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COMPARISON OF UREA FORMALDEHYDE, MELAMINE FORMALDEHYDE, GLYOXAL AND LATEX IN IMPROVING THE WATER RESISTANCE OF THE STARCH COATINGS

BY
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A Thesis submitted in
partial fulfillment of
the course requirements for
the Bachelor of Science Degree

Western Michigan University
Kalamazoo, Michigan
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ABSTRACT

Several coatings colors were prepared and applied. The coated sheets were tested with great emphasis on keeping the conditions constant throughout the course of the experimental work. The study utilized several types of insolubilizers: urea formaldehyde, melamine formaldehyde, glyoxal and latex. Two types of starches were also used: regular and cationic.

Results showed the importance of drying on wet rub development of both urea and melamine formaldehyde as compared to latex and glyoxal. Results also proved the superiority of using insolubilizer additions with cationic starch rather than regular starch.

Glyoxal and latex were superior choices to urea and melamine formaldehyde, even with lower amounts.

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HISTORICAL BACKGROUND

The improvement of water resistance of paper coatings is very important for many commercial applications. Coated paper for highest quality offset printing, particularly those for sheet-fed color work, must be fairly water resis--tant. Coated paperboard for certain packaging applications, laundry tags, or poster board requires a high degree of water resistance to withstand wet-handling and exposure to outdoor conditions (1,2). At the present, water resistance is achieved by using one or a combination of latex binders, protein or casein, and insolubilizing resins. If starch could be used in such commercial applications, it would be preferred to latex or protein or casein because of its much lower cost. In addition to low cost, starch has several other advantages over protein or casein. In formulation, it has excellent rheological properties on all types of coating equipment; it is of relatively constant quality and in plentiful supply. A starch coating formulation can be used at high solid contents on high speed trailing blade equipment with excellent results. The high speed allows increased production, and the higher solid content allows reduced drying capacity. Starch also has good color proper--ties like no odor, good resistance to putrefication, few formulation problems and shows good compatibility with

almost all other materials used in paper coatings. Because of its unique properties, starch readily lends itself to automated coating make-up (3).

Past attempts to replace casein or protein with starch have been unsucessful as a result of the poor water resistance of starch due to its carbohydrate nature (See Fig. 1) (4, 11).

Figure 1

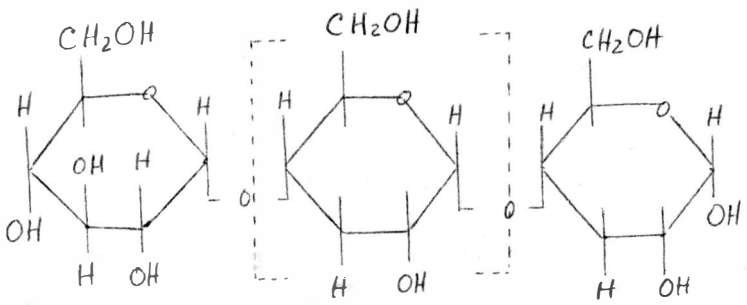


Fig. 1a Amylose fraction of starch

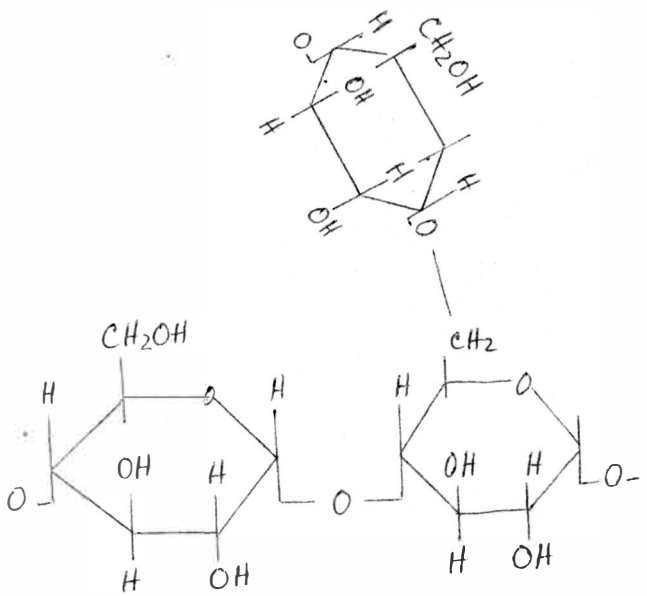


Fig. 1b Amylopectin fraction of starch

According to Ritson (5), there are three general methods of reducing sensitivity of starch film to water as follows:

A- Formations through chemical reaction, of products that are water insoluble or have low water sensitivity:

1- Aldehyde or aldehyde derivatives: i.e. hexa--methylene tetramine, glyoxal, etc... which combine with amine, amide, or hydroxyl groups or the adhesive to pro--duce crosslinking with reduced water sensitivity.

2- Amino-formaldehyde resins: such as urea formaldehyde and melamine formaldehyde which react with amine, amide or hydroxyl groups producing cross linkage and blocking of these groups to further reduce the water sensitivity.

3- Metal salts of chromium and antimony which can form complexes with starch, for example, reducing its water sensitivity. This is probably due to a blocking action by association of groups which contribute water dispersibility to starch.

B- Incorporation of binder of low water sensitivity to protect or simply to blend with the water soluble adhesive particles:

1- Resin dispersions, particularly acrylics, vinyls and styrene butadiene latex (SBR) .

2- Water-soluble polymers, such as polyvinyl alcohol (PVAl) which develop some water insolubility on drying can produce improved water resistance when blended

with the more water sensitive starch.

C- Addition of water-repellent materials: The purpose of these materials is to prevent the wetting of film and disintergration of the starch film. Emulsions of wax and insoluble fatty acids, soaps, and more recently ammonium resinates are typical examples.

Among the above list, four of the most successful methods have employed urea formaldehyde, melamine formaldehyde, glyoxal and acrylic latex. This paper is intended to compare those insolubilizers in terms of their water resistance improvement in the starch coatings.

UREA FORMALDEHYDE

INTRODUCTION

Urea formaldehyde (U.F.) is one of the oldest and best known wet-strength resins used to increase the water resistance of starch coatings. As early as in the early of 20th century, several French and German inves--tigators among whom were Holzer, Einhorn and Goldsmith, have reported on the reaction products of urea and formaldehyde (23). As the urea resins industry grew in volume, most disclosures were in the form of patents (6, 7). The use of urea formaldehyde in coating applications was discussed in some literature (9,10).

CHEMISTRY OF UREA RESINS

Urea resins are essentially thermosetting resins produced by the catalytic condensation of an aqueous solution of formaldehyde with urea. For the preparation of coating resins, reactions may originate in aqueous medium, but are always completed in alcoholic solution. Figure 2 (12) presents a schematic representation of reaction leading to the formation of monomer, and by condensation, dimer and trimer. This is a simplified view of how typical structures develop in solution as reaction is influenced by the medium (water, alcohol and water-alcohol) and catalyst (acid or base). As

Fig.2

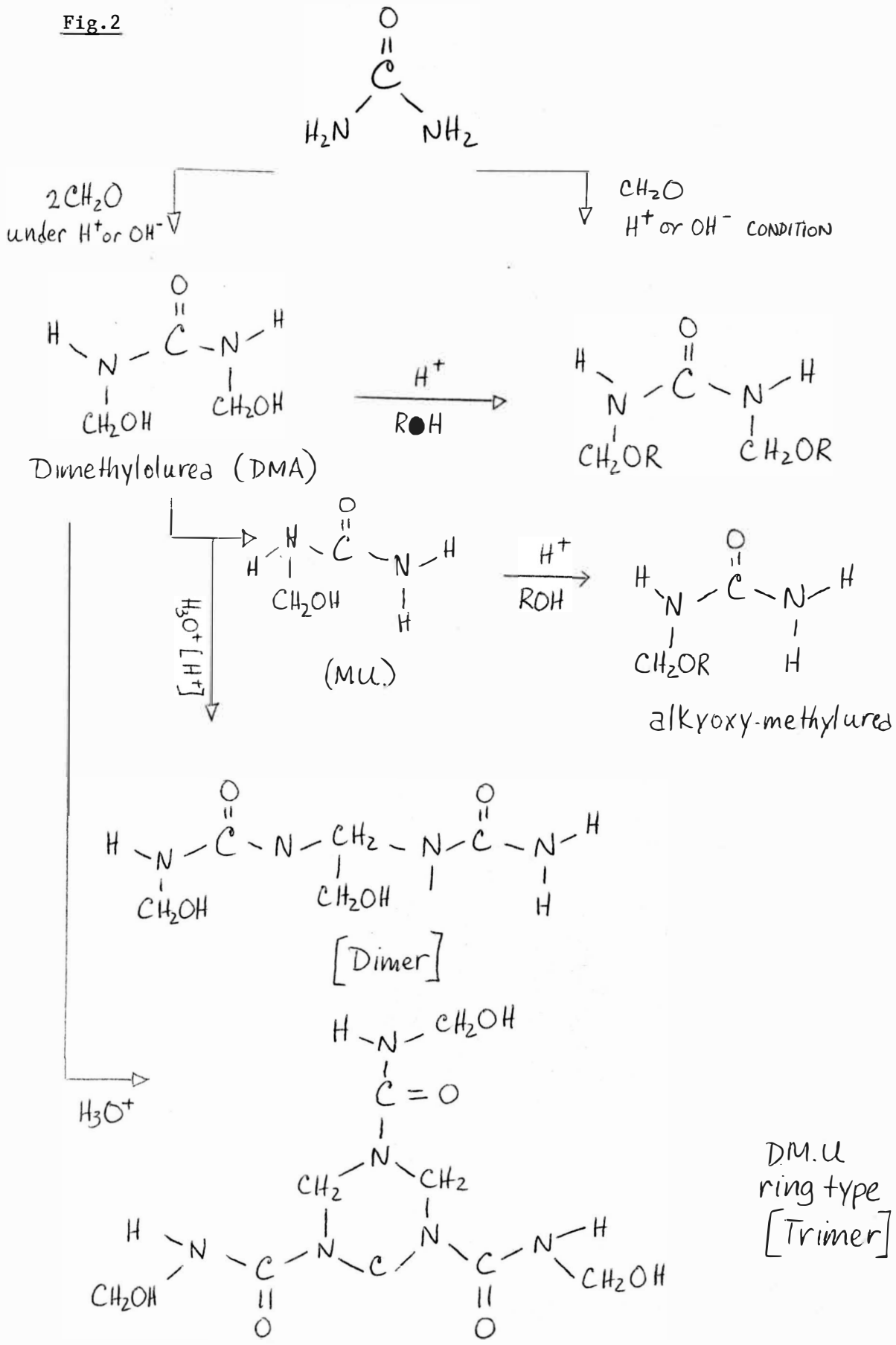


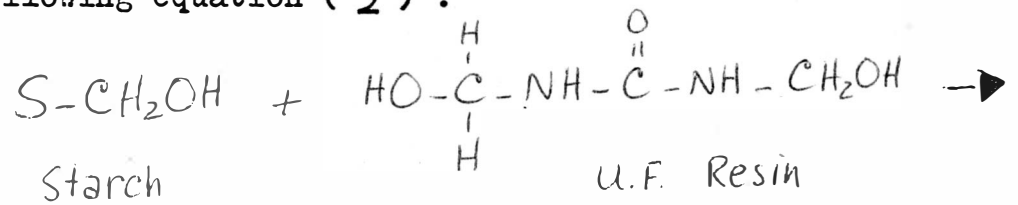
Fig.2 Formations of Dimer, Trimer and Monomer Urea Resins

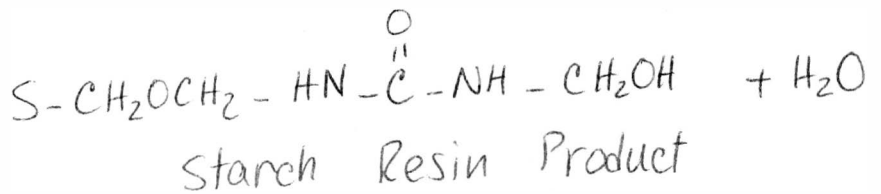
this can be seen in the reaction, the condensation of monomers in aqueous solution with acid catalyst can lead to different structural polymers, including branched chains or chain with rings randomly spaced within the chain depending on the formaldehyde ratio and other reaction conditions. If the ratio of formaldehyde to urea mole ratio is 1:1, the polymer will precipitate. If the ratio is 2:1 or higher, they assume a colloidal state of dispersion. The urea formaldehyde resins manufactured for use in the paper industry are either monomeric or at most, only slightly advanced in poly--merization. The low degree of polymerization (D.P.) is necessary to provide solubility in water or starch coating medium. All the commercial urea resins contain the reactive terminal groups in varying proportions that enable them to condense under the influence of heat, catalyst, or both to yield the infusible cured product. In order to obtain good wet rub resistance, polymerization of urea resins is not carried to the greatest possible degree. That's why some reactive terminal groups are sometimes still present in the cured products (11).

MECHANISM OF UREA FORMALDEHYDE WITH STARCH COATINGS

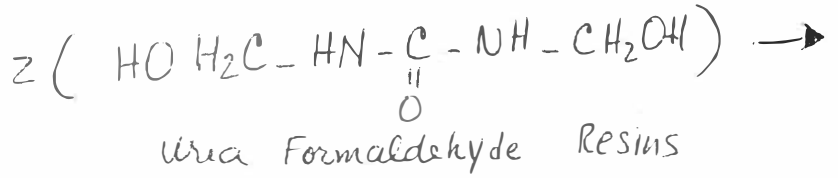
In the reaction of urea formaldehyde resin with starch, it can be considered that a methylol group on

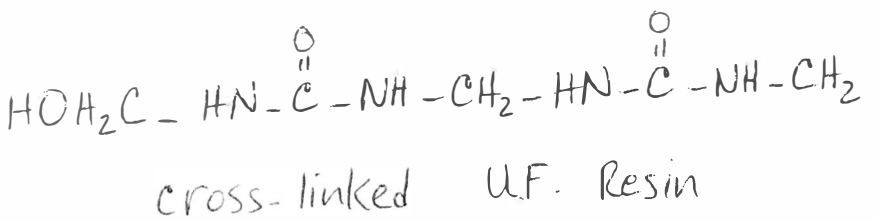
the resin reacts with one of the hydroxyls on the starch (α glucoside) and splits off water as shown on the following equation (5) :





While the resin can function by simple reaction and blocking, there is also considerable opportunity for further reaction of the same resin with the hydroxyls of other starch molecules and the net result would be crosslinking. Moreover, there is opportunity for the urea resin to self-condense to give the insoluble product which can serve to waterproof the starch coatings:





Urea formaldehyde resins are supplied commercially as moderately viscous solution of 55-80% resin solid in water and usually nearly water-white in color. They are produced to the paper industry under several trade names like Beckamine, Cataline, Kymene, Parez, Scriptite, Ufor--mite and Westrez. The properties of various urea resins produced by different companies are compared and discussed (13, 14). Generally, they are characterized by their nearly water-white color, resistance to water and grease, as well as alkali and solvent. They also improve the film gloss and gloss retention, hardness and color retention, and provide good adhesive strength. Usually, only a portion of the potential water resistance is obtained at the machine. The strength develops with storage and a period of 2 to 3 weeks may be required for full cure.

The use of urea resins in reducing water-sensitivity of starch coatings has had many problems. Some of the problems that should be solved are adhesive strength of starch-resin binders, slow-curing , the formaldehyde odor, and viscosity build- up.

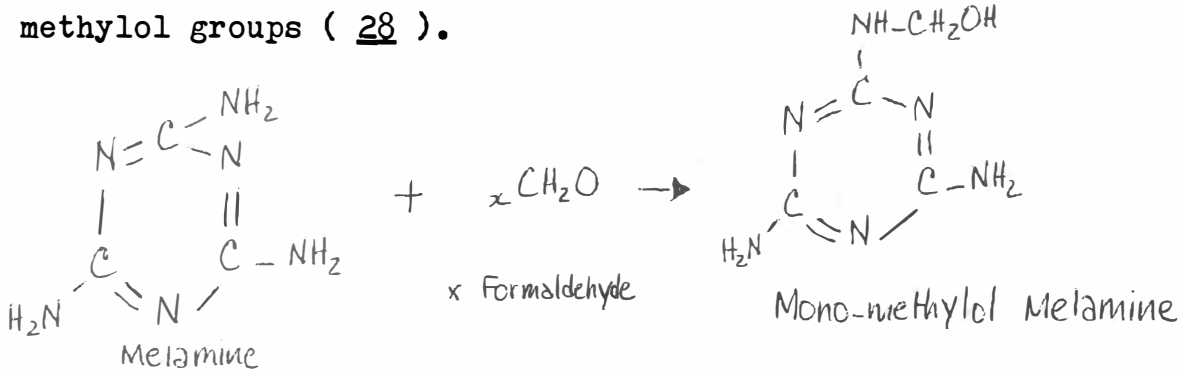
MELAMINE FORMALDEHYDE

INTRODUCTION

Another well-known wet strength resin used to increase the water resistance of the starch coatings is melamine formaldehyde. It was first synthesized by Von Liebig in 1834. Commercial scale production in 1939 by American Cyanamid Company, using dicyandiamide as raw material, was the basis for the first production of melamine resin in the United States.

CHEMISTRY OF MELAMINE RESINS

Melamine is a white, crystalline chemical with very low solubility in water, alcohol or other solvents, but similar to urea resin, it reacts with formaldehyde readily to form a series of methylol derivatives, ranging from monomethylol to hexamethylol melamine, depending on the number of melamine hydrogens that are replaced with methylol groups (28).



The methylol monomers tend to crystallize and become difficult to handle. To overcome this problem, most

commercial melamine products for paper are of higher molecular weight and are obtained by the condensation of two or more monomers units with the elimination of water. The resulting syrups are easy to handle and they spray-dry well (28).

Curing of melamine resins may be accomplished simply by heating. The presence of small amount of acid will accelerate the heat cure, especially for the butylated products; but unlike urea formaldehyde, satisfactory cure is not possible at room temperature for this resin, even in the presence of acid catalyst.

A unique property of methylol melamine resin is its ability to form stable colloids with acids.The colloidal resin so produced possesses a strong positive charge that is readily accepted by cellulose fibers in water dis--persion. New melamine resin (30) eliminates the need for formaldehyde, which tends to thicken the coating and will continue to increase the coating viscosity upon standing.

Melamine formaldehydes are supplied commercially at very high percent solids (usually about 80%). Several familiar trade-names of melamine resins to the paper industry are Parez of American Cyanamid, Resimene of Monsanto Company, Beckamine of Reichhold Company, and Uformite of Rohm& Haas Company. Besides developing

excellent wet rub resistance after curing, its mild odor and low viscosity increase has made melamine resin prefer--able to urea resin in many coating applications.

GLYOXAL

INTRODUCTION

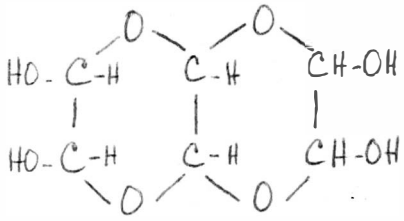
Another method of increasing the wet rub resistance of the starch coatings is by using glyoxal to insolubilize starch. Glyoxal was developed mainly to shorten the curing time and avoid the odor and obnoxious fume which were encountered by the urea resins (15). In the past, glyoxal has been rejected because of the color frequently imparted to the finished paper by the commercial material (2). Modern manufacturing techniques now make available glyoxal which is essentially free of color-forming material and other impurities.

It was found by Buttrick and Eldred (15) that glyoxal, when applied to paper, resulted in very little loss or no loss at all after either natural or accelerated aging. New commercial glyoxal (16) developed good wet rub resistance right off machine and exhibited very modest viscosity increase after addition of the insolubilizer.

CHEMISTRY OF GLYOXAL

Glyoxal, having the formula CHOCHO, is essentially a low molecular weight, and highly reactive di- aldehyde which forms hydrates in aqueous solution . These hydrates which are colorless and nonflammable in aqueous solution ,

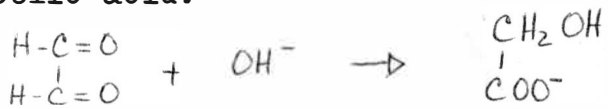
may be represented by the following structure (19) :



The anhydrous form, , which can be pro-
-duced only under most vigorous condition, is hygrosco-
-pic and readily forms a white, solid hydrate on exposure to the air.

MECHANISM OF GLYOXAL WITH STARCH COATINGS

Glyoxal undergoes chemical reactions which are characteristic of aldehyde. Under alkaline condition, an internal Cannizzaro reaction occurs slowly, forming a salt of glycolic acid:

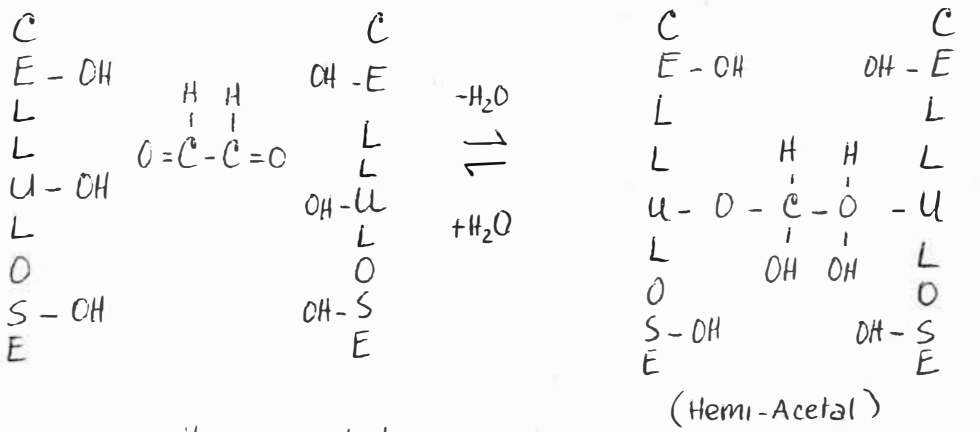


As the hydroxyl ion is consumed, the pH drops to about 5 and the reaction stops. However, under the weakly basic condition (pH 7 to 9) that is often found in paper coatings, reaction with starch in coated paper appears to occur almost as fast as the paper can be dried. The optimum pH of coating color is suggested to be in the range of 6-8.

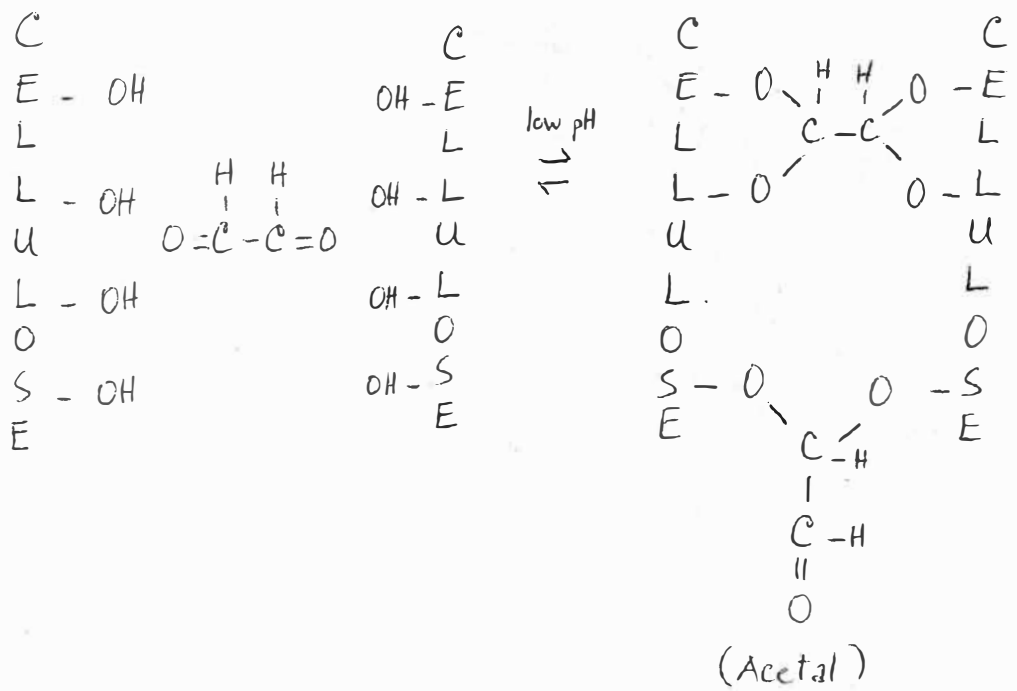
Chemical crosslinks between starch molecules are formed via unstable hemi-acetals bonds. Then on drying, more stable acetals are formed thus rendering the starch

insoluble (4, 17).

It was reported (17) that glyoxal also forms cross--links with cellulose fibers. The reaction occurs somewhat similar to that of with the starch:



Hemi-Acetal Formation



Acetal Formation

Adding glyoxal to the finished coating color produced the lowest viscosity, while addition of the glyoxal to the hot starch cook gives the highest viscosity. Manufac--turers of glyoxal state that cooking glyoxal with starch gives slightly higher wet rub resistance (18).

Buttrick,G.W. and his co-workers (19) revealed that an improvement of wet rub resistance can be obtained with as little as four percent of glyoxal (based on starch concentration) by proper selection of conditions and the use of newly-processed glyoxal. The selected conditions include a) cooking glyoxal with starch together b) main--taining a high starch solid level in the starch-glyoxal cook and c) using high starch binder concentration. They also added that glyoxal was only effective in producing good wet rub resistance as long as the pH was kept under 10. The wet rub resistance decreased as the coatings was too basic.

Glyoxal is usually obtained in the solution with 50% solid. Besides developing good water resistance off machine, it is compatible with most commonly-used coating ingredients and is much more pleasant to work with than urea resins.

ACRYLIC LATEX

INTRODUCTION

One of the most recent methods of improving the water resistance of the starch coatings is by the use of acrylic latex. Acrylics, of course, have been available to the paper industry for several years. Their industrial history dates back to 1927 when a German firm of Rohm and Haas first produced the polymethyl acrylates under the name of " Acryloid ". This was the solution polymer in an organic solvent and it was suggested for use in lacquer and surface coatings. Throughout the years, many monomers have been proposed in the production of acrylic latex, but only few of them were proven economically feasible. At the present time, the commercial production of acrylics uses such materials as acetone, ethylene, ethylene oxide, cyanide, sulfuric acid, acetylene, methanol, ethanol, and other al--cohol (24). The first acrylic latexes to find wide use in the field of paper coating were those developed as binder for pigment in water-base paints. Since many of the desired properties in paints are also those required in paper coatings, the acrylic latexes were evaluated in the paper industry and achieved considerable sucesses.

CHEMISTRY OF ACRYLIC LATEX

Acrylic latex is a colloidal water dispersion of acrylic polymers in water made in a process called emulsion

polymerization. This process is carried out by dissolving in water an emulsifier and a water soluble catalyst. Acrylic monomers are added with the surfactant which are then dispersed together by agitation. The batch is heated and polymerization takes place.

The emulsifier is usually soap or simple surface active agents such as lauryl sulfate. With the rapid development in the field of surfactants, many different systems are used for this purpose. A number of anionic alky-lauryl sulfonates and sulfate yield excellent emulsion of very small particle size and high solid content of low viscosity. Stable latex dispersion has particle size as low as .01 micron and as high as 5 microns.

ACRYLIC MONOMER

The acrylic monomers used in the latex cover a wide range of different vinyl-type chemicals that are essentially based on acrylic and methacrylic acids. These acids can react at the carboxylic functionality like other organic acids to form a variety of derivatives such as ester, salt, alhy--dride, and nitrile. The acid and their derivatives are known collectively as acrylic monomers (27).

Acrylic monomers commonly-used to produce acrylic latex are methyl methacrylate, ethyl acrylate, 2-ethyl hexylacrylate, and butylacrylate. Methyl methacrylate is usually the main constituent due to its toughness which is necessary in durable coating (22, 25). Methyl methacrylate

is produced commercially by a cyano-hydrin process and is well-covered in (24).

MECHANISM OF LATEX WITH STARCH COATINGS

As acrylic latex is added to the starch coating, it is suggested that the existing fiber bonds are rendered resistant to water by the crosslinked polymer network that develops when the latex is cured (24).

Recently, Mlymar L. and co-workers (3, 26) have developed a new approach to the reaction of acrylic latex in starch coating. The newly-developed latex has a strong reactive affinity for clay. It exhibits unusually binding properties (as seen in the I.G.T. pick test) and remark--able wet rub resistance with as low as four parts of latex. The water resistance arises from bonds formed with polymer and clay upon drying, and is not the result of a curing mechanism as are the insolubilizing reactions which occur between urea formaldehyde resin or glyoxal with starch. The new cationic latex does not react with starch, nor does it crosslink with itself in anyway. Evidence was shown by the authors from swelling ratio studies and stress-strain curve analysis. This latex can be used with a high ratio of starch without sacrificing the wet rub resistance of the coatings. It is suggested this latex be used with starch coating under alkaline condition (pH 9 or higher) . In coating with 16 to 20 parts of total binder for every part of clay, a one to one ratio

of starch and latex should provide an excellent water resistance.

Besides improving the water resistance of the starch coating, acrylic latex (either " normal"or " cationic ") can also impart gloss and smoothness to the surface of the sheet. In spite of some disadvantages like high cost and freeze instability, acrylic latex is being recognized more and more by papermakers.

EXPERIMENTAL DESIGN

MATERIALS

Number two Huber clay was the only pigment utilized in the coating color. TSPP (tetrasodium pyrophosphate) was added as the dispersant before blending the pigment by means of a Hamilton Beach Model 936 milk shake mixer. The coating formulation used was as follows:

100 parts of no. 2 Huber clay

.2 part of TSPP

8 parts of cooked starch (regular & cationic)

3-12 parts of various insolubilizers

50% total coating solids

pH 7 for glyoxal, pH 9 for latex and

pH 5 for UF and MF.

The pigment slip used in the experimental work consisted of around 75% total solids clay dispersion. Each clay batch was then subjected to 5 minutes of milk shake mixer action to assure an uniform pigment mixture. The order of addition of the coatings color was as follows:

- Mix TSPP and diluting water
- Add clay to the solution
- Add cooked starch to the above solution
- Add insolubilizer

The urea formaldehyde selected was " Westrez 21-113 " produced by Reichold Company. The melamine formaldehyde used was " Parez 613 " from American Cyanamid Company. Latex A was " Experimental Emulsion E-1209 " from Rohm and Haas Company that reacts specifically with clay. Latex B was " Dow Latex 650 " , obtained from Dow Chemical Company. Finally, " UCAR V " glyoxal from Union Carbide was also utilized for testing the insolubilizing strength.

Two types of starch were used in the study: regular and cationic starches. The regular starch used for the testing was Penford Gum 280, a hydroxy-ethylated starch. The cationic starch used in the study was Cato-kote 485.

PROCEDURE

The starch solutions were prepared by heating a 25% starch suspension on a steam bath for 30 minutes at about 190^{o}F and were kept warm before adding to the pigment slip. All the insolubilizers were added finally with constant stirring. The final total coating solids was maintained at about 50%. pH of the coating color was adjusted using NaOH or dilute H_2SO_4 .

The coating colors were then applied by hand draw--downs with Mayer rod on to a bleached coating raw stock (52.5 lbs/ 25 x 38 - 500 per ream) which was groundwood free and the degree of sizing was 4.6 seconds measured by

the Hercules sizing tester. Coat weights were maintained at approximately 12± 1 lbs per ream by changing appropriate wire-wound rods. The coated sheets were then dried @ 210°F at varying times from 1 to 3 minutes. Curing times of 7 to 15 seconds (similar to mill operations) were tried but found inadequate to produce a reasonably dry sheet. Aging was performed at 73°F and 50% relative humidity for 48 hours. Insolubilizers were used in varying amounts from 3 to 12% (based on pigment) to evaluate the amount of agent needed to produce the optimal result.

Wet rub resistance testing was similar to the TAPPI Routine Control Method RC-184. It involved immersing samples of coated sheet in water for 5 seconds, laying the samples on black glazed paper and firmly stroking the wet surface with the forefinger three times so that any loosened pigment was transfered to the black glazed paper. After drying, the brightness of the spot on the black glazed paper was determined. Low brightness readings indicate good wet rub resistance.

Viscosity readings were taken on a Brookfield Sychroelectric viscosity meter, model RVF-100, using several spindles, operated at different rpm, all at 120°F.

RESULTS

Tabulated test results appear on the following pages.

TABLE I - ETHYLATED STARCH COATINGS WITH 3% INSOLUBILIZER ADDITION

COATING FORMULATION	BROOKFIELD VISCOSITY (cps) @ 120F	WET RUB (FINGER METHOD) % BRIGHTNESS 1min. aging	2min. aging	3min. aging	48 hrs aging
3% Urea formaldehyde 8% Penford Gum-280	640	61	54	50	42
3% Melamine Resin 8% PG-280	620	36	27	19	15
3% Glyoxal 8% PG-280	440	18	16	15	11
3% Latex A 8% PG-280	1320	27	17	18	20
3% Latex B 8% PG-280	965	32	26	19	18

TABLE II - ETHYLATED STARCH COATINGS WITH 5% INSOLUBILIZER ADDITION

COATING FORMULATION	BROOKFIELD VISCOSITY (cps) @ 120F	WET RUB (FINGER METHOD) % BRIGHTNESS			
		1min. aging	2min. aging	3min. aging	48hrs aging
5% Urea resin 8% PG-280	1360	63.2	60.4	48	43
5% Melamine resine 8% PG-280	800	34	28	25	20
5% Glyoxal 8% PG-280	730	25	18	18.5	15
5% Latex A 8% PG-280	840	27	24	24	18
5% Latex B 8% PG-280	1232	28	24	22	22

TABLE III - ETHYLATED STARCH COATINGS WITH 8% INSOLUBILIZER ADDITION

COATING FORMULATION	BROOKFIELD VISCOSITY (cps) @ 120F	WET RUB (FINGER METHOD) % BRIGHTNESS			
		1min. aging	2min. aging	3min. aging	48hrs aging
8% Urea resin 8% PG-280	1050	62	60.5	51	40
8% Melamine resin 8% PG-280	520	33	22.5	21	20
8% Glyoxal 8% PG-280	480	19	18	15	15
8% Latex A 8% PG-280	956	32	18	22	20
8% Latex B 8% PG-280	1200	26	25	23	17.5

TABLE IV- ETHYLATED STARCH COATINGS WITH 12% INSOLUBILIZER ADDITION

COATING FORMULATION	BROOKFIELD VISCOSITY (cps) @ 120F	WET RUB (FINGER METHOD) % BRIGHTNESS			
		1min. aging	2min. aging	3min. aging	48hrs. aging
12% Urea resin 8% PG-280	1300	61	51	35	29
12% Melamine resin 8% PG-280	700	42	34	33	32
12% Glyoxal 8% PG-280	380	17	12	12	12
12% Latex A 8% PG-280	980	26	23	25	25
12% Latex B 8% PG-280	1000	17	14	12	13

TABLE V - CATIONIC STARCH COATINGS WITH 3% INSOLUBILIZER ADDITION

COATING FORMULATION	BROOKFIELD VISCOSITY (cps) @ 120F	WET RUB (FINGER METHOD) % BRIGHTNESS 1min. aging	2min. aging	3min. aging	48hrs. aging
3% Urea resin 8% Cationic	945	48	45	42	42
3% Melamine resin 8% Cationic	924	40	35	21	29
3% Glyoxal 8% Cationic	760	28	17	12	11
3% Latex A 8% Cationic	1140	37	25	24	12.5
3% Latex B 8% Cationic	1000	36	25	29	26

TABLE VI - CATIONIC STARCH COATINGS WITH 5% INSOLUBILIZER ADDITION

COATING FORMULATION	BROOKFIELD VISCOSITY (cps) @ 120F	WET RUB (FINGER METHOD) % BRIGHTNESS			
		1min. aging	2min. aging	3min. aging	48hrs. aging
5% Urea resin 8% Cationic	1100	60	60	54	48
5% Melamine resin 8% Cationic	540	32	27	24	21
5% Glyoxal 8% Cationic	600	15	15.6	14.5	14
5% Latex A 8% Cationic	1100	34	27	21	19
5% Latex B 8% Cationic	1340	28	25	18	16

TABLE VII - CATIONIC STARCH COATINGS WITH 8% INSOLUBILIZER ADDITION

COATING FORMULATION	BROOKFIELD VISCOSITY (cps) @ 120F	WET RUB (FINGER METHOD) % BRIGHTNESS			
		1min.	2min.	3min.	48hrs.
8% Urea resin 8% Cationic	920	57	52	41	41
8% Melamine resin 8% Cationic	780	38	24	19	18
8% Glyoxal 8% Cationic	692	31	18	11	10
8% Latex A 8% Cationic	1020	32	24	20	15
8% Latex B 8% Cationic	1120	31	26	25	10

TABLE VIII - CATIONIC STARCH COATINGS WITH 12% INSOLUBILIZER ADDITION

COATING FORMULATION	BROOKFIELD VISCOSITY (cps) @ 120F	WET RUB (FINGER METHOD) % BRIGHTNESS			
		1min. aging	2min. aging	3min. aging	48hrs aging
12% Urea resin 8% Cationic	1150	60	52	45	45
12% Melamine resin 8% Cationic	540	40	28	22	19
12% Glyoxal 8% Cationic	472	21	10	9.5	12
12% Latex A 8% Cationic	976	12	10	8.5	12
12% Latex B 8% Cationic	1050	21	12	7.7	8

DISCUSSION

Test procedures were the same for all samples. Sufficient readings were taken to make sure test values obtained were representatives of the sample, and each resulting reading was the average of at least four experimental readings. Uncontrollable errors, such as those due to inaccurate readings from the brightness tester, reading level from the test beakers, were unavoidable. However, the pro--cedure was kept as consistent as possible. As the data suggested , the following variables have contributed to obtaining the optimal water resistance of the starch coating:

THE EFFECT OF DRYING TIME

Figures 3a through 3d show the effects of drying time on the wet rub resistance of coating treated with various types of insolubilizers. Figure 3a shows the effect of drying at 12% insolubilizer, figure 3b at 8%, figure 3c at 5% and figure 3d at 3% insolubilizer. The trend is obviously different for all insolubilizers : Drying time is most effective toward urea formaldehyde at 12% addition and overall curing time is most helpful to urea formal--dehyde; and then, secondly, to melamine formaldehyde. 12% addition of urea formaldehyde at 3 minutes drying

time gave the sheet almost the wet rub resistance of melamine formaldehyde at 3 minutes (both with regular starch) . This is a good evidence showing that drying time is very helpful to urea formaldehyde since the wet rub resistance of urea formaldehyde was much worse than that of melamine formaldehyde, with 12% addition and at less than 3 minutes drying time.

In other cases, even though drying helped improve the wet rub resistance of the urea formaldehyde coatings, it was still far less effective compared to coating having melamine formaldehyde, glyoxal and latex. In the latex system, too much drying had adverse effect on latex A (cationic acrylic latex) : As we can see from all four figures, the optimum drying time for latex A was only two minutes and drying longer than 2 minutes lowered the wet rub resistance significantly. This could be because as the sheet was exposed to heat longer, the coatings became more brittle, and when applied by the wet rub test, it came off more easily, thus the wet rub resistance decreased.

For latex B (regular acrylic latex), however, the trend was different : In most cases, drying 2 minutes developed as good wet rub resistance as drying 3 minutes, therefore, it was not necessary to dry the sheet longer than 2 minutes to obtain good wet rub resistance.

For glyoxal, we can see that very good wet rub resis--tance developed right after the sheet finished drying (about 1 minute). There was no substantial increase in wet rub resistance as more drying was allowed. This result was almost identical to the findings of Moyer and Stagg (28).

THE EFFECT OF TYPES OF STARCH

It is obvious from figures 3b and 3d that by changing regular to cationic starch, the wet rub resistance tended to increase significantly. However, in coatings with urea formaldehyde, drying contributed more to regular starch and made regular starch as water resistance as the cationic starch as drying time increased. With 5% and 12% regular starch with urea formaldehyde addition, the wet rub resis-tance was even superior to those obtained by cationic starch at the same amounts. In other cases, at 12% addition of latex A (regular acrylic latex), cationic starch seemed to contribute more binding strength to the coatings than any other insolubilizers studied. However, in general, the combination of cationic starch and glyoxal gave the best water resistance of all. This is, incidentally, in agree--ment with the findings of Mazzarella and Hickey (28).

THE EFFECT OF AMOUNT OF INSOLUBILIZERS

Data shows varying the amount of insolubilizer does not have as great an effect on the wet rub resistance

in the range from 3 - 12% addition as the drying rate. However, it is one of the big contributing factors to the improvement of wet rub resistance of the starch coatings.

In the urea resin case, wet rub resistance increased slowly as more urea resin was added. This was not true in the case of melamine formaldehyde and latex, since 3% of melamine formaldehyde and latex was usually enough to produce good wet rub resistance.

In the case of glyoxal, superior wet rub resistance was found at 12% addition range, but there was no good evidence that wet rub resistance increased with more glyoxal since it was not much better than those obtained at 3% glyoxal addition.

Finally, in the case of latexes A and B, wet rub resistance improved slightly as more latex was added, with latex A (cationic acrylic latex) somewhat better. Cationic starch gave latex A the best wet rub resistance of all insolubilizers at 12% range, much superior to the same amount of either latex used with regular starch.

CONCLUSIONS

The following conclusions can be drawn from the experi--mental tables and data:

1- It took more time for urea formaldehyde to develop the satisfactory level of wet rub resistance than the other insolubilizers studied. Also, the over--all wet rub resistance of urea formaldehyde was always inferior to the rest.

2- Cationic acrylic latex was superior to urea and melamine formaldehyde in improving the water resis--tance of the starch coatings but was generally slightly less effective than glyoxal. Melamine formaldehyde was slightly better than regular acrylic latex. However, with the use of cationic starch, cationic acrylic latex began to gain the superiority to the rest at 12% latex addition.

3- Good wet rub resistance developed right after the coated sheet was dried for regular and cationic acrylic latexes and glyoxal. For urea and melamine formaldehyde, it took much longer times.

4- In comparing the efficiency and ease of operation, glyoxal developed excellent water resistance and produced very little increase in overall coating viscosity, thus it was found to be the best insolubilizer for starch coatings.

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APPENDIX

Figure 3a : Effect of drying on starch coatings with 12% insolubilizer

Figure 3b : Effect of drying on starch coatings with 8% insolubilizer

Figure 3c : Effect of drying on starch coatings with 5% insolubilizer

Figure 3d : Effect of drying on starch coatings with 3% insolubilizer

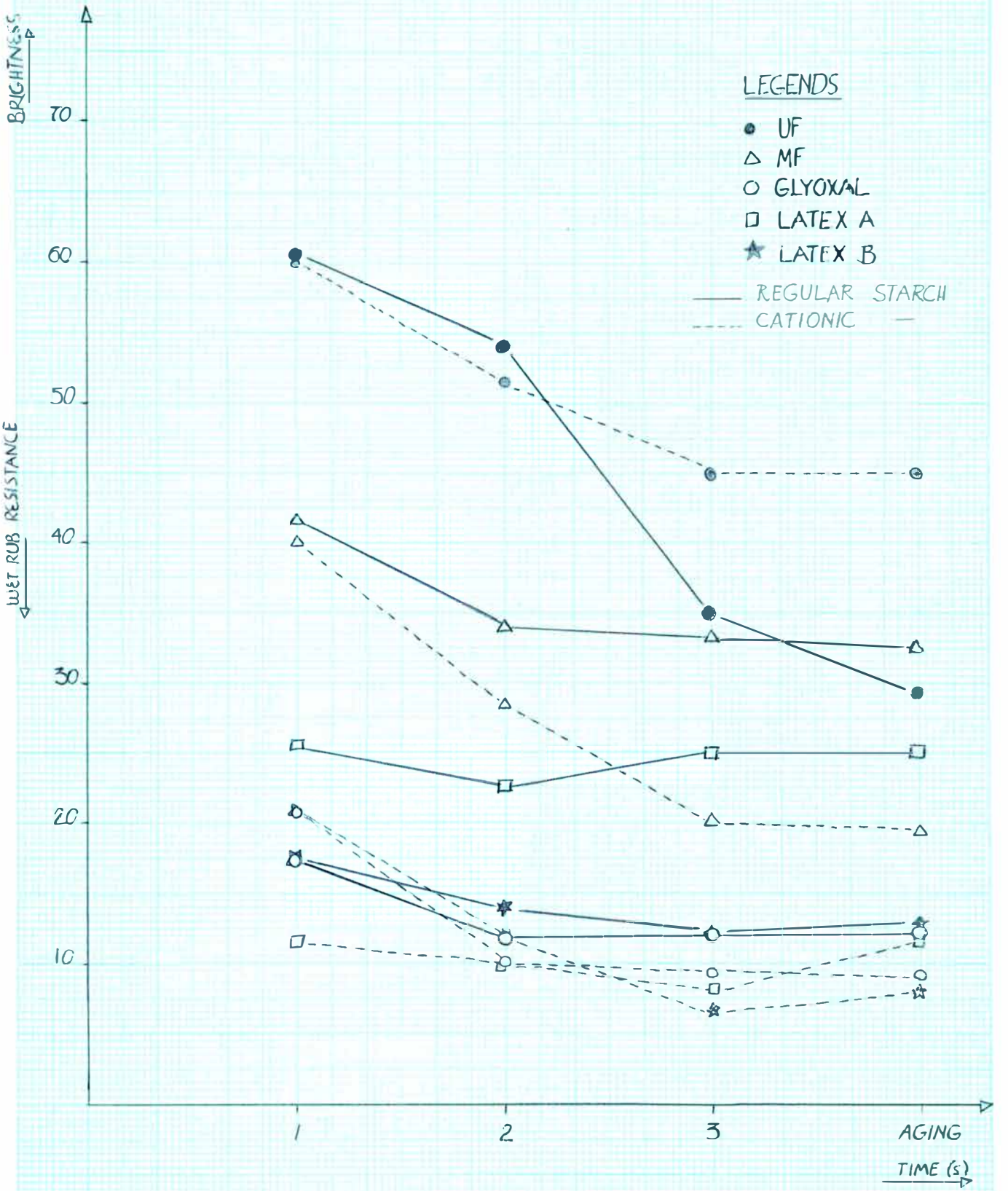
EFFECT OF DRYING RATE ON
12% INSOLUBILIZER + STARCH COATINGS
BRIGHTNESS
WET RUB RESISTANCE
70
60
50
40
30
20
10
LEGENDS
UF
MF
GLYOXAL
LATEX A
LATEX B
REGULAR STARCH
CATIONIC
1
2
3
AGING
TIME (s)

Fig. 3a

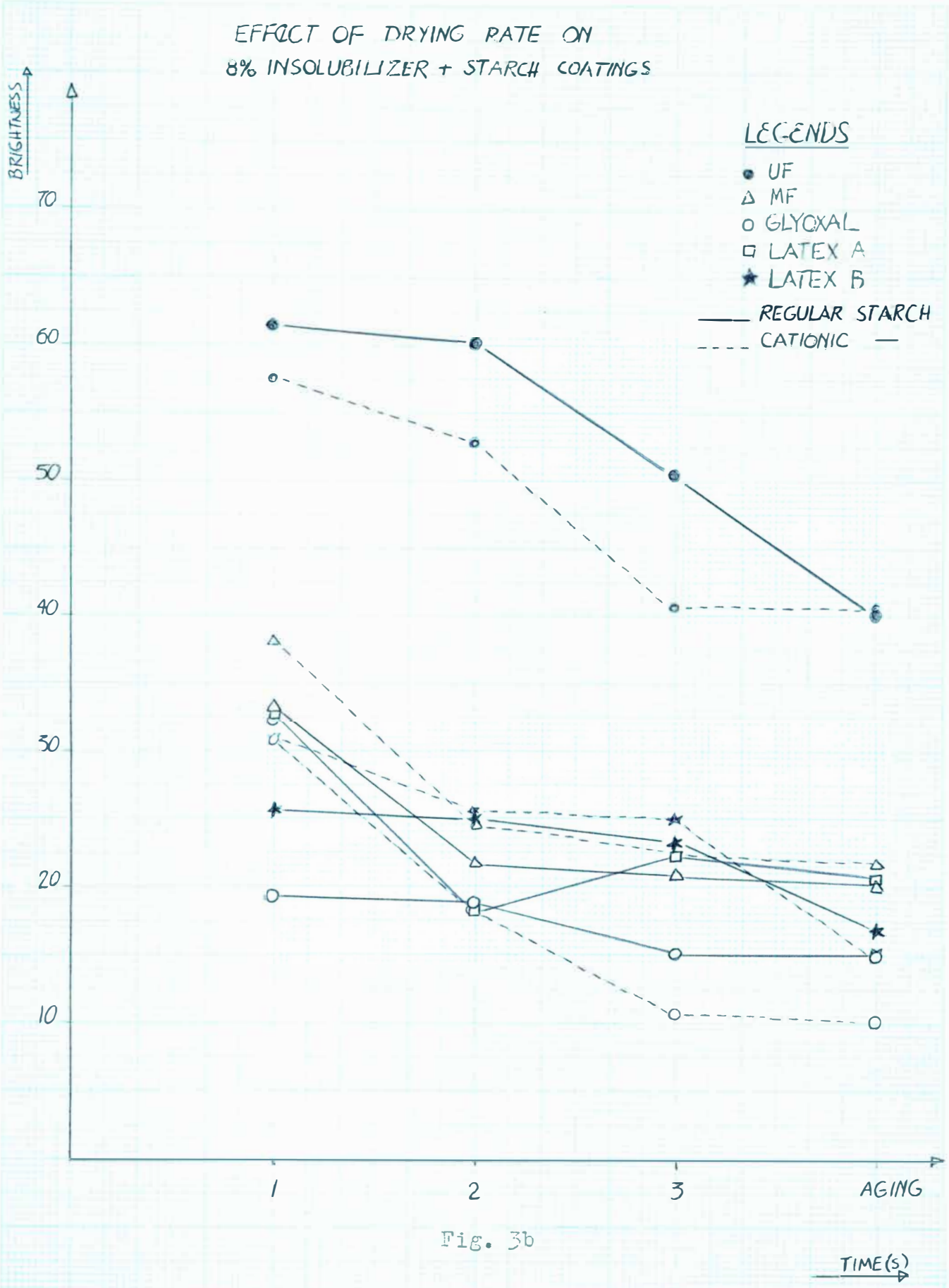
EFFECT OF DRYING RATE ON
8% INSOLUBILIZER + STARCH COATINGS
LEGENDS
UF
MF
GLYOXAL
LATEX A
LATEX B
REGULAR STARCH
CATIONIC
BRIGHTNESS
70
60
50
40
30
20
10
1
2
3
AGING
TIME(s)

Fig. 3b

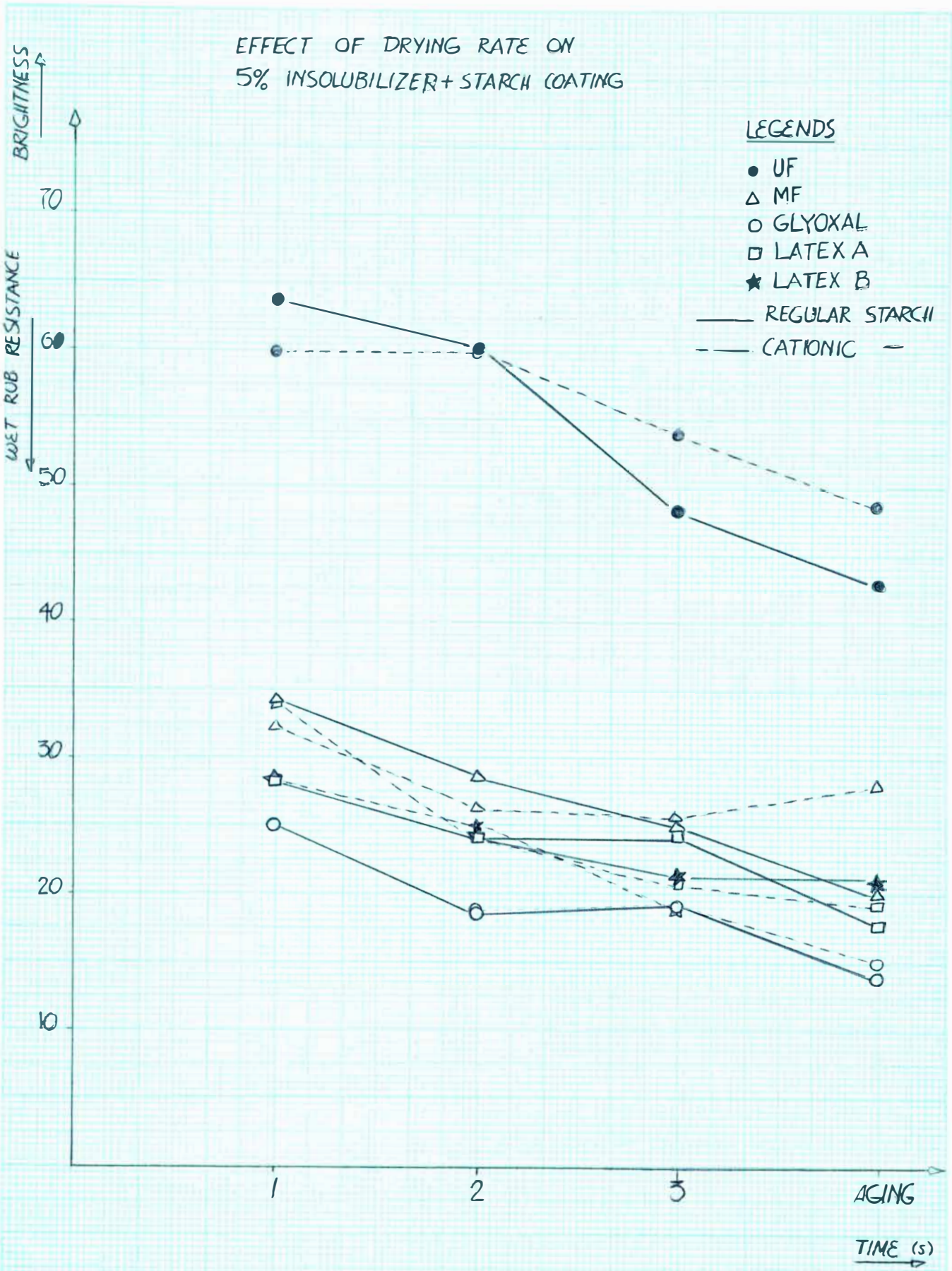
EFFECT OF DRYING RATE ON
5% INSOLUBILIZER + STARCH COATING
LEGENDS
UF
MF
GLYOXAL
LATEX A
LATEX B
REGULAR STARCH
CATIONIC
BRIGHTNESS
WET RUB RESISTANCE
70
60
50
40
30
20
10
1
2
3
AGING
TIME (s)

Fig. 3c

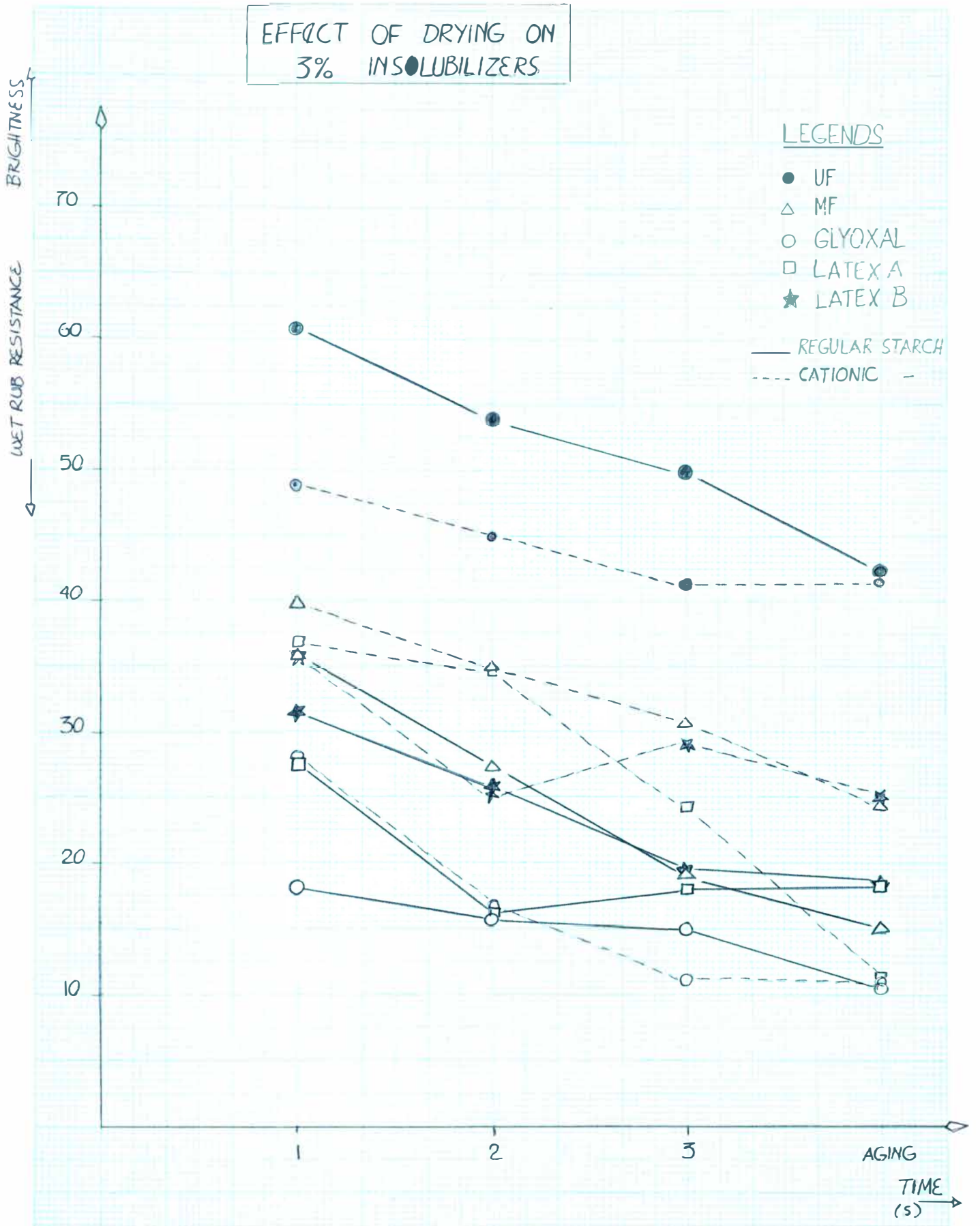
EFFECT OF DRYING ON
3% INSOLUBILIZERS
BRIGHTNESS
WET RUB RESISTANCE
70
60
50
40
30
20
10
LEGENDS
UF
MF
GLYOXAL
LATEX A
LATEX B
REGULAR STARCH
CATIONIC
1
2
3
AGING
TIME
(s)

Fig. 3d