Paper Colouring and Whitening

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Introduction

Colour is the sensation produced on eye. The pleasing appearance required of the finished paper depends very largely upon the proper colour or whiteness imparted to it.

The colouring of different substances has engaged the attention of man from the earliest age. Records of the colouring go back as far as the year 2000 B C.

With the beginning of manufacture of handmade papers, it is recorded that vegetable stains and minerals were used for colouring purposes.

Many of the earliest Chinese papers were coloured yellow by colour derived from Phellodendron amurense and a 7th century edict specified that it should be used in all religious and other important documents. As reported by Hunter in 'HISTORY AND TECHNIQUE OF THE ANCIENT CRAFT OF PAPER MAKING' the yellow colour was used not for aesthetic reasons but to protect them from insect and mildew attack.

Before we peep in to the history of paper making let us examine the definition and theory of dyeing.

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Dyeing may be defined in simple words as the act of colouring or to be most precise changing the colour of any material.

The colour of paper, like that of all other substances, is due to differential or selective absorption of different wave-lengths present in the incident white light. The incident light penetrates a small distance into the body of the paper, and undergoes some absorption, and is then reflected in diffused form. Colour of paper is determined by the reflected light, that is the wavelength least absorbed by the paper. If the paper absorbs chiefly yellow and red, it will appear blue.

Paper making has progressed in the previous 1000 years from a very laborious manual process gradually to a highly sophisticated capital intensive continuous sheet making process, but untill the beginning of sixties the principles of Korean established methods were used in most paper mills. Till dyes were added in the form of solution or dispersion to stock before the web formation and dyeing operation was considered a separate operation.

During the last decade the importance of batchwise addition of dyes, Optical Brightening Agents (OBA) and other chemicals to the beater, hydrapulper or machine chest has been felt and that it has been fitted in well with the craft of paper making. During this period advances in refining, continuous processing control instrumentation etc. have become proven and established with full scale production units. This has led to increase in rate of production not only in the case of new machines but in the case of old machines by alterations and modernisations. With increase in speed the emphasis changed to continuous processing and control. Even the traditional method of batchwise addition of dyes and OBAwere re-examined and it was found that traditionally long contact times between the dye and the pulp-known as 'beating-in' of the dye were in most of the cases unnecessary. The experiments were made and as reported by HINTON in 'APPITA (1966) conference proceedings' if dye or OBA was added at a suitable addition point a contact time of 1 m. with continuous addition of dyes and OBA would give results similar to traditional batchwise dyeing method of one hour or more contact time results. It has now been accepted principally and established practically that a short time dye or OBA contact was adequate for all except the deepest colours shades.

Lately use of applying OBA and even dyes to the surface of paper than at the wet-end is reported, and greater attention is now being given to surface application. This is in part a reflection of the current emphasis on the protection of the environment; thus if the technical effect i. e. colour can be achieved by surface application the problems of retention of effect chemical i.e. dye on the fiber are considerably lower than in wet end addition. Thereby the pollution load is minimised.

For the sake of convenience we shall discuss the wet-end dyeing and surface application dyeing separately.

Wet-end Dyeing

The mechanism of dyeing depends on the nature and structure of both dyes and fibres. Vegetable fibres are built up from long chain molecules having crystalline regions known as crystallites or micelles, and amorphous regions mainly due to hemicellulose. When placed in water, the fibers swell in the amorphous parts producing open pores, large enough to permit the passage of dye molecules which then diffuse along the parallel chanel in the miscellar region and are attached by hydrogen bonding (FINAR K. L.-Organic Chemistry Vol. I)

Dyeing in the pulp (BEATING-IN) is the most widely used method. Most dyes and OBA are applied to the pulp slurry before the pulp goes on the wire to form a sheet. When the dyes and sizing materials are added in the paper stock at the wet-end before sheet formation, the dyeing efficiency is greatly influenced by :

1. Nature of the pulp fiber used.
2. The type and the amount of sizing materials added and, particularly with OBA performance.
3. The type and amount of retention aids added.

And in light of the above it is not surprising that some of the most interesting and relevant study results on the aspect of dye absorption on paper fibers have been those investigating the sizing process.

The colouring matters generally used in colouring paper are broadly classified in to two classse : (1) DYES (2) PIGMENTS. Dyes are further classified in three classes: (a) ACID (B) BASIC (C) DIRECT.

The choice of dye depends largely on the properties required in the finished sheet and on economic factors. Generally speaking, only direct dye on bleached pulp and basic dye on unbleached pulp are adequately retained in the absence of other 'mordanting' or fixing chemicals such as rosin size, paper maker's alum, electrolytes, retention aids, dye-fixing agents, etc.

If the dye or OBA possesses substantivity for the fiber, straight forward adsorption process takes place, although probably incompletely in normal mill practice, this process will be negligible with weakly substantive (acid) dyes, but important with substantive (direct) dye. This is the first process.

If conventional sizing materials (rosin size and alum) are then added, a charged dye-rosin-alum colloid complex is produced; the adsorption of which on the pulp fiber forms the second stage of dyeing process.

The importance of surface chemistry in studies relating to properties of suspensions of pulp fibers is suggested by the fact that gm. of I beaten pulp fibers may contain 8 million individual fibers, ranging in length from 3.0 to 0:3 mm and possessing a total surface area variously estimated to lie between 5,000 to 50,000 sq.cm. (CHASE, TAPPI, 43 No. 8 (1960) 197a)

Various workers have worked on the surface chemistry of suspension of pulp fibers-equilibrium of dye uptake-the nature of the charge on the fines and longs fractions of beaten pulp. HINTON & QUINN, in studying fiber surface characteristics in relation to the problem of two sided dyeing of paper examined this using a simple electro-osmosis technique, and concluded that the fines possess a more highly charged surface than the longs. The recorded zeta potentials were :

Although results of the studies of what happens as the dye as ions approaches the fiber are now known the reason for the differance in the substantivity between direct and acid dyes is less well understood. It has been suggested that the forces that cause direct dye to aggregate in solution, a phenomenon that occurs to a much less degree with acid dye, must play a part.

We have discussed the mechanism of dyeing at the biginning of this wet-end dyeing subject and have mentioned that the behaviour of dyed fibers towards plane polarised light would seem to support the idea that the dye lies lengthwise along the cellulose chain, and the exothermicity of dyeing ($-\Delta H = 10-30$ Kg cal/mol.) indicates atleast two H-bonds per mol. of dye. However some dyes (e. g, Benzidine dyes) appear to diffuse in to cellulese perpendicularly rather than parallel to the fiber axis. As reported by CETOLA & BORRUSO-FUNDAMENTAL ASPECTS OF FIBERS (PAPER) SYMPOSIUM, 1957, evidence suggests that some direct dyes, e.g. Congo Red, Benzo Purpurine 4B. Chicago Blue 6B, and Direct Blue 2B enter the amorphous regions of paper fibers and so plasticise the structure; this is found to accelerate beating.

So to summarise the most important variable affecting dyeing in the absence of sizing agents are :

i—Source, nature and state of fibrillation of pulp.

ii– dyes under consideration.

iii–nature of the water pH & hardness).

In light of the above studies we can safely regard dyeing as a two stage process: (a) attraction of the dye to the fiber close enough for dyeing to occur, and (b) the dyeing or attachment of the dye to the fiber.

The first of these two processes is assisted by:

(a) increasing the degree of the pulp by beating, which increases both the specific surface area for dye adsorption and the electronegativity of the fiber.

(b) decreasing the fiber length (cutting) by means of beating which increases the specific surface area.

(c) decreasing the pH, which depresses the ionisation of either the dye or the electronegative groups in the cellulose, thereby reducing repulsion between dye and fiber.

(d) adding electrolyte (in case of dyeing in hard water), which also reduces the repulsion.

The second process–the attachment of the dye to the fiber is dependent upon the spatial geometry of the dye molecule and the position of groups that can form bonds with the cellulose structure, and broadly explains the difference in performance between direct and acid dyes in paper making.

The above ideas explain most of the phenomena observed in colouring absoarbent soft toilet and table napkin tissues. With a few exceptions–e. g. C. I. BASIC BLUE 33, only direct dyes and OBA are suitable for dyeing toilet tissues, because on resins, dye–fixing aids or other additives are normally employed Looking to the marketing popularity of the shades, satisfactory dyeing performance. and experience of freedom from dermatological problems dyes are selected from the following :

Crysophenine G (C.I. 24859), Serius Yellow GC (C.I. 29000), Benzo Viscose Yellow RL (C.I. 29025).

Direct Fast Orange S (C. I. 29150).

Direct Fast Scarlet 4 BS (C.I. 29160), Direct fast Scarlet 4BA (C.I. 29185), Sirius Red 4B (C.I. 28160) 27905).

Direct Sky Blue FF (C.I. 24410) Benzo Blue BGS (C.I. 31635), C.I. Direct Blue 199.

As noted above, reducing the pH improves the retention of direct dye, but on the other hand the addition of alum imparts a hard feel to tissue, and to reduce absorbency; often therefore alkali is added to raise the pH to 7.5–8.5 to improve softness and absorbency. This practice may result in higher dye coats or need to use dye–fixing aids to improve dye retention.

Although it has been recorded above that decreasing the fiber length by beating improve dye retention, the replacement of lightly beaten long-fibered pulps by short fiber pulps, e. g. the soft wood sulphate with soft wood sulphite hardwood sulphate in toilet tissues increases by 20-40% the amou t of dye required to achieve the given colour shade. In this respect, sulphite pulps are worst than sulphate pulps. It is not however clear whether the differance results from reduced dye retention,or from differences in opacity between the different pulps.

DYEING IN PRESENCE OF SIZING AGENTS :

The term "sizing is a loose term. It is used to express resistance to penetration of liquids such as water, writing inks etc. In this sense, the term refers to a property of paper, but it is also used as descriptive of the process for obtaining resistance to liquid penetration.

The sizing agents used in the paper industry cover a wide range of materials, including animal glue, rosin size, synthetic resins, casein, polyvinyl alcohol, starch, wax emulsions, and many more similar substances. But more popular and conventional sizing is brought about by the addition of natural or modified, partially saponified or unsaponified wood rosins to the pulp slurry, followed by paper makers alum. A great deal of dyeing is simply lake production, that is the formation of an insoluble dye by precipitation of the dye with alum.

Since dyes are generally added before the sizes, a better understanding affecting rosin sizing should lead to a better understanding of dye fixation. On the basis of studies of the sizing the value of investigation related to surface-charge characteristics, and it is hoped that further work will extend the technique to study the behaviour of dyes in greater detail in both conventional and newer and modern sizing systems.

In the production of coloured and whitened sized papers therefore the dyeing process consists of two stages as established by HINTON in his review of progress in colouration (May 1972), 10-17.

i—The process of substantive exhaustion of dye, or OBA, but with a limited interval before the sizing agents are added followed by

ii–A process entailing adsorption of a charged colloidal complex comprising rosin, alum and dye or OBA, formed on adding the sizing materials, influenced by the dye or OBA itself (charge, substantivity, structure and solubility) the nature of the rosin size used (saponified, fortified or dispersed) and the amount of alum present, and other additives, both intentional (wet-strength resins, fixing aids and flocculating agents) and fortuitous (e.g. hardness salts).

MEERSMAN and KUKOLICH, proc. 14th Annual Pulp & Paper Conf. W. Mich. Univ. M 1431 (1970) 150.

Kletz has reported that when additions are made to a system of high pulp consistency, with sluggish agitation e. g. beater or machine chest) it is probable that the first process is incomplete even with substantive dyes. The second process is the most important one for dye adsorption on the sized papers and the dye ion itself plays an important role in influencing the charge on the complex and its ultimate attachment and adhesion to the fiber.

OBA may be considered similar to direct dyes in their substantivity for cellulose. Although the products currently employed are all based on similar structures (i. e. disubstituted 4-4-diamino-stilbene-2, 2 (-disulphonates), they may differ markedly in their under different condition of sizing owing to the influence of substituents in the triazinyl rings. More soluble compounds desired for products of OBA for application to paper, and in this connection there has been interest in the use of polysulphonated amines as one of the triazine substituents. One of the difficulties encountered in the paper-making industry with regard to OBA are the lower pH conditions which are often employed. A similar difficulty is associated with high quality finishing, and previous known Optical Brightners have often been incompatible with these acidic conditions. Careful but realistic testing is essential if the correct choice is to be made from the neumerous products available.

Although basic dyes are used widely for the colouring of unbleached furnishes because of their affinity for lignified fibers, particularly unbleached sulphite little information exists on the nature of dye adsorption. It is generally assumed that dyeing occurs by reaction of the dye cation with acid group present (e.g. carboxyl, hydroxyl or phenolic group) in the lignin of unbleached fibers, although reaction of the dye cation with the negatively charged rosin sol. is also thought to have an influence. The marked reduction in retention of basic dyes at low pH may be explained by a suppression of the ionisation of the acid groups in lignin or a tendency for H+ ions to replace the dye cation in the size colloid, thereby reducing the amount of dye finally adsorbed on the fiber.

Studies on the retention of pigments are even lesser than those on basic dyes, although it is traditionally that a pigment required 'beating in' in the fiber, and for this purpose it should be added as early as possible, so that it undergoes prolonged beating together with the stock. The longer the dye takes part in the beating operation. it is generally assumed that by better beating time the particle size of the pigment is further reduced, but most synthetic organic dispersed pigment pastes are having a controlled particle size distribution and are sufficiently small in average particle size for beating to have little or no effect. Since the pigment is expected to possess a negative charge retention on fiber by adding alum or cationic agents, thus reducing this charge. In the production of absorbent base papers for plastic lamination, the use of melamine resin, alum and sodium aluminate at pH 5.5-6.5, together with a polyacryamide filler retention-aid ensures adequate retention of pigments, even at heavy depths (e. g. 10-30%).

In practice the dyes used by a paper mill will be chosen to represent the best compromise between several factors-retention, cost, fastness properties, broke usability and bleachability, general runnability, ease of handling, protection of environment, pollution control etc. Normally, ease of handling with trouble free running is more important than low dyeing cost per ton as a reason for selecting particular dyes.

The problems of retention of acid dyes, and the secondary problems of reduced sizing, increased foaming and low water fastness in the dyed paper have led to their gradual repalcement by direct dyes. Direct dyes are of major importance in paper dyeing and are increasingly used instead of acid dyes, even though they may be more expensive, with the major benefit of improved stability on the machine, leading to increased productivity, outweighing higher cost.

Basic dyes, form the second main dye class, and the use of this class of dyes is confined mainly to the dyeing of unbleached or substantially unbleached, furnishes, for which their high brightness and tinctorial power and good substantivity are essential and the low light fastness of this class of dyes is no disadvantage.

In the use of pigments two hurdles or short comings come in the way. One is the problem of two sidedness which the use of pigment tends to promote, and the other one is generally inferior colour value in terms of cost and efficiency as compared to other water soluble dyes.

Pigments are used when particularly good fastness properties are required which otherwise cannot be achieved with water soluble dyes. C. I. Vat Blue-4 or monastral Blue XBV Pastes are frequently used in archival, bank, ledger and government papers where permanance is important. pigments satisfy an important need in colouring specialised grades of paper which is unlikely to be met by soluble dyes.

Advances in Sizing

Effect of newer sizing system on retention of dye is of importance to us to review the same here, When considered in the light of current conditions facing the industry these changes introduced as alternative to traditional methods are not only proving economically viable but also offer additional advantages. Take the example of alkaline-sizing system. This is an alternative to traditional 'acid' method (rosin-alum sizing). This new system not only answers to the printers' complaints about acid reducing the drying-ink drying time but also to provide added benefits in lowering the cost of whitening (better whitening value from OBA), reducing machine corrossion, improving the ageing resistance of paper (e. g. ledger and archival).

Surface colouring and Whitening

As discussed at the end of the topic-introduction–there are two main reasons for the attention to be given to the development of technique for the surface treatment and surface colouring and whitening of paper.

With the changing phase in the speeds and breadth of the machine a thought has been given to surface colouring and whitening with an objective to permit a series of colours to be run in quick succession at the end of a standard (white or a coloured) making, with a minimum of machine downtime.

The second main reason is the increasing attention being paid by rever a sewage–treatment authorities to the pollution caused by industrial discharges. This is providing additional impetus to studies aimed at achieving technical effects by surface treatment rather than by additing chemicals at the wet end. Surface treatment produces less total pollution and no problem of retention.

Many difficulties are faced in surface colouring and we have yet to hear of a foolproof method to achieve (1) uniform, non-patchy colour, free from orange peel' effect (2) proper fixing of dye to provide adequate water fastness.

In case sized base paper is taken a wetting out agent addition will be essential to overcome the sizing and to assist penetration of the dye. The coloured paper thus produced will be too absoarbent to be acceptable for writing or for printing.

Otherwise if an unsized base paper is used, both the colouring effect and the sizing must be achieved from a single treatment.

Many claims are reported on this line but much work has to be done on this subject to achieve at a popular method to overcome difficultles in surface colouring.

Howevr same problems are not faced when surface application of OBA is done, this is possibly because any non-uniformity in application is non-visible to the human eye and these flows if any can only be detected under ultra violet illumination. We find an increasing acceptance of this method of whitening, due mainly to development of improved qualities of OBA, greater stability of surface applied OBA to pH fluctuations, low cost of whitening as the OBA is applied only to the surface unlike wet-end addition where it is lost in thickness of sheet.

Lot more work is on the way and yet more work has to be done to study the newer methods of application of dyes and OBA to wet-end as well as surface applications.

The newer trends forecast much faster production of paper with automation in dye and OBA additions, quality suface sizing, dyeing and whitening.

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