The chemistry and technology of modern synthetic and national polymers for coating of paper and boards

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SUMMARY

This paper outlines the chemistry and important structural modifications of present day, natural polymers such as cationic starch, oxidized low viscosity starches and modified gums carboxy methyl cellulose etc. and their technical merits over conventional polymers.

Synthetic Acrylic Binders and their typical formulations used in paper coating are also discussed.

The chemistry of cross linking reagents used for improving adhesion and film formation and their reactions with cellulosic films is discussed at length.

The role of fillers such as Titanium Dioxide, Calcium carbonate and colored pigments, is also described along with various other consumer criteria such as matte and High Gloss finishes, strength improvements, High Brightness and Brightness retention.

Typical coating formulations and various physical/optical properties of coated Paper and Boards are described,

The subject of Coating/Finishing of Paper and Boards was only a technique and largely upon the experience and knowledge of the coater, in the past. Today, it has reached a scientific level which demands a thorough knowledge of the chemistry and the reaction mechanisms of various components used.

Of particular interest are the natural and synthetic polymers whose chemistry is as complex as that of the cellulose fibers. In addition, competetion from synthetic laminates is a constant threat and thus demands better standards of quality and durability of the finish, every day.

Coating of the base paper or board is usually done to improve the brightness, smoothness, opacity, surface gloss, printability and other related properties.

In a simpler term the coating process involves preparation of the coating color and its deposition on the paper or board surface. This can be either "on machine" process or "off machine" process. The coating color preparation is done by dispersing a filler such as clay, talc, $CaCO_3$, TiO_2 etc. in a dispersing medium, usually water; with

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the use of a dispersant. Binder is used to hold the various components to the paper or board surface. Though, the process looks simple, knowledge of the chemistry and mechanisms is essential to obtain high performance standards. Thus, each component has a different role to play in the coating formulation and for a given role a number of differant compounds are available.

The type of coating selected depends upon its end use and hence, it varies from one mill to another or from one operation to another. Low gsm coating with a binder and little filler is given, usually, to improve printing whereas higher gsm coating gives other properties like brightness, gloss, opacity etc. The requirements of high gloss involves altogether different composition and coating equipment/conditions. Thus, generalization of the coating process is a difficult job and is also dependent on the operator's skill apart from above mentioned variables.

A simple look towards this vast and complex subject reveals that the two most important and

*Parkhe Research Institute Khopoli 410 203, Maharashtra inseperable constituents of any coating mix are the fillers and the binders. An attempt has been made in this paper to discuss the chemistry and technology of some of the modern synthetic and natural polymers as binders and the role of fillers.

COATED PAPER VARIETIES

Some of the common grades of coated varieties are :

Book

It usually refers to sheets C2S used for books, catalogues, advertising etc by letter press printing.

Litho

These papers are usually C1S and are designed for offset lithography. Label papers are often lithographed on the coated side, the other side being uncoated for gluing to bottles or packages. **Enameled**

These are high gsm coated and super calendered papers having porcelain like finish and can be either C1S or C2S grades.

Letterpress enamel

These are super calendered papers in the 45-100 lb, basis weight range.

Offset Enamel

It is usually a C2S grade and though appears similar to letter press grade, it has improved ink tack resistance and wet rub.

Double Coated

It is coated either twice or twrice to get the quality.

Metal

These are coated with different powdered metals and either friction calendered or supercalandered.

Waterproof

High class box covers, school note books and other such uses require water resistance. A top or water proofing second coat of shellac or casein was used, but latexes and extruded films are now frequently preferred.

Cast coated

Papers made by this method are characterized by extremely high gloss obtained by drying the coating in contact with a highly polished drum. They have more bulk than papers which have been super calendered.

Dull finish or Matte coated

These are coated papers having little or no gloss produced by use of special coating pigments with or without super calendering. Those designed for letter press are super calendered, those for offset lithography may or may not be. They are used in sheets or webs. Special matte papers are used for photographing of copy for plate making.

Other grades are, Label, Litholabel, Dual purpose, Publication, Brush enamel, Playing card, Cover. etc.

PAPER OR BOARD COATING : OBJECTIVE

The very purpose of paper or board coating is to develop or improve the surface properties. The advantages of the coated sheet over the uncoated sheet for the printing purpose lie in its having a) better surface smoothness b) uniform reflectance characteristics c) more uniform opacity d) improved dimensional stability and e) uniform ink receptivity. Ink penetration and receptivity are better controlled by coating process rather than surface sizing.

Coating Color Constituents

The main components of any coating color are as under.

Pigments

ii Vehicles (usually water)

iii Binder or Adhesive and

iv Additives.

COATING PIGMENTS

The choice of a particular pigment or a pigment cambination is mainly dependent upon the end use requirements of the coated paper. Equipments available for coating color preparation and its application, also play a decisive role in the selection, along with the economic factor.

Clay

Clay is a major pigment which is relatively inexpensive and has excellent physical and optical characteristics. Clay is a natural, earthy fine grained material composed largely of a group of crystaline minerals known as clay minerals. The kaolin forming clays are hydrous aluminum silicates of approximately the composition $2H_2O$. Al_2O_3 $2SiO_2$. The clay used for coating purpose is usually processed and purified by the wet process. Typical chemical analyses of some of the clays are given in Table I.

The desired properties or the specifications of the coating grade clay has been recorded in Table II.

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S.No.	Particulars	Georgia Kaolin	English Kaolin	Theoretical Kaolin	English-India Chyna-Clay
			с. 		
1 2 3 4 5	SiO ₂ , % Al ₂ O ₃ , % Fe ₂ O ₃ , % TiO ₂ , % MgO, %	45.30 38.38 0.30 1.44 0.25	46.77 39.79 0.56 0.02 0.24	46.30 39.80	46.20 38.80 0.55 0.10 0.05
6 7 8 9	CaO, % Na ₂ O, % K ₂ O, % Loss on ignition at 950° C (combined wa	0.05 0.27 0.04 ter) 13.97	0.13 0.05 1.49 12.79	 13.90	0.10 0.05 0.25

TABLE – I CHEMICAL ANAIYSES OF DIFFERENT CLAYS

TABLE-II

SPECIFICATIONS FOR A COATING GRADE CLAY

S.No.	Particulars	Values
		,
1	Brightness (457 nm, Elrepho), %	Min 85
2	Yellowness $(\underline{R_9}-\underline{R_{11}})\times 100$, %	Max 5
3	R ₁₀ pH value (20 % w/w slurry) (T 645 TS-54)	3.8 — 7.2
4	Moisture, % (T 645 TS-54)	Max 5
5	Grit, % (residue on 325 mesh wet sieving)	Max 0.01
6	Particle size distribution (IS: 5282-1969)	
-	$\begin{array}{ccc} - & 10+2 \text{ micron}, & \% \\ - & 2 & \text{micron}, & \% \end{array}$	Max 20 Min 80

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Clay particles are stacks of flat hexagonal crystals. The particle size distribution analysis reveal whether the clay is a coating grade or coarser filler grade material. A superior coating grade clay consists of more than 90% by weight particles less than 2 micron in diameter. The particle size distribution of a typical No. 1 coating grade clay is given in Table III.

TABLE-III

PARTICLE SIZE DESTRIBUTION OF A TYPICAL No. 1, COATING CLAY

Comparable spherical diameter, microns	percent by weight
78	0.5
67	1.0
56	1.5
45	2.0
34	2.5
2—3	2.5
<2	90.0

Clay is easily dispersed because of its hydrophilic surface character. To obtain the maximum efficiency of a coating clay, each and every particle must be completely dispersed. Use of a dispersing agent is necessary to deflocculate kaolin to obtain maximum fluidity. The most efficient and economical dispersing agents for kaolin in aqueous systems are alkali phosphates and silicates e.g. sodium-hexameta phosphate and tetrasodium pyrophosphate. Wetting and stability of the dispersion are aided by a neutral or slightly alkaline pH.

Superior gloss and improved smoothness can be obtained with clay coatings. Generally, clays are characterized by low adhesive demand (10-18%) and a well dispersed coating clay of fine particle size and the use of -adequate binder gives the highest film strength.

Two grades of koalin, which are thermally treated, have been developed to achieve special porperties. These are a dehydroxylated or partially calcined kaolin and fully calcined kaolin. Use of this, helps in improving brightness, opacity and light scattering power.

Titanium Dioxide.

These are finely divided white powders which are nonreactive with any of the coating color constituents. These are manufactured pigments either by the chloride or the sulphate process. These appear in two crystalline forms 'anatase and rutile' tetragonal. In their finely divided form these pigments are intensely white and possess the highest refractive index of any pigment used in coating systems. The refractive indices of rutile and anatase are 2.76 and 2.54 with specific gravities as high as 4.2 and 3.9 respectively. The optimum particle size for titanium dioxide for maximum light scattering is 0.25 μ m.

These pigments are available as a dry product or a high titanium dioxide slurry in water which is in completely dispersed condition ready for direct use in coating systems. The dry pigment require dispersion in liquid media to wet out and deagglomerate the particles to obtain maximum optical performance. The dispersant demand of this pigment is rather low and either tetrasodium pyrophosphate or sodium hexameta phosphate can be used.

This pigment is usually used as a minor component in the coating color, i. e. usually upto 25-30% by wt. of the pigment. Titanium dioxide pigment is comparatively more abrasive than other pigments. However, this property is influenced by the particle size and the degree of dispersion

Titanium dioxide pigments contribute in a major way in improving the optical properties such as brightness and opacity of the coated paper or board, and high brightness is achieved at lower coating weights. The use of this pigment will ensure a smaller decrease in opacity after calendering as compared to that obtained only with clay or clay and calcium carbonate mixtures. TiO_2 is a relatively costly pigment.

Calcium Carbonate

Calcium carbonate contributes to brightness, opacity, smoothness and ink receptivity. Only for speciality coatings it is used as sole pigment but in most of the other coating applications it is used along with clay.

Calcium carbonates are generally obtained by grinding lime stone, or by precipitation reactions.

The natural form of calcium carbonate is either calcite or aragonite of which the former is the stable form. The precipitated forms of calcium carbonates are produced by the following reactions.

i.	Ca(OH) ₂	+	CO_2	\rightarrow	CaCO ₃	+	H_2O
ii.	Ca(OH) ₂	+	Na ₂ CO ₃	→	CaCO ₃	+	2 NaOH
iii.	CaCl ₂	+	Na_2CO_3	→	CaCO ₃	÷	2 NaCl

Finest natural calcium carbonate produced until recently was approximately $1.5-1.7 \ \mu$ m average diameter size whereas the most commonly used precipitated product has an average particle size of 0.6-0.8 μ m.

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The awareness to have a fine particle size led to the development of ultrafine ground lime stone. Some of the chemical analyses of natural and precipitated calcium carbonates are given in Table IV. The data reveal that the synthetic products are of higher purity than the natural products. The latter contained higher amounts of mg and silica impurities. The presence of magnesium can result in yellowing. The various properties of these calcium carbonate pigments are also listed in Table IV.

The synthetic products are of a higher brightness than the natural products (1-2%). The ultrafine ground lime (UFGL) had a higher surface area than the precipitated varieties but had a comparatively lower oil absorption. This difference would indicate that synthetic materials possess some degree of agglomeration. Inorganic polyphosphate compounds are the most effective dispersants for CaCO₃ pigments. Talc

It is a hydrous magnesium silicate having a composition 3 MgO $4SiO_2$. H_2O . Fine ground talc contains plate like particles of irregular outline. The flat surface of the platy talc is hydrophobic and organophilic. The refractive index of talc is 1.54 - 1.59 and it has a specific gravity of 2.75. Ultrafine ground talcs vary in brightness between 90-96% G. E. As talc is highly hydrophobic and organophilic, it is difficult to disperse and requires a combination of additives.

In addition to the wetting agent, a normal dispersing agent of the polyphosphate type is required. Potassium tripolyphosphate $(K_5P_3O_{10})$ is the most efficient disperser.

Ultrafine grind talc is being used as a portion of the pigment content principally in the area of

TABLE IV CHEMICAL ANALYSIS OF CALCIUM CARBONATES

S.No.	Particulars	Natural products		Precipitated products		
		FGL	UFGL	PCC-C	PCCA	
1	CaCO ₃ , %	97.73	9 7.62	98.?6	98 60	
2	MgCO ₃ , %	1.33	1.48	1.28	0.70	
3	SiO ₂ , %	0.59	0.70	0.09	0.45	
4	$Al_{2}O_{3}$	0.28	0.15	0.20	0.20	
5	Fe ₂ O ₃ , %	0.07	0.05	0.07	0.05	
	PROP	ERTIES OF	THE PIGMENTS			
1	Brightness, % 457 nm	94.6	94.4	95.9	96.8	
2	pH	9.9	10.0	10.0	9.8	
3	Oil absorption.cc/100 g	13.0	22.8	27.1	34.8	
4	Surface area, m^2/g	2.7	9.4	6 .9	8.4	
5	Residue on 325 mesh. %	0.008	0.002	0.037	0.122	
6	Valley abrasion, mg	42.2	8.5	5.1	6.2	

Ref. : Tappi 61 (5): 47 (78)

FGL : Fine ground lime stone

UFGL : Ultra fine ground lime stone

PCC-A : Aragonitic precipitated CaCO₃

PCC-C : Calcitic ppted CaCO₃

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rotogravure, label and impact printing grades. It has limited application in offset and latter press sheets. Pigmented size press coating are probably the major area of application especially where the talc is used as the sole pigment.

It has been reported that 10-40% addition of talc improves the print smoothness of rotogravure. Use of talc improves gloss on calendering easily.

Satin White

It is a white pigment with the chemical composition as 3CaO. Al_2O_3 . $3CaSO_4$. $31H_2O$. It is composed of needle shaped crystals approximately $1-2\mu$ m in length and $0.1-0.2\mu$ m in cross section. The specific gravity of satin white ranges from 1.5-1.82 depending on the age and composition. The particle size of European satin whites is 93-95% by weight of it, smaller than 2μ m size. Because of its acicular 'shape, satin white particles pack in a "jack straw" configuration resulting in a large void volume and numerous reflective interfaces. As a result high brightness and excellent filling properties of satin white coatings are realized.

The high degree of hydration of satin white makes the development of high gloss possible under mild calendering conditions. In the presence of another pigment such as clay, minor amounts (up to 5 %) of satin white promote high gloss even at comparatively low relative humidity. It also improves the wet rub resistance in the presence of the small amounts of protein adhesive by the formation of an insoluble calcium proteinate.

Satin white has a high dispersant demand. Its use is mainly limited in the production of high gloss art papers and also in the coating of photographic papers.

Amorphous Silicas and Silicates

There are several artificially precipitated amorphous silicious pigments composed of silicon dioxide either alone or in combination with various other elements. They generally exhibit high brightness and opacity values. They are sometimes known as "titanium dioxide extenders" and impart opacity, high bulk and low gloss They are capable or replacing 25-50% of TiO₂ pigment without any drop in opacity and brightness values.

Zinc Oxide Pigments

Its role in paper coating is limited to the coating of those papers used in electrophotography.

Barium Sulphate

Its usage in paper coatings is restricted to the field of photographic papers. Here, despite of its high cost per unit of hiding power, it is the

choice pigment because of its purity and chemical inertness.

COATING BINDERS

The important function of the binders is to bind the pigment particles to each other and to the paper or board surface very firmly so that during drying, calendering, etc. the coating will not be removed. Apart from this major role, the binders also influence the rheology of the coating, and some of the important properties like brightness, opacity, gloss, printing properties, dusting tendency, varnishability etc. depending upon the type of the binder, quantity used and certain other factors. Some of the important binders are given below.

A. Natural Binders

- i) Starches (oxidized, cationic, dialdehyde etc.).
- ii) Casein.
- iii) Soya protein.
- iv) Carboxymethyl cellulose etc.

B. Synthetic Binders

- i) Styrene-butadiene latexes.
- ii) Acrylic emulsions.
- iii) Polyvinyl alcohol, polyvinyl acetate etc.

Natural Binders-Starch

Like cellulose, starch is a high polymer compound made up of chains of anhydro glucose residues with alpha 1-4 linkages. It has two different types of polymers. These are straight chained linear amylose molecules and branched amylopectin molecules. (20-30% amylose and the rest amylopectin). The amylose molecules contribute to the jellying characteristics of cooked and cooled starch whereas amylopectin molecules impart the cohesive and tacky properties.



If starch is cooked with water, the result is a thick viscous gel which would be quite unsuitable as a coating adhesive. So, various methods are employed to reduce the viscosity such as:

Thin Boiling Starch

These are also known as fluidity starches.

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They are manufactured by adding acid to a starch suspension and heating to a temperature below the gelatinizing point. After the required degree of conversion, the acid is neutralised and the starch filtered and dried. Acid hydrolysis tends to break up the branched amylopectin molecules, as a result the amylose fraction becomes more predominant and viscosity reduces. Acid modified starches are not very often used in coating.

Oxidized Starches

These are also known as chlorinated starches. These are prepared by suspending starch in water below the swelling temperature and treated with a hypochlorite solution with about 8% of available chlorine based on the starch and a slight excess of NaOH is added to control the pH (alkaline). When the reaction has proceeded to the desired level sodium bisulfite is added and the slurry is washed and filtered before drying. Starches with a wide range of viscosities can be made in this way. The solutions are clear and they donot tend to set up when they cool and age. Dried films tend to be quite hard so additives are often used to plasticize them.

Enzyme modified starches

These are prepared by shortening the starch chains by an enzyme to the desired level and then the enzyme is destroyed. Depending on the degree of action the viscosity is controlled.

Dextrins

These are prepared by roasting starches upto 400°F temperature to break down the molecular chains to reduce the viscosity. They are also known as British gums. They are soluble in cold water and their films rewet very easily. Hence, they are seldom used for the coating of printing papers.

Dialdehyde Starches

These are obtained by the periodate oxidation of starch. The dextrose units are broken up with the formation of two - CHO gps in C_2 and C_3 positions.



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In order to minimize the rewetting and solubilizing tendency of starch-modified starch films, are made. Formaldehyde, glyoxal and amino resins work as effective insolubilizers for improving the wet rub resistance.

Formaldehyde as a starch Insolubilizer

It is a cross linking agent for starch in various applications. The initial reaction takes place between starch hydroxyl groups and HCHO to form a hemiacetal, with the HCHO being rather loosely bound. The hemiacetal is stable in the pH range of 5-7. The full acetal (cross linking) occurs only at a lower pH.

Glyoxal as starch insolubilizer

i)

It also forms hemiacetals and acetals with starch and cellulose by crosslinking to impart excellent wet-rub resistance property to starch pigment coatings, The type of starch employed is the most important variable affecting the degree of wet rub resistance which has been illustrated in Table V.

Amino resins (Melamine and Urea resins) as starch insolubilizers

These are the polymeric intermediates formed by the condensation polymerization of formaldehyde with urea and melamine. These are heat sensitive and are called as thermosetting polymers. The three principal reactions that take place in their manufacture are :

The HCHO adds to the amino compound to give a methylol intermediate.

 $R-NH_2+HCHO \rightarrow R-NH-CH_2OH$

- ii) The methylol intermediate condenses with a free amino group forming a methylene bridge. $R-NH-CH_2OH+H_2N-R \rightarrow R-NH-CH_2$ -HN-R+HOH
- iii) This addition involves the alkylation step in presence of an acid. An excess of alcohol is used so as to suppress the competing self con-



Dialdehyde unit

Type of Starch	Glyoxal %	Coating viscosity	Wet	rub resistance
	on dry starch	CP. Brookfield (No. 3 spindle, 10 rpm)	Air dried	Cured 10 min at 110°C
Hydroxyethyl	0	2320	5	8
J - J - J -	2.5	3980	83	88
	5.0	5560	91	97
Oxidized	0	3340	3	6
	2.5	4720	26	57
	5.0	5480	54	73
Enzyme converted	0	1200	2	4
	2.5	1400	35	75
	5.0	2400	55	9 5

TABLE – V EFFECT OE GLYOXAL INSOLUBILIZER ON PROPERTIES OF VARIOUS STARCH COATINGS.

densation. After neutralization the excess alcohol is stripped off.

 $\begin{array}{l} R--NH--CH_{2}OH+HOR^{1} \rightarrow R--NH--CH_{2}-\\ OR^{1}+HOH \end{array}$

The most popular type of resin for insolubili-Zation of paper coatings has been the methylolated melamine formaldehyde compositions.

Reactions of Amino resins as starch insolubilizer

The principal reaction involved in the insolubilization process is the reaction between methylol group of the thermosetting resin and the hydroxyl group of the starch.

S-CH ₂ OH	+Resin-CH ₂ OH	$I \rightarrow S - CH_2 OCH_2$
-	-	-Resin+HOH
(Starch)	(Resin)	(Starch-resin)

By this reaction it blocks the water sensitive hydroxyl groups of starch. Apart from this there is also an apportunity for self condensation between resin malecules as well as cross linking between binder molecules.

Casein

It is a protein adhesive. It constitutes about 3 % by weight of milk and is obtained by precipitation with either mineral acid such as HCl or H_2 SO₄ or lactic acid. The type of acid used is not important but a pH of 4.5 is important as it is the isoeletric point at which casein is precipitated. The precipitate is washed free of all traces of minerals, lactose and fats. This operation and the quality of milk govern the quality of the finished product. After washing, it is centrifused to about 50% water content and then dried slowly at 150°F to about 12% moisture content. It is ground and sieved through screens of various sizes to the customer specifications.

Chemistry of Casein

The chemistry of casein is quite complex. It is a globular amphoteric heterogeneous phosphoprotein, generally regarded as a polypeptide condensation of amino acids with the elimination of water. Most authorities consider it to consist of chain like compounds united through the peptide linkage as

Where R can vary according to the individual amino acids. A polypetide chain typical of those found in casein has been symbolically represented as below.



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The alpha amino acid residue is enclosed by the dotted lines. The side group R may be -H— CH_3 , $-CH_2$, $C_6H_6(CH_2)_4NH_2$, CH_2COOH etc.

Solvents or cutting agents for casein

There are many alkalis which can be used alone or in combination but practically about 6 of them are used. They are :

i) Amonia ii) Borax iii) Soda ash iv) Caustic soda v) Trisodium phosphate and vi) Disodium phosphate.

The first two are effectite solvents and are mostly used. In dissolving casein, it is common practice to use more solvent than is necessary to produce a natural solution. The amounts of the various solvents necessary for a natural solution and also the quantities used in the actual mill practice are given in table VI.

Casein can be dissolved in three different ways.

i) As a seperate solution.

- In the presence of a pigment at fairly low viscosity in a high speed mill (Kady or Abbe mills)
- iii) In the presence of a pigment at high viscosity in a kneader type mill (sigma blade or Z type bar)

Fromaldehyde as a Protein (casein) insolubilizer

Formaldehyde probably reacts in various ways with proteins, but the insolubilizing effects obtained can be represented by the following two reactions.

i) The HCHO reacts with the free amino groups of the protein (prot) to give a methylol compound and thus blocks the hydrophilic amino groups.

 $Prot-NH_2+HCHO \rightarrow Prot-NHCH_2OH.$

ii) Further cross-linking of the methylol compound with another protein molecule takes place as: Prot-NHCH₂OH + Prot-NH₂ \rightarrow Prot-NH CH₂NH-Prot + HOH

(cross-linked protein)

Formaldehyde has been applied as a wash coat or as a gas to insolubilise protein coatings, but at the present time these treatments are used only to a limited extent.

Glyox1l in protein coatings as an insolubilizer

Glyoxal reacts with casein, soyaprotein and animal glue and can be used to provide good wetrub resistance to coated papers containing these binders. The possible mechanism is given as below.

2 Prot-NH₂ + CHOCHO→Prot-N : CHCH : N-Prot + HOH (cross linked protein)

About 3-5% (active) glyoxal on the weight of protein gives good wet rub resistance.

Amino resins as protein insolubilizers

The primary reaction that takes place can be given as :

$$\begin{array}{c} Prot-NH_2 + Resin-CH_2OH \rightarrow Prot-NHCH_2 \\ - Resin+HOH \end{array}$$

(protein-resin).

Apart from this various other reactions of the reactive groups of amino resins can take place.

Metal salts as protein insolubilizers

Divalent and polyvalent metal ions have been used to improve the wet rub resistance of paper coatings containing such proteins as casein, animal glue and soyaprotein.

Advantages of Casein as a binder

Case in is a superior binder in many respects As compared to starch, it is a better adhesive. However, it is a very costly product. Where water proofness, durability and appearance of coated paper are of importance, case in is extensively used even at high price levels. Some of the properties posses-

S.No.	Solvents	Solvents requirements, (c	on O.D. basis of casein)
		For neutral solutions, %	Common Mill practice%
1	Ammonia	5.2	6-8
2	Caustic soda	3.5	4-6
3	Soda ash	4.6	6-12
4	Borax	14.7	.15
5	Trisodium phosphate	12.3	12-14
6	Disodium phosphate		14

TABLE—VI SOLVENTS FOR CUTTING CASEIN

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sed by case in which make it a good binder are :

- i) Suitable and stable viscosities at medium solids concentration.
- ii) Good adhesive strength and pigment binding power.
- iii) Good film forming properties and hence good ink, varnish and grease resistance.
- iv) Moderate degrees of insolubility easily attained.
- v) Good finish after calendering.
- vi) Good water binding characteristics.

Soya Protein

It is insolated from soya beans. The beans contain approximately 40-44% protein and 20-22% fat. They are cracked, dehulled and then flaked before the fat is extracted with hexane. This oil free meal is treated with alkaline solutions to take as much as possible of the protein contained therein into solution. The dissolved protein is then separated from the liquor extract by the addition of an acid, such as H_2SO_4 . The acid is added to the liquor extract in sufficient amounts so as to bring it to the isoelectric pH. This precipitates the protein as a curd which is then washed, filtered, dried, ground and then bagged.

The different types marketed are unhydrolysed, hydrolysed, chemically modified and enzyme digested. In use and solution they are similar to casein, although each has special properties. They are light brown powders which contain from 80 to 90% protein.

Isolated soyaprotein solutions

The commonly used alkalies are soda ash, ammonia, caustic soda, and borax. These alkalies are used in different combinations and some of the important typical combinations are as follows :

100	100	100	100	100	100	100	100
12		—	<u> </u>	8	—	_	· ·
	— ,	3.5	3	—	—	3.5	3.8
_							
2	10	6	5.4	4	11		8
	5		3.3	<u> </u>			<u> </u>
	100 12 	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Use of different insolubilisers

Formaldehyde, glyoxal, amino resins and certain divalent and polyvalent metal ions have been used as the insolubilisers to improve wet rub resistance or to develop water proofness. The mechanism of actions with different chemicals is the same as that described for casein. The properties developed by glyoxal casein and glyoxal soya protein coatings has been given in Table VII.

Advantages of soyaprotein as a binder

Some of the important properties of soya protein as the binder are listed as below :

- i) It is as effective as case in in adhesive power.
- ii) It gives better flowing coating color. Hence improved coating spread or application is possible as compared to that obtained with casein.
- iii) It develops improved wet rub resistance with the different insolubilisers.
- iv) It gives fine printing characteristics when used as a binder. The bulk portion of the binders

used for Washable wall papers are soyaproteins.

Carboxy methyl cellulose

Sodium carboxy methyl cellulose is commonly

TABLE-VII

Insolubilizer. %	Coating color Viscosity, cp Brookfield No.3 spindle 60rpm	Brightness,	%	Wet rub resistance T. UM 462
Glyoxal-Casein 0	3680	79		10
1	7870	78		23
3	7740	78		86
- er e i i i i i i i i i i i i i i i i i	9000	78		98
Glyoxal-Soyaprotein				
0	1470	79		4
1	1910	78		18
3	1850	76	··· ··.	89
5	2010	76		97

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known as CMC or cellulose gum. It is avilable in several grades varying in viscosity, degree of substitution and purity. The more common types (carboxy methyl substitution 0.7 or higher) are free flowing white solids which are soluble in hot or cold water.

Production of Sodium Carboxy Methyl Cellulose

It is produced from pure wood pulp or cotton linters pulp by alkali treatment to produce alkali cellulose followed by reaction with sodium monochloracetate. Sodium chloride is formed as the byproduct of this latter reaction. The typical reaction may be represented as: imately 1 % solids and very viscous of solutions at lower concentrations. They are very effective where it is advantageous to increase the viscosity of solution. Other products made from celluloses with shorter chain lengths are less viscous and can be used with higher concentrations. It is possible to prepare 10-15% solids solutions with some commercial products. The effect of temperature on viscosity is appreciable and the viscosity decreases as the temperature increases. Also, as the pH increases the viscosity drops.

Uses of CMC in coating

Apart from its numerous other uses, CMC finds some place in coating. Its use as the binder



The glucose units in the cellulose have 3 reactive hydroxyl groups in 2, 3 and 6 positions. Hence, it is theoretically possible to introduce a maximum of 3 carboxy methyl groups per glucose unit. Such a product would be said to have a degree of substitution of 3. The degree of substitution reported for a commercial product is actually an average figure. A purity of 99.5 + % CMC are commercially available.

Solubility of CMC in water

The more common types of CMC available have a degree of substitution of 0.7 or higher and are soluble in hot or cold water. Somewhat lower substituted types are soluble in 5% NaOH solutions and below about 0.2% substitution, sodium carboxymethyl cellulose is insoluble in water and water solutions.

Factors affecting viscosity of CMC Solutions

The Important factors affecting viscosity of CMC solutions are, a) degree of substitution b) concentration c) temperature and d) PH. Products made from high viscosity celluloses without degra dation have high viscosities at low concentrations. These may be gels at concentrations above approx-

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has very limited applications. However, it is used mostly as the modif er or additive in coating formulations where other binders are used. Some of its main uses in coatings are :

i) As a viscosity increasing additive.

2) As a water retention agent etc.

SYNTHETIC BINDERS

Some of the important binders of this group include the latexes formed by the polymerization of monomers such as styrene, butadiene, acrilonitrile, chloroprene etc. and also include polyvinyl alcohols and polyvinyl acetates.

Manufacture of synthetic latexes

These are manufactured by the emulsion polymerization process. The monomers either alone or mixed are charged into a pressure vessel with water and an emulsifying agent. The monomers may be added all at once or step wise. As an emulsifier a single compound or a blend of two or more compounds may be used. This emulsifying agent is very important since it profoundly influences the coarse of the reaction and the mechanical stability

of the final product. In some instances polymerization accelerators may be controlled by the use of chain stoppers

The degree of polymerization and the molecular weight of the polymer are influenced by the additives, the temperature and the pressure of polymerization. In addition, the monomers and their ratio to each other and also to the amount of water are important. As so many variables are involved in the manufacture of latexes, they will vary in properties from one manufacturer to another unless all the conditions are kept exactly the same.

General properties of latexes

These are usually milky in appearance and posses characteristic odour. The odour results from the content of monomers and low molecular weight polymers that is charactəristics of the products of emulsion polymerization. Although, they consist of dispersions of 30-60% solids in water, they are generally water thin. The usual range of particle size is from about $0.1-0.2/\mu m$. The dispersions are usually stable and can be stored for over longer periods of time. Upon exposure, to atmosphere, there is skinning over.

Most of the synthetic latices are anionic but a very few of them are cationic which are not in general use. Because of the electrical charges on the particles latexes are some what sensitive to electrolytes. As is normal with the colloidal systems, synthetic latex will tolerate relatively large amounts of the monvalent ions (i.e. Na⁺, K⁺.) However they are readily coagulated by divalent and trivalent ions (i.e. Ca⁺⁺, Mg⁺⁺, Al⁺⁺⁺) The degree of sensitivity of a latex to these ions is largely influenced by the method of manufacture. Once a latex is coagulated it can not be redispersed to its previous condition.

The styrene butadiene copolymer latex which is being used in relatively large quantities commercially, as a paper coating adhesive can be considered as a typical latex. Its physical characteristics have been given in Table VIII.

Synthetic latexes as Coating Binders

Latexes have approximately the same adhesive strength as casein and it can be substituted on a 1:1 basis These are stronger binders than starch. Although, latex can be used as a sole binder, in most of the cases, it is used alongwith the natural binders for reasons of cost as well as for the properties imparted to the sheet. some of the advantages in favour of the use of latex are :

- i) It lowers the viscosity of the colour, with the conventional adhesives so that higher solids can be used.
- ii) It can be used as received and does not require cooking or dissolving, although for some applications it has to be stabilized with about 3 % casein to prevent coagulation under mechanical shear.
- iii) It contributes to more uniformity in the coating color and the coated paper.
- iv) The finishing operation is aided and gloss and smoothness are more easily obtained.
- v) Dusting on super calenders is reduced, and the coating is more flexible, so that cracking and flaking on folds and score lines is also reduced.
- vi) Better dimentional stability is achieved and curl is reduced.
- vii) Better printing is usually obtained and ink and varnish holdout is improved.
- viii) Wet rub for lithographic papers is enhanced although, other agents are usually necessary.

TABLE-VIII

PHYSICAL CONSTANTS OF A TYPICAL STYRENE-BUTADIENE LATEX

S No.	Particulars	Values
1.	Solids by weight, %	48+0.5
2.	Water by weight. %	52+ 0 .5
3.	Sp. gravity at 25°C.	1.05
4.	pH of latex	10.5 + 1
5.	Viscosity at 25°C, cp	28-30
6.	Average particle size micron	0.2
7.	Surface tension at 25° C. dynes/cm	37.5
8.	Specific gravity Of solids	1.02
9.	Refractive index of solids	1.565
10.	Styrene : Butadiene ratio	60:40

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Polyvinyl Alcohols

These are water soluble synthetic resins having unusually high tensile strength and when plasticized excellent flexibility. They are nontoxic, practically odourless and produce colorless transparent tough films. Films and oatings made from these resins are unaffected by animal and vegatable oils, grease, and most organic solvents and are impervious to practically all gases. These are the important properties which recommended the use of polyvinyl alcohols in the paper industry as sizing, coating and binding materials.

Production of Polyvinyl alcohols

In the manufacture of polyvinyl alcohols, acetylene and acetic acid are first reacted to form vinyl acetate which is then polymerized to polyvinyl acetate. This on hydrolysis gives polyvinyl alcohol. The reactions can be represented as follows.



Polyvinyl alcohols as Coating Binders

The high viscosity completely hydrolysed grades of polyvinyl alcohol offer outstanding advantages as binders in pigmented coatings for paper. It is such a powerful adhesive that as little as 2-5 parts is sufficient binder for 100 parts of pigment. It is interesting to note that polyvinyl alcohol bound coatings which exhibit as low a "pick "test as" 2" print very well. Aqueous coating mixtures containing polyvinyl alcohol flow on smoothly when applied by ordinary coating machines. They form tough, flexible coatings on paper which show little tendency to curl, even under extremely humid conditions.

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Polyvinyl alcohol starch mixture containing relatively small amounts of the former are of particular interest, since even 1 part of polyvinyl alcohol to 20 parts of starch give marked increase in film strength. Polyvinyl alcohol tends to increase rather than diminish the brightness of white coatings, and it also improves the printing qualities of paper.

COATING ADDITIVES

These may be defined as substances which are added to the coating mix to enhance optimize or improve the coating layer properties or to remove operating problems during the preparation of coating color, its application, drying, calendering or finishing stages. Thus, all materials excluding pigments, adhesives and vehicles are broadly classified as additives. These additives include the following.

1) Dispersants

These are the compounds when added in small quantities improve the rheology or the flow properties of the pigment slip. The most important ones fall into the following five broad classifications.

- i) The polyphosphates.
- ii) The alkali silicates.
- iii) The alkalies (rarely used as sole dispersants)
- iv) The anionic polymer dispersants (Auxiliary dispersants)
- v) The nonionic polymer dispersants.

Mechanism of ionic dispersant action

The common dispersants ionize when dissolved in water and these ions are preferentially absorbed from the solution on to the surface of the pigment particles. As a result of this adsorption the particle receive an electrostatic chargeequal to the charge of the adsorbed ions and it is localized at the particle surface. The magnitude of the charge depends upon the number of ions absorbed and up-on the charge of each ion. The dispersant in solution furnishes both positively and negatively charged ions. The pigment particles adsorb and remove a number of ions of one charge and leave an equal number of ions of opposite charge in solution. The net balance of charges is not affected but the action of the dispersant causes a redistribution of the charges. The ions on the pigment surface attract the oppositely charged ions that are excess in the solution and they cluster around the pigment particles. Thus, ionic electrical double layer is formed which can be shown as follows :



the — ions adsorbed on the particle surface uniform distribution of+and — ions.

The excess ions in solution as a result of the adsorption of oppositely charged ions on the Pigment surface are called counter ions. The counter ions will not attach themselves to the oppositely charged ions on the surface inspite of the strong electrostatic attraction. The factors that caused the dispersant to ionize make the separation of these ions a stable condition. The creation of this electric double layer stabilises the dispersed pigment particles.

Protective Colloid Mechanism

The nonionic polymer diapersants and/or surfactants mostly consist of condensation products of fatty alcohols and ethylene oxide. In this the more hydrophobic end of the surfactant molecule attaches to the pigment surface while the hydrophilic polyoxyethylene chains project in to the aqueous phase. These projecting chains produce a layer of sufficient mechanical strength around the particles that the collisions that occur between particles do not permit the closeness of approach necessary for flocculation to occur. This has been termed as a "protective calloid" phenomenon.

Foam control agents

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Some of the chemical foam control agents are:

a) pine oil, b) Silicon emulsions c) Tributyl phosphate d) Higher alcohols etc.

Viscosity modifiers

The theology of the coating color can be modified to a great extent by the use of additives to accomplish such ends as increasing or decreasing the viscosity, changing the amount of thixotrophy or oven converting the flow pattern from Neutonian to pseudo plastic and soon. These additives are called viscosity modifiers.

a) Viscosity decreasing additives

i) Urea ii) Dicyandiamide iii) Esterified ethers of fatty acids iv) Latexes etc.

b) Viscosity increasing additives

i) Ethylene diamine ii) Diethylene triamine iii) Alginates iv) CMC v) Hydroxyethyl cellulose etc.

c) Laveling agents

These are the surface active agents used to control the surface tension of the coating color. Some of the compounds are :

i) Pine oil ii) Wax emulsions iii) Sulfonated oils iv) Soaps etc.

Water retention agents

These are the additives which improve the ability to hold water within ccatings after application and decrease the migration to the surface, or into the base shest. These can be also classed as hydrophilic polymers of hydrophilic colloids.

Most of them also function as binders, lubricants, protective colloids or dispersants. So all these functional properties must be considered before its section. Some of them are :

i) Inorganic polymers such as modified silicates.

- ii) Sodium alginates.
- iii) Polyacrylates.
- iv) CMC.
- v) Methyl celllose etc.

Lubricants

These are the additives which perform multiroles when added to the coating mix. Some of them are :

- i) Insoluble soaps and dispersions.
- ii) Soluble soaps.
- iii) Wax.
- iv) Sulfated and sulfonated oils etc.

Preservatives

These are the compounds which prevent or minimize the spoilage by microbial attack of a coating color. Some of the important compounds are:

i) Organosulfur compounds.

- ii) Organo halogens.
- iii) Heterocyclic nitrogen, compounds.

iv) Boron compounds etc.

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Colorants

These are used in aqueous pigmented coatings to produce a wide variety of colored coated papers. The principal colorants used in coatings are the highly dispersible colored pigments of both the synthetic organic and inorganic types.

a) Inorganic colored pigments

The most widely used inorganic colorants are :

- i) Chrome yellow (pigment yellow 34).
- ii) Iron Oxide pigments.
- iii) Molybdated orange (Pigment Red 104).
- iv) Cadmium red (pigment Red.

v) Prussian Blue (Pigment Blue 27) etc.

b) Organie colored pigments

These are considered to be the most important in aqueous pigmented coatings. There are a number of compounds which fall in the following categories.

- i) Azo pigments.
- ii) Phthalocganine pigments.
- iii) Vat dye pigments.
- iv) Thio indigo pigments.
- v) Anthraquinone pigments etc.

c) Lakes

These are organic colorants derived from water soluble acid, basic or direct dyes, made insoluble by treatment with suitable inorganic or organic compounds. Some of the important colors are :

- i) Reds (pigment Red 81).
- ii) Violets (pigment, Violet 3).
- iii) Blue (pigment Blue 1, 2, 14, 53)
- iv) Green (pigment Green 1)

d) Soluble dyes

These consist of acid dyes, basic dyes and direct dyes.

Insolubilizers

These reduce the water solubility or sensitivity of the pigment binders used in the coating colors so that dry pick improvement, dry rub improvement, wet pick improvement, wet rub improvement and water resistant properties are developed. The different types of compounds and their reaction mechanisms has already been given earlier.

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End use modifiers

These are used to serve a number of purposes as listed below.

- i) Gloss ink holdout.
- i) Grease and oil resistance.
- iii) Water resistance.
- iv) Plasticizing and fold improvement.
- v) **Rewetting**.
- vi) Antistatic properties.
- vii) Electro conductivity.
- viii) Glossing and
- ix) Abrasion resistance.

Coating color preparation and some Typical Coating Formulations :

Coating color preparation

a) **Preparation of the pigment slip**

The Procedure for the pigment dispersion is as follows :

- i) In the dispersing unit take required quantity of water+alkali so that the pH will be around 8.5-9.0
- ii) Wetting agent to be added.
- iii) add dispersing agent.

b)

- iv) Add pigment gradually. The final solids will be more than 65-70%.
- v) color pigments and dye etc. to be added, if needed.
- vi) Lavelling agent to be added.
- vii) Plasticizer, whitening agent and lubricants to be added.

All mixed well, till a uniform rigment slip will be formed.

Preparation of Binder Solution

(In case of proteins)

Required quantity of water+ pine oil+protein to be added gradually under agitation. To this, urea, borax, TSP and NH_3 are to be added in the required quantities. Continuous agitation and heating helps in reducing the swelling time. The final pH should be around 9-9. 5.

c) Addition of the Binder to the pigment slip

The binder has to be added to the pigment slip under constant agitation but not the latter to the former to avoid the protein shock.

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After this hardening agent to be added. The coating color should be screened and kept in a vessel having slow agitation. The synthe tic binder component has to be added just sometime before the use. A finall screening may or may not be necessary.

Some Typical Coating Formulations

Some typical binder formulations for various paper grades are given in Table IX. It is found that acrylic based latexes are used extensively for the production of LWC rotogravure papers whereas styrene-butadiene type latexes find wider applications in the offset sector. Some main properties of coated papers are given in Table X.

The knowledge of the different coating color components, their properties and different reaction mechanisms and reactions involved during preparation or use of the coating colors will definitely help in either selection or formulation of a typical coating color depending on the end use requirements.

TABLE-IX

SOME TYPICAL BINDER FORMULATIONS

Particulars	Sheet offset			Wet offset		Gravore
	All latex	Latex/PVOH	Latex/starch	All latex	Latex/starch	
Pigment	100	100	100	100	100	100
Latex	12-14	9-11	8-15	10-11	6-8	5-7
Starch		<u> </u>	2-8		4-8	
PVOH		2-3		·		
Hydro colloid	1			1		1

Ref. : TAPPI 63 (3) : 59 (1980)

TABLE-X

PROPERTIES OF MAJOR COATED PAPER GRADES

Properties	Wood free			Mechanical	
	Art	Standard	Matt	Web offset	Rotogravure
Gloss	65-75	60-70	7-35	50-60	50-70
Brightness (ISO)	80-85	78-85	78-87	68-70	. 68-72
Opacity	94-97	89-93	91-95	89-91	90-9 3

Ref. : TAPPI 63 (3) : 59 (1980)

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