Optical Whitening agents in Paper Industry

V. K. ATRE *

The Author has attempted to enlighten the role of Optical whitening agents in the high grade paper making. Optical whitening agents have great affinity for cellulose and they get fixed to cellulosic fibres directly from their aqueous solutions. The molecules of Optical Whitening Agents absorb the invisible ultra voilet radiation which is remitted in the invisible region. The Whitening agent can only enhance the whiteness of the Pulp which is already highly bleached. The whiteness imparted by an optical whitening agent to paper depends upon the solubilities of the agents, concentration and the wavelength at which the highest emergy emission occurs.

The author has also attempted to detail various methods of evaluation and laboratory testings of the whiteness.

Optical Whitening Agents, though of comparatively recent introduction play a very important role in the manufacture of paper of a high order of whiteness.

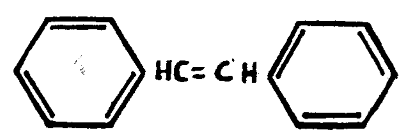
Many paper mills in our country have been incorporating Optical Whitening Agents in their better grade papers.

I would like to make a modest attempt in the brief time at my disposal to throw light on the function of the Optical Whitening Agents and the methods of evaluating their efficiencies.

What are Optical Whitening Agents ?

The common Optical Whitening Agents employed in the paper trade are pale yellow to off-white Organic Compounds which essentially belong to the class of substantive dyes or direct cotton dyes. It means that they have a great affinity for cellulose and they get fixed on to cellulosic fibres directly from their aqueous solutions. The most important chemical group present in their molecules is the system of conjugated double bonds like the stilbene group. It is this group which is responsible for the fluorescent nature.

Stilbene Group Structure :



The molecules of O.W.A., by virtue of the conjugated double bonds absorb the invisible ultra violet radiation and get existed to a higher state of energy with re-emission of light in the visible region. As some energy is lost in this process the re-emitted light is of longer wavelength, (lower frequency) than the absorbed light. To act as a brightening or whitening agent the compound must re-emit at the blue end of the spectrum, so that the emitted light is essentially complementary to the pale yellow. colour normally shown by 'white' cellulosic material.

However, it should be noted that the Ultraviolet content of the sunlight is limited. Therefore, a limited amount of yellowness only can be corrected by the optical whitening agent. Thus it can enhance the whiteness of the pulp which is already highly bleachd by chemical means. You will also notice that when all the u.v. radiations available in sunlight are already utilised by the optical whitening agents, any

*Hickson and Dadajee Ltd. Bombay

further additions of the whitener will not be of any help in increasing the brightness. On the other hand, it would result in what we call "quenching" or the suppression of the fluorescence by the intrinsic colour of the unexcited molecules. I hope you will now appreciate why too high concentrations of optical whitening agents are not advised because they defeat the very purpose which we want to achieve.

I should like to touch upon the solubilities of the whiteners which are attracting much attention during processing.

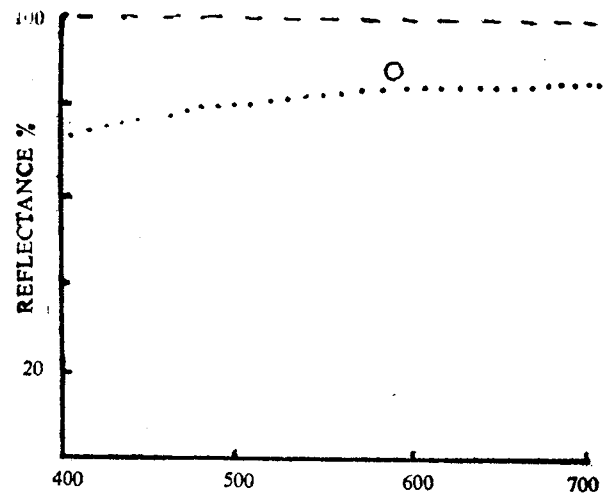
The solubilities of the various whiteners on the market for cellulosic fibres are between 2%—8%. As a general rule the less soluble the optical whitening agent the more substantive it is on the fibres, and more the substantivity, better are the fastness properties to light etc.

As such, effect of less soluble optical whitening agents on paper is likely to last longer than in the case of the more soluble ones. It will be seen that the quantities of the Optical Whitening Agents required are so small say 0.5 kg. to 5.0 kg. per tonne paper and the quantities of water handled are so enormous that the whiteners even if they are less soluble should not create any appreciable difficulties in the process.

The whitening effect given by the fluorescent brightening agents, therefore, is an additive effect. The yellow colour is corrected by the addition of blue light and the total light reflected from the material is greater than that from the untreated material. On the other hand the old blueing method by pigments, worked by a substractive process ; the blue pigment absorbed the yellow light equivalent to the blue light absorbed by the yellow colour of the untreated material. Although the material thus treated looked whiter, in fact, the total reflected light was much lower. Such agents were correctly designated as 'blueing' agents, whereas the fluorescent compounds are both blueing and brightening agents.

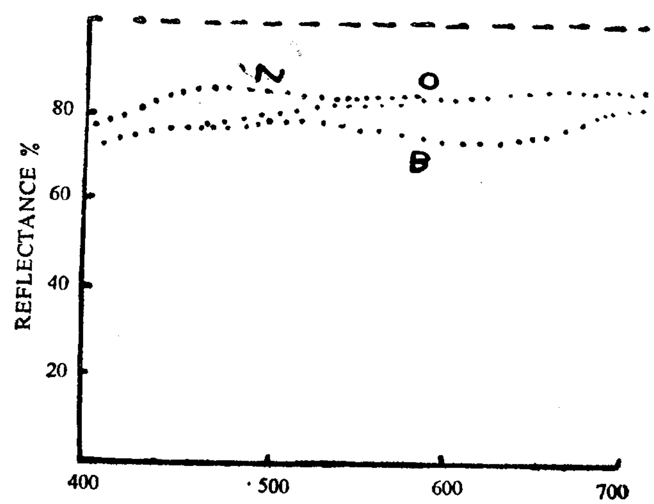
Figure 1 shows the reflectance curves, one of magnesium oxide, which is commonly accepted as a standard of whiteness and the other the paper made from chemically bleached but untreated pulp, (o). The curve for the paper is lower than that of

Fig 1 MAGNESIUM OXIDE



WAVELENGTH mμ

Fig 2 MAGNESIUM OXIDE



WAVELENGTH mμ

magnesium oxide indicating less brightness. The slope indicates the yellowness. Figure 2 shows the reflectance curves of : (i) paper made from untreated pulp (o), (ii) paper made from pulp treated with optical whitening agents (w) and (iii) paper made from pulp treated with a blueing agent (b). It can be seen that the overall slope of the curve is lessened in the case of (ii) and (iii), which means a decrease in yellowness. However, the height of (w) is more than that of (o) indicating a higher reflectance, while that of (b) is less. The blueing agent has rendered the paper less bright.

Shade of Whiteness :

The whiteness imparted by the optical whitening agents to paper will have different hues depending upon the wavelength at which the highest energy emission occurs. Figures 3 and 4 indicate the absorption curves and the corresponding emission curves of two typical brighteners giving red and green shades respectively.

Fig 3 ABSORPTION CURVES

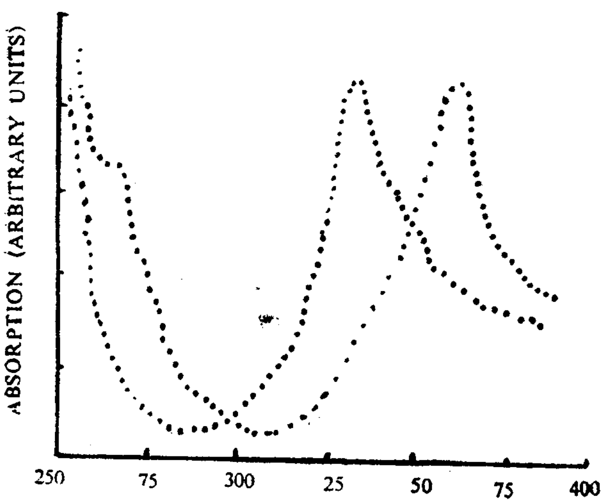
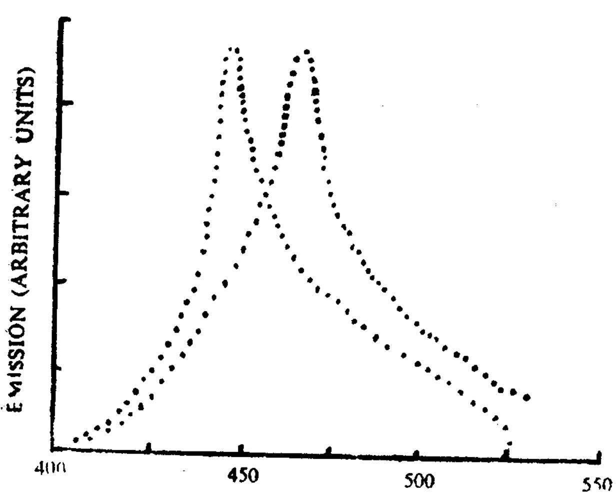


Fig. 4 EMISSION CURVES



Evaluation and Comparison :

The efficiency of an optical whitening agent is directly proportional to the fluorescence emitted by the treated material. Hence, the fluorescent brightness of papers made with different whiteners under similar conditions afford a measure of the relative efficiencies of the products.

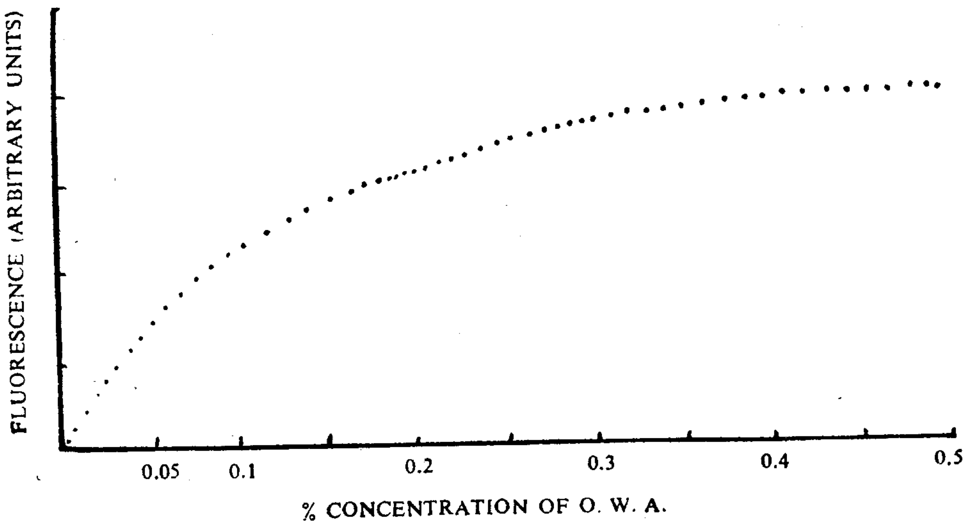
The assessment of fluorescence is by no means simple. Visual examination in day light would appear to be the answer. However, the human eye is highly individualistic. It soon gets fatigued and loses its sensitivity. Further, daylight varies in spectral quality from day to day and from minute to minute. As such, visual examination is not a reliable method of assessing fluorescence brightness.

Alternatively instrumental methods are adopted for this purpose. However, the instruments commonly employed in the paper mills for measuring the intrinsic brightness of chemically bleached pulp —such as the G. E. Brightness Tester—are unsuited for the purpose as the source of illumination in these instruments is a tungsten filament lamp which does not emit any u.v. light.

Various other instruments have been developed for the purpose based on the following principle. Ultraviolet light enanated from a mercury discharge long is passed through a filter to cut off the visible component and made to fall on paper treated with the O.W.A. The light reflected by the paper is passed through a.u.v. filter and made to fall on a photocell which is connected to a millivoltmeter or galvanometer and the readings are recorded. Readings are also similarly recorded for a piece of paper made from the same stock but not treated with optical whinening agent. The difference between the two readings will be a measure of the fluorescence which of course will be in arbitrary units.

Such an instrument is useful to a certain extent for the comparison of any two optical whitening agents. It can evaluate the fluorescence against concentration characteristics of a single optical whitening agent. It can also be used with fair accuracy for assessing the efficiencies of optical

Fig. 5



whitening agents which have the same absorption maxima.

Laboratory Testings :

Laboratory testings of optical whienting agents should be carried out on bleached pulp (thoroughly washed free from chlorine) using white water for diluting the furnish. Blueing agents should be avoided in the tests as these mask the effects of the brightener. The pH of the furnish should be adjusted with alum to the level prevailing in machine house at the point where the optical whitening agent is added. After beating, the optical whitening agent, rosin and alum are added in the given order to end up with the pH prevailing in the machine chest and paper sheets prepared. The sheets may be read on the fluoremeter and also visually examined.

Concentration vs. fluorescence data for a given optical whitening agent can be obtained by making paper sheets under similar conditions employing 0.05 to 0.5% of optical whitening agent on the weight of dry pulp. Fluorescence readings of the sheets are then plotted against concentrations. A typical curve is given in figure 5. As can be seen, at lower concentrations the increase in brightness is nearly directly proportional to the concentration, whereas at higher concentrations the ratio is no more linear. The concentration above which the proportionality starts deviating heavily from the linear should be the maximum economical limit.

Based on this data mill trials can be carried out.

Before I conclude I would like to emphasise that while selecting any O. W. A.s for papers it would be advisable to choose a more substantive product because the whitening effect would last longer.