 30 per cent of solid matter) which, when added to water, shows very small particle size and settles very slowly. The commercial product is characterized by varying degrees of alkalinity and a tendency to react with other materials, notably with borax, of the coating mixture, especially when heated. Coating mixtures which contain satin white require a larger proportion of adhesive than when clay alone is used.

Blanc fixe or precipitated barium sulphate is largely used in the manufacture of coated papers for lithographing and for photography. Such papers are characterized by the pure whiteness, with a tendency to bluish tones, of their color, although their total reflection of light is less than that of papers coated with satin white. On account of its high specific gravity the use of blanc fixe increases markedly the weight of the coating and sometimes causes operating difficulties due to its tendency to settle out of the coating mixture. Since, in the process of manufacturing blanc fixe, the precipitated barium sulphate is carefully washed with water until free from acid, this material is chemically neutral and therefore does not react with the other constituents of coating mixtures. It is commonly marketed as a pulp containing about 25 per cent of moisture. Blanc fixe is characterized by requiring smaller proportions of adhesives in coating mixtures than clay.

Barytes, or natural barium sulphate, is prepared for use by simply grinding the mineral. In general, the commercial types contain relatively large amounts of grit (8 to 15 per cent) and may be more or less discolored, and the particle sizes are more coarse and variable than in blanc fixe. It is not used in the best grades of papers.

Of late considerable use has been made in coating paper of a mixture of hydrated carbonates and hydroxides of calcium and magnesium.

(b) ADHESIVES.—As indicated previously, the adhesives chiefly employed in coating paper are casein and glue. It should be noted that both these commonly used materials are nitrogenous and therefore subject to decay, a factor which must be borne in mind in the preparation of coating mixtures.

The following qualities are desired in adhesives for coating purposes: Freedom from insoluble matter, such viscosity as to permit the use of ordinary equipment at the desired dilution of the color mix and within the temperature range of working conditions, high adhesiveness, good clay-suspending power, freedom from foam-causing impurities and from grease.

(1) *Glue*.—In the past it has been the custom of some paper converters to manufacture their own glue. This practice has largely been discarded in favor of purchasing prepared glue as, in addition to being more economical, the latter procedure renders it possible to obtain a more nearly uniform and regular supply. Glue is sold in well-recognized and sharply differentiated grades based primarily on considerations of jell strength and viscosity. The best hide glues form the highest grades; the poorest bone glues, the lowest grades; the medium and highest grades of bone glues overlap the lowest and medium grades of hide glues in the middle zones of the commercial scales. Most grades are offered for sale in both sheet and ground form, the latter possessing the advantage of requiring a shorter time for soaking and therefore for the preparation of their solution. In preparing solutions of glue excessive heating should be avoided, as comparatively slight exposure to high temperatures tends to hydrolyze the proteins to proteoses, causing decreased strength in the product. If thorough soaking has taken place ordinary glues will dissolve freely at temperatures not higher than 140° F. The use of live steam for dissolving glue and the maintaining of high temperatures in the glue solution should be avoided.

The adhesiveness of glue as measured by the amount required to hold the mineral matter of a paper coating firmly to the body stock may be determined by a laboratory modification of the coating process known as the sealing wax pick test.²

The higher grades of glue possess greater strength and therefore may be used in smaller quantities than the lower ones. The proportion of high-grade glue to clay that may be used in coating mixtures is not entirely limited by the binding qualities of the adhesive. The respective clay-suspending powers of a comparative series of glues do not improve uniformly with increasing grades. Even within any particular grade of glue a marked difference may exist in the clay-suspending powers of lots from different sources. Therefore, the lower limit for the amount of glue needed in a coating mixture is affected by the clay-suspending power as well as by the adhesiveness of the glue under consideration. Comparisons for clay suspending power may be readily made by preparing small batches of the coating mixtures from the different glues and examining the mixtures at suitable time intervals for rate of settling.

(2) *Casein*.—Commercial casein is marketed in a number of kinds, generally designated to indicate the manner in which the protein material has been separated from the other constituents of milk, as "rennet," "self-soured," "lactic," "sulphuric (acid)," and "muriatic

² Chemistry of Pulp and Paper Making, by Edwin Sutermeister, pp. 341-342. John Wiley & Sons; 1920. The Manufacture of Pulp and Paper, 5, pp. 38-39 of section on coated papers. McGraw-Hill Book Co. (Inc.); 1925. A slightly different method of procedure, used in the bureau tests, is given on pp. 316-317 of Griffin's Technical Methods of Analysis, McGraw-Hill Book Co. (Inc.); 1921.

(acid)." Within each of these major divisions there exist wide variations of quality, depending on the care with which the material has been prepared, dried, and stored. These variations in quality require different modifications of the dissolving process and cause differences in the types of the liquids obtained.

Casein is insoluble in water and treatment with alkali is required to bring about its solution. Depending on the type of material and the requirements of the coating process and product, there is generally employed some combination of the following alkalies: Soda ash, crystalline sodium carbonate, ammonia, borax, or trisodium phosphate. The adhesiveness of casein and its clay-suspending power may be tested for as indicated under "Glue" in the preceding section.

III. MATERIALS USED IN THIS INVESTIGATION

1. PAPER

Throughout the investigation the paper stock used for coating has been chiefly of sulphite fiber and from slack to medium rosin sized. The weight of the raw stock was approximately 50 pounds, 500 sheets 25 by 38 inches in size. For most of the coating runs the paper stock was made on the Fourdrinier machine of the Bureau of Standards' experimental paper mill. This stock was much the same as that used for commercial mimeograph work. It was composed chiefly of sulphite fiber, with some waste paper from experimental paper runs, contained generally about 10 per cent of fillers, and was sized with approximately 2.8 per cent of rosin. The comparatively large amount of rosin was largely offset by the filler present, therefore the paper was rather slack sized. Several runs were made using stocks obtained from commercial coating mills. These stocks were largely sulphite papers, and as they contained little or no clay they were somewhat harder than those made at the bureau. A typical sample tested 1.3 per cent of rosin with no filler. A representative sample of Bureau of Standards, coating stock when tested for sizing value by the indicator³ method transuded water in 39.2 seconds. A typical commercial stock transuded water in 56.7 seconds.

The limitations of the small-scale coating equipment employed necessitated a higher dilution of the coating mixtures than is used generally with commercial machinery. Such dilutions required a relatively more absorbent raw stock than those used in commercial operations in order to obtain uniform medium-weight coatings. When coated with the dilute color mixtures referred to the commercial stocks tended to curl excessively on the drying festoons.

³ Testing paper for permeability to liquids, by F. T. Carson (Bureau of Standards) Paper Trade J., 89, No. 10, pp. 59-62, Mar. 5, 1925.

FIG. 1.—Paper coating machine with festoon dryers, Bureau of Standards

FIG. 2.—Paper coating mixers, Bureau of Standards

FIG. 3.—*Paper supercalender, Bureau of Standards*

2. COATING MATERIALS

(a) MINERALS.—Three different brands of imported clay were obtained for use in this investigation. All of them were of medium grade, varying somewhat in color as well as in plasticity, and therefore in the proportion of adhesive required to obtain satisfactory coating mixtures. Most of the coating runs were made with some one of these three clays, but several runs were made using imported clays obtained from commercial coating plants.

In addition to those runs made with clay alone as the mineral matter a considerable number were made with mixtures of clay with satin white and clay with blanc fixe. The satin white and blanc fixe so used were good commercial grades.

(b) ADHESIVES.—Eight lots of glue, four each from hide and from bone stock, were procured from manufacturers. Through laboratory studies as described in the sections on "Test methods" and "Development procedure" the less desirable glues were eliminated from consideration and the development and semicommercial coating runs were chiefly made with three glues, representing high, medium, and low grades.

In order to compare products obtained under parallel conditions coating runs were made frequently with casein as the adhesive. In these runs there was used a good grade of French casein, obtained from a commercial coating mill.

IV. PAPER-COATING EQUIPMENT USED

The paper-coating equipment of the Bureau of Standards consists of a 14-inch Waldron flat-bed brush coater with festoon drier and rewinder. (See fig. 1.) The festoon rack is 15 feet in length and holds a maximum of 380 feet of paper in 27 loops, each 7 feet in length. It is not inclosed and has no provision for heating, so that in all the full-sized runs made the festoon was filled and allowed to dry overnight.

Auxiliary equipment includes small power-driven agitators of the wooden-gate type which were used in stirring the color mixes. (See fig. 2.)

The bureau does not possess the special type of calendar that is ordinarily used for coated paper. A nine-roll Holyoke super-calendar was used to finish paper for printing tests. (See fig. 3.)

Five runs were made in a commercial coating mill, using their ordinary full-sized coating equipment.

V. TEST METHODS

1. LABORATORY STUDIES OF GLUES

Prior to the larger-scale work, involving the use of the bureau's semicommercial coating equipment, a thorough laboratory study was made to determine the suitability for coating purposes of the eight lots of glue obtained from manufacturers for this investigation. Test data as ordinarily used in describing glues were first obtained. These included the following items: Stock origin, form, moisture, ash, jell strength, viscosity, grease content, acidity, and observed odor. In addition, there were considered those factors which are of importance to the paper coater—the relation between adhesiveness and clay-suspending power, the effects of color on the finished coated paper, and the reactions with hardening, softening, and waterproofing agents. The effects of the acidity on the degree of deflocculation of the mineral portion of coating mixtures were also considered.

(a) STANDARD DATA.—Information regarding the type of stock used in manufacturing the respective glues was obtained from the manufacturers.

The moisture was obtained by heating a weighed sample at 105° C. until constant weight was obtained. The dried samples were then incinerated in porcelain crucibles to find the ash content.

The jell strength and viscosity were measured by the approved methods of the National Association of Glue Manufacturers.⁴

(b) GREASE CONTENT.—A comparison of the grease content of the different lots of glues was obtained by the "fisheyes" method; that is, by taking the average of five counts of the number of "fisheyes" in 5 square inches of the coating obtained by painting on a sized paper a 25 per cent glue solution to which 2 ml of a concentrated magenta solution had been added.⁵ This method is not quantitative but serves for comparative purposes or to eliminate excessively greasy glues. It should be noted that by this means there is indicated the presence of free grease, which is objectionable in coating practice because of its tendency to "spot" on coated surfaces, and little or no indication is given of the presence of combined grease or soap. The count of "fisheyes" is not quite as satisfactory with bone glues as with those made from hide stock.

In the laboratory study there were noticeable variations between the results of the fisheye count and those of the Kissling extraction method⁶ commonly used in glue analysis. This method specifies a

⁴ Standard methods of glue testing, *Ind. and Eng. Chem.*, **16**, pp. 310-315, March, 1924.

⁵ Teesdale-Bezeau, *Modern Glues and Glue Handling*, Chapter V, Glue Testing, pp. 28, 33, and 34.

⁶ R. Kissling, Determination of grease in glue, *Chemiker-Zeitung*, **11**, pp. 691, 719. Also in Allen's *Commercial Organic Analysis*, 4th ed., 1913, 8, p. 606.

rather long period of heating with hydrochloric acid and relatively high concentrations of the acid used. These conditions favor decomposition of any soaps present to their respective fatty acids, and in the extraction such material is added to the free grease removed from the sample. The "grease" obtained by the Kissling method was found to be completely saponifiable. It could therefore not contain decomposition products of the glue, and the larger amounts found as compared with the indications from the fisheye count must have been due to the splitting up of soaps by the acid.

The presence of soaps in the samples was checked by extracting a dried powdered glue with anhydrous petroleum ether until the relatively small amount of free grease was removed.⁷ The residue from the ether extraction was then extracted with alcohol, and a small amount of soap was obtained.

(c) EFFECT OF COLOR OF ADHESIVE ON THAT OF COATED PAPER.—Hand-brushed samples of coated paper were prepared to determine the effects of the various colors of different glues and those of tinting agents when used with glues. The samples were air-dried and, without being calendered, color comparisons were made with the Pfund colorimeter.⁸ The same clay was used for all the coating mixtures, and the coatings were applied as uniformly as possible. In all cases the weight of the coating was sufficient to minimize any variations in the coating stock. For comparison, similar samples were prepared, using casein, starch, and gum tragacanth as adhesives.

(d) ADHESIVENESS AND CLAY SUSPENDING POWER.—Small amounts of coating mixtures were prepared and subjected to the sealing-wax pick test. In this way comparisons were made between the adhesive qualities of different lots of glue. The relative clay-suspending powers were graded by comparing the amounts of mineral matter which settled out from these coating mixtures in a given length of time. Cylinders were filled to equal depths with the different coating mixtures, and the volume of the respective precipitates noted at suitable time intervals.

(e) WATER RESISTANCE.—The effects of a considerable number of glue-hardening agents were studied to check their influence on improving the water resistance of glue-bound coated paper. Among these materials were the formate, acetate, and sulphate of aluminum, chrome alum, sodium bichromate, and formaldehyde. Preliminary studies were made by forming films from glue solutions to which the respective hardening agents had been added. Later work included different methods of incorporating such materials in the finished coated paper and observations of their effects on coating mixtures.

⁷ R. H. Bogue, *The Chemistry and Technology of Gelatin and Glue* (1922), p. 455.

⁸ A Measure of the Color Characteristics of White Papers. B. S. Tech. Paper No. 244, R. E. Lofton; 1923.

(f) **SOFTENING AGENTS.**—The effect of materials commonly used for softening glue—that is, for lowering its viscosity and setting point, such as glycerin—was studied with films of glue and through the preparation of hand-brushed coated paper samples. These observations included consideration of glues to which hardening agents had been added as well as the normal glues. Materials, such as soaps, wax emulsions, and “vegetol,” used in commercial coating practice were likewise tested.

(g) **ACIDITY.**—The acidity determinations were made by titration of a 1 per cent glue solution with tenth-normal sodium hydroxide solution, using phenolphthalein indicator. As this indicator changes color only when the solution has become distinctly alkaline (at 8.0 pH) the acidities as thus determined are too high; an attempt to substitute brom-thymol blue for phenolphthalein failed because of the lack of a sharply distinguishable end point under the conditions of titration.

The hydrogen ion concentrations were determined colorimetrically.⁹ The pH values show smaller hydrogen ion concentrations than would correspond to the titration values even at complete dissociation if the acid were strong and with a correction for the high results obtained with phenolphthalein. This indicates that much of the total acidity determined by titration is weak acid, probably of the type of the amino acids formed by hydrolysis during the glue-manufacturing processes, and hence is little dissociated. Laboratory studies were made of the effects of the degree of acidity of the different glues on the deflocculation of the mineral matter in preparing coating mixtures. The results of the additions of small amounts of different alkalies, calculated to neutralize the acid present in the different glues, on the degree of deflocculation were noted through study of the particle size of the mineral on coated sheets. At the same time any changes in the clay-suspending power of the glues were observed.

2. DEVELOPMENT PROCEDURE

(a) **CHOICE OF GLUES.**—The eight lots of glue, test data of which are given in Table 1, represent the various types which are commercially available.

Hide glue No. 1, when tested by the count of “fisheyes,” was deemed to be too greasy for coating use and was therefore eliminated from experimental work. Hide glue No. 2 was free from grease, but was slightly greenish in color and made up to rather thin solutions of relatively poor clay-suspending power. Only small-scale work was therefore done with this glue. Glues Nos. 3, 7, and 8 were high-grade bone glues. The solutions of Nos. 7 and 8 possessed dis-

⁹ The Determination of Hydrogen Ions, W. M. Clark (1920), p. 307.

tinctly unpleasant odors, especially noticeable when heated, and as the solutions of glue No. 3 were free from this objectionable quality this glue was used in many of the experimental coating runs. Glues Nos. 4 and 5 were representative high-grade hide glues. While both lots were used in much of the earlier work of the investigation, the superior clay-suspending power of glue No. 5 caused it to be chosen for much of the later work, especially where smaller proportions of glue to pigment were used. Lot No. 6 was a low-grade bone glue, and was used throughout the investigation when a cheap glue was desired.

TABLE 1.—*Test data of glues*

Number	Stock	Form	Moisture	Ash	Jell strength (1)	Viscosity ¹	Number of grease "fish-eyes" per 5 square inches	Acidity		Odor, warm solution
								Titration equivalent to sulphuric acid	pH colorimetrically	
			Per cent	Per cent	Grams	Millipoises		Per cent		
1	Hide	Flake	11.9	2.44			141	0.6	6.75	Slightly putrid.
2	do	do	13.1	2.80	229	59.0	0	.3	6.95	Sour.
3	Bone ²	do	13.1	2.46	228	68.0	14	.8	6.00	Sweet.
4	Hide	Ground	12.1	1.50	295	85.1	30	.5	6.10	Do.
5	do	do	12.8	2.90	255	79.3	1	1.0	6.10	Do.
6	Bone	do	11.6	2.79	120	39.0	25	1.4	5.50	Do.
7	do	do	13.1	2.52	224	61.0	16	.9	6.20	Strong.
8	do	do	12.3	2.42	228	61.0	10	1.1	6.00	Do.

¹ As measured by the approved instruments of the National Association of Glue Manufacturers.

² Probably a blended glue.

(b) DETERMINING THE PROPORTION OF GLUE IN COATING MIXTURES.—Since the laboratory pick test gives results that are merely comparative, it was necessary to apply larger-scale methods to find the amount of glue required to make the coatings resistant to lifting during the printing operation. The following procedure for determining the proportion of glue needed was adopted: Experimental machine-coating runs were made, using progressively increasing amounts of each glue in the coating mixture, and the series of papers were then subjected to the sealing-wax procedure as prescribed for the laboratory pick test. Any coated paper that was not torn completely through the paper on pulling off the sealing wax was considered as containing insufficient adhesive. In this manner there was obtained at least the lower figure for the amount of each glue required in practice. Such figures were checked by printing tests of the papers coated, and where these tests indicated insufficient adhesiveness of the coating the amounts of glue were increased.

(c) DEVELOPMENT OF COATING FORMULAS.—The small coating machine of the Bureau of Standards was not equipped with heating

devices and so was not suitable for determining whether or not commercial coating with glue would be facilitated by the continuous heating of the color mixture with automatic control of the temperature. Experimental work was therefore concentrated on the development of formulas which would produce coated papers of satisfactory printing qualities with the equipment available.

Using the method referred to in the previous section for determining the proportion of glue, working formulas were evolved which could be applied at room temperatures averaging about 80° F. Data sheets for typical experimental coating runs are given in Appendix B.

3. SEMICOMMERCIAL COATINGS

Following the laboratory study of coating materials and the development of coating formulas a considerable number of runs were made on the semicommercial equipment as follows: (a) To check the optimum conditions for the preparation of coating mixtures; (b) to develop the best operating technic for the coating formulas which appeared most satisfactory; and (c) to obtain samples of coated paper representative of various combinations of the variables involved for the purpose of making printing tests.

VI. RESULTS

1. VARIATIONS IN QUALITIES OF GLUES

(a) GREASE CONTENT, EMULSIFYING AND ANTIFOAMING AGENTS.—The use of the "fisheye" count method for eliminating glues which contained excessive amounts of free grease has been noted in an earlier section on "Choice of glues." References were found in early paper-coating literature, especially that of European origin, to the use of milk, soluble oils, and similar materials for the purpose of overcoming the bad effects of the grease associated with commercial adhesives. Since glues so free of grease as to cause no trouble in coating work were readily available, it was not necessary to use materials designed to overcome such difficulties.

When appreciable amounts of soaps of the alkali metals, sodium, potassium, etc., are present in the adhesive there is a tendency to objectionable foaming during the stirring operation while preparing the coating mixture. The soaps of the alkaline earth metals, such as calcium, unless present in unusual proportions do not cause this trouble and in small amounts seem to increase the clay-suspending power of glues.

None of the glues investigated contained sufficient quantities of soaps of the alkaline metals to cause difficulties in the preparation of color mixes. Throughout this work it appeared that the formation of foam and its persistence with resulting bad effects on the coating

were more largely influenced by the mechanical factors and by the concentration and viscosity of the coating mixture than by the small amounts of soaps present in the different glues. Such variables as the type of agitator used, the speed of agitation, and the length of time of stirring seemed of prime importance.

When foaming of the color mixtures was encountered during the experimental coating runs, small amounts of turpentine or gasoline were generally added or, in a few instances, commercial "antifoam" or "antifrothing" preparations. It was found that lowering the viscosity of the coating mixture by warming slightly in cases where glue was the adhesive or by modifying the alkalies used in dissolving casein aided in freeing the mixtures of entrapped air. Reducing the period of agitation and extra care in the screening of the coating mixtures so as to prevent the absorption of air as far as possible tended to reduce the foam largely.

There was no difference observed, respecting tendencies to foam, between coating mixtures containing glue and those made with casein.

(b) COLOR.—Although the various types of glue appear to contain amounts of dark coloring matter which vary largely in the different lots, and which in some cases are noticeable even in the coating mixtures, the color and brilliancy of the finished papers were practically the same as with casein.

Since chrome alum possesses considerable value as a hardening agent for glue and tends to increase the damp proofness of glue-bound coated papers, the influence of additions of this violet-colored salt on the color tone of the coat was studied by laboratory methods. It was found that when small amounts of chrome alum—that is, up to 1 per cent of the weight of glue—were added, more evenly balanced papers of slightly reduced brilliance were obtained than with the glue and clay alone. Although the reflection of red light was somewhat in excess with larger amounts of chrome alum, the balance of reflection was not materially altered and the brilliance was generally further reduced.

Ultramarine is largely used as the tinting agent in commercial paper coating practice, and its effect on glue-bound coated paper was therefore tested. As when chrome alum was used, the balance of color in the paper was improved and the brilliance slightly decreased by such additions.

The results of this study as indicated by the Pfund colorimeter measurements are given in Table 2.

TABLE 2.—Comparison of color measurements of coated paper¹

Test No.	Coating stock	Adhesive	Tinting agent	Other materials	Coefficient of diffused reflection (Pfund colorimeter)			
					Red	Green	Blue	Mean
1.....	A	Starch.....	None.....	None.....	82.8	81.4	79.3	81.2
2.....	A	Gum tragacanth.....	do.....	do.....	84.2	82.5	80.5	82.4
3.....	A	No. 4 glue, 9 per cent.....	do.....	do.....	83.1	81.6	79.3	81.3
4.....	A	do.....	5 per cent ultramarine.....	do.....	78.0	77.2	77.5	77.6
5.....	A	No. 5 glue, 9 per cent.....	None.....	do.....	82.1	80.4	77.5	80.0
6.....	A	do.....	0.5 per cent chrome alum.....	do.....	82.6	80.9	78.4	80.6
7 ²	A	do.....	None.....	do.....	81.2	79.1	75.6	78.6
8 ²	A	do.....	0.5 per cent chrome alum.....	do.....	81.0	78.9	75.8	78.9
9.....	A	do.....	1 per cent ultramarine.....	do.....	81.5	80.1	78.3	79.6
10.....	A	do.....	2 per cent ultramarine.....	do.....	79.4	78.2	77.8	78.5
11.....	A	No. 6 glue, 10 per cent.....	None.....	do.....	83.6	82.0	79.3	81.6
12.....	A	do.....	1 per cent ultramarine.....	do.....	81.9	80.4	79.3	80.5
13.....	B	No. 1 glue, 15 per cent.....	None.....	3 per cent soap.....	78.7	76.4	72.8	76.0
14.....	B	do.....	0.9 per cent chrome alum.....	do.....	78.1	75.1	74.7	76.0
15.....	B	do.....	3 per cent chrome alum.....	do.....	71.0	67.4	67.7	68.7
16.....	B	No. 2 glue, 18 per cent.....	None.....	None.....	79.8	78.0	74.4	77.4
17.....	B	do.....	7.5 per cent chrome alum.....	do.....	67.6	64.4	64.2	65.4
18.....	B	No. 3 glue, 18 per cent.....	None.....	do.....	78.9	76.7	73.4	76.3
19.....	B	do.....	2.5 per cent chrome alum.....	do.....	75.0	71.5	72.0	72.8
20.....	B	No. 4 glue, 15 per cent.....	None.....	do.....	80.1	78.6	75.0	77.9
21.....	B	do.....	2.5 per cent chrome alum.....	do.....	72.3	69.6	69.2	70.4
22.....	B	No. 5 glue, 15 per cent.....	None.....	do.....	78.7	76.7	72.2	75.9
23.....	B	do.....	2.5 per cent chrome alum.....	do.....	72.1	68.9	68.0	69.7
24.....	B	do.....	do.....	1.2 per cent soap.....	72.0	67.6	68.0	69.2
25.....	B	No. 6 glue, 18 per cent.....	None.....	None.....	79.6	77.7	73.8	77.0
26.....	B	do.....	2.5 per cent chrome alum.....	do.....	73.9	71.1	70.8	71.9
27.....	B	No. 6 glue, 14 per cent.....	None.....	2 cc glycerin.....	80.2	78.9	76.0	78.4
28.....	B	do.....	0.5 per cent chrome alum.....	do.....	78.7	76.9	76.0	77.2
29.....	B	Casein, 12 per cent.....	None.....	None.....	80.8	79.3	76.4	78.8

¹ Measurements made by R. E. Lofton, Bureau of Standards.² Nos. 7 and 8 are different samples from the same materials as Nos. 5 and 6 and were reported by a different observer.

In interpreting the color measurements of the Pfund colorimeter it should be noted that approach to balanced reflection is indicated as the coefficients of diffused reflection for the individual colors approach uniformity; that is, with equal values for the three constituents no color tone would predominate. Any variation in the total reflection of light is shown by a change in the mean of these values. Therefore, approach to complete whiteness is determined by uniform and high values for the coefficients of diffused reflection. Thus, referring to Table 2, in test No. 12 the value for each of the three primary colors is high, and there is little difference between them. This denotes a brilliant color with little predominating tint, therefore a relatively good white. On the other hand, while in test No. 28 there is also little excess tint, the values are low, and this color as a whole is a somewhat poorer white than test No. 12. Test No. 19 is an example of a paper with a predominating tint, the red being noticeably in excess of the other colors.

In general, it is indicated that light-colored bone glues decrease the whiteness of a coating to the same extent that casein does;

ordinary bone glues make the coating more yellow than casein does, but the difference is not readily discernible to the eye; ordinary hide glues make the coating less white than casein, although this may be offset to some degree by the smaller amount of hide glue required for a given degree of adhesiveness of the coating.

While the results of the above tests are indicative of the differences in color under parallel conditions which existed between the adhesives employed, the degree of such differences was less than that which would be experienced in commercial practice through variation between different coating stocks, pigments, and similar influences and, moreover, was within the range of correction of the tinting agents employed in such practice.

Since the effects of tinting agents on glue-bound coated papers were found to be similar to those in which casein was used, in the machine coating runs such materials were omitted.

(c) WATER RESISTANCE.—Considerable attention was paid to improving the water resistance of the glue-bound coated papers through the use of glue-hardening agents which tan glues and lower the rate and amount of their swelling with water. The most satisfactory materials for these purposes were chrome alum and formaldehyde. While applications of processes involving the bichromate-light reaction were studied, it is felt that such methods are impractical for paper coating.

It was found that through the addition of small amounts of chrome alum, varying from $1\frac{1}{2}$ per cent of the weight of high-grade hide glues to $3\frac{1}{2}$ per cent of the weight of low-grade bone glues, the water resistance of the coating was somewhat improved. Such additions removed practically all stickiness of the coat as tested with a moist finger and also raised the setting and melting points of the glue. Although chrome alum tends to cause clay to settle out of its suspensions, this did not interfere noticeably with its use in the coating mixtures. In commercial practice where a thorough study of all the factors involved has been made amounts of chrome alum considerably larger than those just indicated are used, especially with medium grade glues.

The water resistance of glue-bound coated papers is also markedly increased by treating the coated paper with formaldehyde or by additions of this material to the coating mixtures.

The amounts of hardening agents that may be added to glue containing coating mixtures without bad effects on the viscosity and length of working life of the mixes vary with the individual glues. In general, larger amounts may be used with bone glues than with hide glues and with low or medium grade glues than with those of higher grades. With the same amount of hardening agent added the water resistance is increased more with hide glues than with

bone glues and more with the higher grades than with lower ones. The viscosity and length of working life of glue-containing coating mixtures to which formaldehyde has been added are adversely affected by exposure to abnormal temperatures.

The use of combinations of two or more hardening agents offers no advantage over the use of individual materials.

(*d*) **SOFTENING AGENTS.**—Laboratory experiments indicated that the use of specific softening agents for glue, such as glycerin, sugar, or ammonium thiocyanate, possesses no distinct advantages over the use of materials ordinarily employed for rendering coated paper less brittle. With commercial softening agents, wax emulsions, etc., the results with the glue-bound coated papers were similar to those in which casein was employed. Consequently in the later semi-commercial runs the use of such softeners and similar materials was largely avoided, as it was felt that though their use is general and often leads to improved products, the choice of substance and its application is a matter of adjustment to strictly local conditions, such as cost and the effect on the degree of damp proofness or on calendering and printing practice.

(*e*) **ACIDITY.**—Preliminary tests indicated that the acidity of the different glues investigated was in no case sufficient to inhibit deflocculation of the mineral matter in preparing coating mixtures. The amount of acid present in these glues was too small to produce any noticeable reaction, even with as alkaline a mineral as satin white. The addition of small amounts of alkali to the glue-containing color mixes had little if any effect on the particle size observed in coated sheets. It may be noted, however, that the clay-suspending power of the most acid glue studied, lot No. 6 ($\text{pH}=5.5$), seemed to be somewhat improved when enough alkali to neutralize to $\text{pH}=7.0$ was added to the coating mixture and the whole heated to approximately 135°F . There was no noticeable improvement in the clay-suspending power of the more neutral glues when subjected to this treatment.

2. OPTIMUM CONDITIONS FOR THE PREPARATION OF COATING MIXTURES

In the preparation of the color mixes for runs on the small-scale coating machine about 3 pounds of dry pigment were taken for each batch; for coating with clay alone, 3 pounds; for clay-satin white mixtures, 2 pounds of clay and 2 pounds of satin white pulp (35 per cent solids); for clay-blanc fixe mixtures, 2 pounds of clay and 2 pounds of blanc fixe pulp (75 per cent solids). The pigments were allowed to stand overnight with part of the water used in the color mix in order to deflocculate them as completely as possible. In the case of color mixtures containing glue No. 6 (the low-grade

glue used with clay only) sufficient dilute caustic soda solution was added to the water in which the clay stood overnight to neutralize the acidity of the glue to $\text{pH} = 7$.

In the comparative runs using casein as the adhesive the formula of the mill from which the casein was obtained was adopted with slight modification in regard to the dissolving of the casein.

The glues were soaked overnight with four times their weight of water and heated to not more than 135°F . for solution. Making all glue solutions of standard strength facilitated changing the proportions of glue in the color mixes in the course of the individual experimental coating runs.

The casein was soaked for one hour in approximately four times its weight of water, and after the addition of the casein solvents, was heated with agitation to 150°F . for solution.

In the earlier stages of the investigation, after adding the glue solution and any desired water to the pigment-water mixture, the whole was stirred by a motor-driven agitator of the wooden-gate type for a comparatively long period, as up to four hours. After studying the causes of foaming in the color mixtures the time of agitation was decreased to one-half hour, with the result that the foaming was reduced materially without interfering appreciably with the deflocculation of the pigment.

After agitating the coating mixtures were screened through metal sieves. In several runs the mix was divided into two portions and run, respectively, through a 100-mesh and a 200-mesh screen. In every such case the paper coated with the 200-mesh mixture had less blotchiness than the paper coated with the 100-mesh mix; in other words, the quality of the finished paper was much improved by removing even very small amounts of flocculated pigment or other particles of unusual size. In large-scale work a preferable method is to screen first through a 100-mesh screen, then through a 200-mesh.

3. COATING TECHNIC

The small-scale coating machine available did not permit the refinement of operating control to obtain the thin uniform coatings with relatively high concentrations of coating material that may be obtained with commercial equipment. In the work of the investigations the desired lightweight coatings were obtained by diluting the coating mixtures with water.

This dilution of the coating mixtures was found to increase the range of glue concentrations within which the color mixtures remained fluid at room temperatures of about 80°F . Experiments indicated that with the use of high-grade hide glues at concentrations of 160 parts of water for 100 parts of clay, a ratio of water to clay that is

common in commercial practice, it was necessary to employ higher temperatures to obtain color mixes sufficiently fluid to insure uniform weights of coating. It appeared that with each combination of a clay with a different type of glue there was a distinct temperature range within which optimum working conditions and results were obtained. This temperature was higher and the range was narrower with decreasing amounts of water in the coating mixture and with improved quality in the grade of the glue. Laboratory studies indicated that the greatest change in the viscosity of coating mixtures, even at commercial concentrations, takes place between 75 and 85° F. when medium-grade glues are used.

With the lower concentrations referred to, heating of the coating mixtures was not resorted to save in cases when the low-grade bone glue No. 6 was used. Experiments indicated that the clay-suspending power of this glue was improved by heating it to 135° F. and then permitting it to cool to room temperatures.

In studying the effects of raised temperatures on the behavior of glue-bound coating mixtures there was encountered, to possibly a slightly less degree than with casein-bound mixtures, the difficulty of the thickening of mixtures which contained satin white. No such difficulty was met with in using reasonably neutral glues with satin white at ordinary temperatures. The limit to which it was possible to carry the dilution of the color mixtures was set by the clay-suspending powers of the individual glues. The clay-suspending qualities of the glues were generally superior at the low concentrations employed to those of the casein, although in the case of the latter adhesive this quality was found to be influenced by the solvents and the temperature maintained in dissolving.

Aside from the lower concentrations of the coating mixtures, regardless of the type of adhesive and studies of the effects of higher temperatures already noted, the actual coating procedure was the same as in commercial practice.

4. COMMERCIAL TEST

Five lots of about one ream each 500 sheets, 26 by 38 inches were prepared at a commercial coating plant. The paper was coated on one side, using clay as the mineral. Three different glues were used; a high-grade hide glue, a high-grade bone glue (probably blended), and a low-grade bone glue. No difficulties were experienced by the operators in coating with the glue-clay mixtures, even in the adjustment of the machines, to obtain the proper weight of coating. The preparation of the glue for coating was noted as being simpler than the preparation of casein inasmuch as the glue required less stirring and no chemicals for its solution.

There was a slight disadvantage in coating with the glue-clay mixtures, especially those containing the higher-grade glues, as at the concentration of the color mix employed it was necessary to warm the color mixes somewhat.

5. DEMONSTRATION OF RESULTS

A demonstration of the use of glue in coated paper was given at the Bureau of Standards and at the Government Printing Office to representatives of the glue and the coated-paper industries.

The actual coating work of the demonstration was divided into four parts. Formulas developed during the investigation were used. For adhesives three glues were selected that varied widely in grade, but were of ordinary commercial types. For comparison, one trial was made using casein as the adhesive. A high-grade casein was obtained from a coating plant and the mill recipe was used in the coating formula.

The stock coated throughout the demonstration was a sulphite paper made on the experimental Fourdrinier machine at the Bureau of Standards. It contained about 10 per cent of clay filler and was only slightly rosin sized. Data sheets for the four runs are given in Appendix C.

Test data of the glues used may be found in Table 1. The glues used in the demonstration were Nos. 3, 5, and 6, respectively.

At frequent round-table discussions during the demonstration many factors relating to the uses of glue in the coating industry were discussed. The employment of glue in the manufacture of special papers, such as flint glazed, where a higher finish was said to be obtained with glue-bound than with casein-bound papers, and in metal-coated papers; the wider range of colors available for use with neutral glue as compared with alkaline casein; and the avoidance of troublesome side reactions by using glue with satin white were mentioned as advantageous uses of glue in the industry. It was noted that a considerable number of manufacturers were using glue in conjunction with casein in their processes. The value of high-grade hide glues, which may be used in relatively small proportions, to obtain a higher degree of elasticity for papers subjected to embossing and similar processes was also mentioned.

The printing tests of the papers coated in the demonstration are referred to in the following section.

6. PRINTING TESTS

During the course of the investigation printing tests of the papers coated were occasionally made at the Government Printing Office. Acknowledgment is hereby made of the valuable assistance rendered

in this respect by the Government Printing Office, such printing tests being a very essential part of the investigation. These printing tests proved that no adjustment of the inks used with casein-bound papers was required by the glue-bound papers. Inasmuch as the introduction of casein-bound papers was marked by difficulties of this sort, the results with glue were rather unexpected. The explanation is offered that thinner, more fluid inks can be used with glue-bound paper than with casein-bound paper, but that the heavier, more viscous inks that must be used with the casein-bound paper work with the glue-bound as well as they do with the casein-bound paper.

The paper manufactured in the large-scale runs of a commercial mill was subjected to tests by two commercial printing houses. These tests indicated that the characteristics of the reproduction were influenced somewhat by the kind of glue used as binder, the finest results being obtained with the highest-grade glues. It is believed, however, that the differences in other factors of the production processes have much more effect on the final results than do the different grades of glue.

Variations in the kind of stock coated, the materials entering into and the methods of preparing coating mixtures, equipment, and working conditions of the coating, drying, and finishing operations were found to influence profoundly the appearance of the paper produced and the amount and proportion of adhesive required to obtain a coated paper of satisfactory printing qualities. Similarly, variations in inks and in printing practice influenced the tendency of coated papers to "pick" or "lift" during the printing operation.

The effect of variations such as are referred to in the preceding paragraph was strikingly shown by the behavior of glue No. 5 during the course of this investigation. This was the glue referred to earlier in this report which when used in the coating mixture to the extent of only 8 per cent of the clay, and applied with the small experimental machine at the Bureau of Standards produced a coated paper which stood the sealing wax picking test as well as commercial papers. When applied under commercial conditions at coating plant A, with the coating stock and the clay ordinarily used at this mill, the coated paper produced from a color mix containing 9 per cent of the glue gave a doubtful test with sealing wax, and could be printed only by reducing the speed of the press and by softening the ink. A second run at this mill under the same working conditions and with the same stock and clay, but using 12 per cent of the glue, produced paper which met the sealing-wax test and which was printed at two different plants without difficulty. In the proofs from one firm excessive absorption of ink took place, the printing showing through the back of the paper. This defect was not present in the work of the second company. The manufacturer

of this glue reported that at another coating plant, B, using their stock and clay, it was necessary to use 15 per cent of glue in order to obtain coated paper which passed commercial printing tests. This paper was considered as being close to the safety margin by one printing company, although it was passed without question by another.

On the last day of the demonstration referred to samples of the paper just coated were printed in the half-tone press room of the Government Printing Office. A commercial order consisting of illustrations from half tones of varying screen fineness was interrupted to permit the changing of the feed for the different size of the sample sheets. The samples were printed, and the commercial run continued with the casein-bound paper being used without any other adjustment of printing procedure or of ink. Inspection of the samples showed no evidence of picking, lifting, or dusting of the coating. Variations in the degree of clearness of high lights, depth and smoothness of solid blacks, and fineness of gradations in the middle tones were consistent with the variations in type of coating employed and weight of coat. There was no difference in the printing quality of the glue-bound coatings and those made with casein.

VII. DISCUSSION OF RESULTS

1. COMPARISON BETWEEN CASEIN AND GLUE FOR COATING PURPOSES

The two reasons generally cited for the preference of casein above glue at the present time are the factors of price and waterproofness.

(a) PRICE.—The price question is rather an open one, for when the cost of casein solvents is taken into consideration, the influence of the type of stock coated and the weight of coat upon the amount of adhesive required, the choice of glue, the method of preparing casein or the relative spreading or covering powers of the particular casein and glue compared, may influence the cost of the finished paper more than variations in the market price of the adhesives. It may be noted that the reason given for the recent change in French coating procedure from casein to glue was the lower cost of glue.¹⁰

In this connection it should be noted that the frequently observed statement that five parts of glue are required to replace four parts of casein in coating formulas is extremely misleading, as it ignores the fact that glue, unlike casein, is sold in a number of well-recognized and sharply differentiated grades. Experiments have shown that the required proportion of glue to mineral matter as used in coating mixtures varies almost inversely as the grade of the glue. For example, as much as 20 per cent (based on the weight of clay) of a low-grade bone glue (jelly strength, 120 g; viscosity, 39 millipoises)

¹⁰ Notes on current paper-coating practice, by Elie Caylers, in *Le Papier*, July, 1925, p. 777.

was required to give a good pick test, and as little as 8 per cent of a high-grade hide glue (jelly strength, 257 g; viscosity, 79.3 millipoises) was sufficient for a clay coating that stood the sealing wax picking test as well as do commercial casein-coated papers. Similar experiments with a number of glues give the figures, 150 g jelly strength and 50 millipoises viscosity, representing a medium grade for a glue that is about equivalent to casein in binding power. In other words, a glue of this grade could be substituted pound for pound in place of casein in a coating formula. It should be noted that the adhesive power of casein may be influenced markedly by the method of "cutting" it; that is, by the kind and amounts of alkalies employed to dissolve it as well as by the time and temperature factors of the solution process.

(b) **WATER RESISTANCE.**—The question of damp proofness is to some extent also open. There is little doubt but that an ordinary glue-bound coated paper is less water resistant than an ordinary casein-bound coated paper, even though casein-bound paper as ordinarily made is not really waterproof. Yet in investigating the claim that glue-bound paper tends to stick together experiments showed that it is difficult to find conditions under which properly made glue-bound paper would become sticky enough to adhere when two sheets are pressed together. In one test, sheets of glue-bound coated paper were exposed to the steam rising from the dryer rolls of the experimental paper machine, then rapidly placed with coated surfaces together between heated aluminum plates and pressed for one-half hour. At the end of this time when the plates were removed the sheets of paper were easily separated without injury to the coated surfaces.

The insistence on a high degree of waterproofness in the coating of the paper is difficult to understand, inasmuch as, except in high-grade lithography and possibly in the offset processes, moisture has but little effect in printing. Coated paper finds its greatest use in ordinary printing and half-tone illustrating work, such as enters into magazine, book, catalogue, or advertising lines, and these processes and products do not require extraordinary damp proofness. Similarly it would appear that where it is desirable to increase the damp proofness of glue-bound coated papers, this may be accomplished by the use of glue-hardening agents. By study of the local conditions prevailing, it should be possible to apply such materials to individual problems. Among coated-paper manufacturers interviewed, the general idea is expressed that since the waterproofness of casein may be obtained without extra cost, it is cheap insurance against possible printing trouble. It seems reasonable to expect that with a price differential favoring glue, there would follow a trend of coating practice toward more strict segregation of the

products for special uses, such as obtains in European mills where the use of glue is quite universal. Such a condition would call for a better coordination of effort and more successful cooperation between the paper coater, the ink manufacturer, and the printer than is now the case in this country. It may be noted that through the addition of chrome alum the setting and melting points of the glue are raised, which may be of significance in facilitating the drying process.

(c) OTHER FACTORS.—The reputed variations in acidity, grease content, odor, color, etc., are matters of specifications and are so treated in later sections of this report.

Factors favorable to the use of glue in paper coating are the obtaining of a higher finish with glue-bound than with casein-bound papers, as in the manufacture of glazed papers; the wider range of colors available for use with neutral glues as compared with alkaline casein; the avoiding of troublesome side reactions by using glue with satin white; and the influence of a higher degree of elasticity as obtained through the use of high-grade hide glues as adhesives in papers subjected to embossing and similar processes.

VIII. SPECIFICATIONS FOR COATERS' GLUE

The results of this investigation have indicated that glues of widely differing types may be used for coating purposes. It has therefore appeared that from the viewpoint of the individual coater it is essential, if uniformly satisfactory results are to be obtained, that the glue used be of known quality and properties. The grade as determined by the official jelly-strength and viscosity tests, is of primary importance. This is followed by the factor of clay-suspending power and considerations of acidity, grease content, odor, and color.

The grade of glue to be used must be determined from considerations of price, product requirement, and local coating conditions. When the desired grade has been fixed upon, there should be no difficulty in duplicating the material, because the glue industry is already organized on a grade basis.

Again, in the matter of clay-suspending power, the local condition of the choice of pigment has interfered with the development of a standard method of testing. It has appeared during this investigation that the clay-suspending power of different glues is influenced by the methods of manufacture and that when the grade of glue is agreed upon a choice between two glues is readily made by making up for comparison small amounts of a standard coating mixture, using the mill formula with each of the glues under consideration, and examining these mixtures for the rates of settling at suitable time intervals.

As to the incidental properties of acidity, grease content, foaming tendency, odor, and color, these were found to have no standards for coating purposes.

While glue is most water resistant when very slightly acid, for coating with alkaline pigments, such as satin white, it has been found that neutral glues do not tend to react with the pigments and are therefore more easily handled. Inasmuch as it is the free hydrogen-ion concentration rather than the total amount of acid that determines the behavior of glue solutions, it is felt that the pH determination is of value in specifying glues for coating work, as nearly neutral glues only slightly acid appear to introduce the fewest complications in the preparation of color mixes. Since glue makers have generally adopted some method of determining hydrogen-ion concentrations in the control of their manufacturing processes, this measurement may be specified for limiting acidity.

In consideration of the factors of grease content and foaming tendency, it should be noted that these are to some extent interrelated characteristics. Thus, with a given glue, reduction of the grease content is generally accompanied by an increased tendency to foam. Glues in which these factors are at their optimum balance are offered in most of the commercial grades.

The question of odor is largely determined by the stock and manufacturing conditions. In any grade, glues free of objectionable odor are readily obtainable. Although the color of various glues varies considerably, when coatings are made with different glues the finished papers seldom show a difference visible to the eye. Where desired, especially light-colored glues may generally be procured.

IX. SUMMARY AND CONCLUSIONS

Paper has been coated on the coating equipment of the Bureau of Standards experimental paper mill, using glues of different grades as adhesives and using casein for comparison, with the different types of minerals, clay, satin white, and blanc fixe. The coated paper has been calendered and subjected to printing tests at the Government Printing Office. A demonstration of the use of glue in coated paper has been given to representatives of glue manufacturers and of the coated-paper industry, at which there were employed formulas which had been evolved to produce coated papers of satisfactory printing qualities.

The results of laboratory studies of the individual factors involved, of upward of 100 experimental coatings on semicommercial equipment, of 4 demonstration trials on semicommercial equipment, and of the coating of 5 lots of paper on commercial equipment point to the following general conclusions:

1. The proportion of glue required in coating mixtures varies almost inversely with the grade of the glue chosen, and the amount of the better-grade glues required may be less than that of casein.

2. The use of glue introduces no new difficulties in the preparation and application of coating mixtures containing either neutral minerals, such as clay and blanc fixe, or alkaline substances, such as satin white.

3. With proper selection of the glue used and adaptations to local conditions and product requirements the use of glue requires little change in equipment and involves little change in operating technic from procedure with casein.

4. The various types of glue available permit considerable latitude in choice within which local conditions may be met.

5. Variations in the other materials employed and in coating procedures influence largely the proportion of adhesive required to produce coated papers of satisfactory printing qualities.

6. The use of ordinary glue-bound coated paper offers no new difficulties to the printer and engraver, at least as regards printing processes other than those lithographic and possibly offset processes where a high degree of water resistance is required.

7. The need for an extraordinary degree of waterproofness and of water resistance in coated paper for other than some lithographic and offset work is questionable.

8. Uniformity in glue for coating processes may be attained by drawing specifications to meet local and product requirements.

APPENDIX A.—BIBLIOGRAPHY

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APPENDIX B.—DATA SHEETS OF EXPERIMENTAL COATING RUNS

Run No. 101A

SAMPLE.—First third of festoon.

COATING MIXTURE.—

0.9 kilos clay.	} Let stand overnight.
0.9 kilos blanc fixe pulp (73.65 per cent solids).	
1 liter water.	
0.2 kilo glue No. 5 (hide).	} Soaked overnight, heated to 135° F. for solution.
0.8 liter water.	
Stirred for one-half hour at room temperature.	
Screened through 100 mesh.	
Specific gravity, 1.43; 44° Bé.; at 85° F.	

FORMULA.—

- 100 parts mineral—57.6 clay, 42.4 blanc fixe (dry basis).
 12.6 parts glue.
 129 parts water.

WEIGHT.—

	Pounds
500 sheets, 25 by 38 inches { Coated paper would weigh.....	95.5
{ Body stock would weigh.....	50.0
{ Coating would weigh.....	45.5

Ratio, coating: body stock, 0.91.

REMARKS.—No settling of mineral. Mix was heavy, but not viscous. Wet coat had some bubbles and large particles. Coat very heavy but did not run. Dry coat even, with no pinholes, but too heavy.

Run No. 101B

SAMPLE.—Second third of festoon.

COATING MIXTURE.—To the remainder of the color mix from run No. 101A was added 0.1 liter water; specific gravity, 1.37; 39° Bé.; at 85° F.

FORMULA.—

100 parts mineral—57.6 clay, 42.4 blanc fixe (dry basis).
12.6 parts glue.
139 parts water.

WEIGHT.—

	Pounds
500 sheets, 25 by 38 inches { Coated paper would weigh.....	77
	50
	27

Ratio, coating: body stock, 0.54.

REMARKS.—Some pebbles on wet coat. Dry coat even, with no pinholes. Pick test satisfactory.

Run No. 101C

SAMPLE.—Last third of festoon.

COATING MIXTURE.—To the remainder of the color mix from run No. 101B was added 0.08 liter water; specific gravity, 1.32; 36° Bé.; at 85° F.

FORMULA.—

100 parts mineral—57.6 clay, 42.4 blanc fixe (dry basis).
12.6 parts glue.
153 parts water.

WEIGHT.—

	Pounds
500 sheets, 25 by 38 inches { Coated paper would weigh.....	75.9
	50.0
	25.9

Ratio, coating: body stock, 0.52.

REMARKS.—Wet coat smooth. Coating still heavy but of good appearance. Pick test satisfactory.

APPENDIX C.—DATA SHEETS OF DEMONSTRATION COATING RUNS

Run No. 113 (demonstration run A)

COATING MIXTURE.—

0.9 kilo clay.
0.9 kilo satin white pulp (35 per cent solids).
1.50 liters water.
0.48 liter water added before mixing.
0.15 kilo glue No. 3.¹¹
0.60 liter water. } Soaked overnight. Heated to 135° F. for solution.
Stirred for one-half hour at room temperature.
Screened through 200 mesh.
Specific gravity, 1.22; 26° Bé.; at 76° F

FORMULA.—

100 parts mineral—74.1 clay, 25.9 satin white (dry basis).
12.2 parts glue.¹²
258 parts water.

¹¹ See Table 1, p. 647.

¹² Printing tests indicate that this proportion of this glue is the smallest that could be employed to produce a satisfactory product under the coating conditions employed.

WEIGHT.—

	Pounds
500 sheets, 25 by 38 inches—	
Coated paper would weigh.....	69.9
Body stock would weigh.....	50.0
Coating would weigh.....	19.9

Ratio, coating: body stock, 0.38.

REMARKS.—Color tests, calendered samples:

Pfund colorimeter.—Red, 0.818; green, 0.769; blue, 0.733.

Ingersoll glarimeter.—81.5 per cent gloss.

Run No. 114 (demonstration run B)

COATING MIXTURE.—

0.9 kilo clay.
0.9 kilo satin white pulp (35 per cent solids). } Let stand overnight.
1.5 liters water.
0.217 kilo casein. } Soaked for one hour.
0.830 liter water. }
0.018 kilo borax. } Added to casein mixture and heated to 150° F. for
0.010 kilo soda ash. } solution.
0.2 liter water. }
5 mil liters concentrated ammonia solution. } Added to casein solution and
50 mil liters water. } let cool to room temperature.
Stirred for one-half hour at room temperature.
Screened through 200 mesh.
Specific gravity 1.24; 27° Bé.; at 82° F.

FORMULA.—

100 parts mineral—74.1 clay, 25.9 satin white (dry basis).
17.7 parts casein.¹³
2.7 parts casein solvents.
25.8 parts water.

WEIGHT.—

	Pounds
500 sheets, 25 by 38 inches—	
Coated paper would weigh	70
Body stock would weigh.....	50
Coating would weigh.....	20

Ratio, coating: body stock, 0.40.

REMARKS.—Color tests, calendered samples:

Pfund colorimeter.—Red, 0.819; green, 0.773; blue, 0.727.

Ingersoll glarimeter.—81.5 per cent gloss.

Run No. 115 (demonstration run C)

COATING MIXTURE.—

1.36 kilos clay.
20 mil liters 1:10 NaOH solution. } Let stand overnight.
1.47 liters water.
0.2 liter water added before mixing.
0.26 kilo glue No. 6.¹⁴ } Soaked overnight; heated to 135° F. for solution.
1.04 liters water. }
Stirred for one-half hour at room temperature.
Heated to 135° F.
Screened through 100 mesh.
Specific gravity 1.27; 31° Bé.; at 106° F.
Coated at approximately 100° F.

¹³ Printing tests indicate that this proportion of this casein offers an ample margin of safety to produce a satisfactory product under the coating conditions employed.

¹⁴ See Table 1, p. 647.

FORMULA.—100 parts clay.

20 parts glue.¹⁵

200 parts water, plus sufficient dilute caustic-soda solution to neutralize the acidity of the glue.

WEIGHT.—

	Pounds
500 sheets, 25 by 38 inches—	
{ Coated paper would weigh.....	64.9
{ Body stock would weigh.....	50.0
{ Coating would weigh.....	14.9

Ratio, coating: body stock, 0.30.

REMARKS.—Color tests, calendered samples:

Pfund colorimeter.—Red, 0.739; green, 0.733; blue, 0.676.

Ingersoll glarimeter.—77.5 per cent gloss.

Run No. 116. (Demonstration Run D)

COATING MIXTURE.—

0.9 kilo clay.

.9 kilo blanc fixe pulp (74 per cent solids). } Let stand overnight.

1.5 liters water.

.2 kilo glue number 5,¹⁶ } Soaked overnight; heated to 135° F. for solu-
.8 liter water. } tion.

Stirred for one-half hour at room temperature.

Screened through 100 mesh.

Specific gravity, 1.39; 41° Bé.; at 83° F.

FORMULA.—

100 parts mineral—57.6 clay, 42.4 blanc fixe (dry basis).

12.6 parts glue.¹⁷

161 parts water.

WEIGHT.—

	Pounds
500 sheets, 25 by 38 inches—	
{ Coated paper would weigh.....	103.3
{ Body stock would weigh.....	50.0
{ Coating would weigh.....	53.3

Ratio, coating: body stock, 1.06.

REMARKS.—Color tests, calendered samples:

Pfund colorimeter.—Red, 0.802; green, 0.766; blue, 0.697.

Ingersoll glarimeter.—73.0 per cent gloss.

WASHINGTON, March 23, 1926.

¹⁵ Printing tests indicate that this proportion of this glue offers an ample margin of safety to produce a satisfactory product under the coating conditions employed.

¹⁶ See Table 1, p. 647.

¹⁷ Printing tests indicate that this proportion of this glue offers an ample margin of safety to produce a satisfactory product under the coating conditions employed.