Effective Utilisation of Optical Whitening Agents-A Fresh Look at the Theoretical & Practical Aspects

VENKOBA RAO G.*

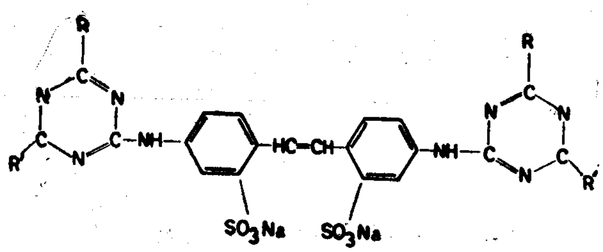
SUMMARY

In this paper, a comprehensive review on the optimisation of the dosage of the optical whitener is made. Basing on the extensive work done in our laboratories, an attempt has been made to elucidate the mechanism of action of optical whiteners. It is postulated that the mechanism of action of optical whiteners also involves atleast partly, the hydration of C-2 and C-3 Ketonic functions of the cellulose molecules catalysed by the protons of the sulfonic acid function present in the OWA molecule.

One of the most important optical properties of paper is the shade or colour of the paper : optical whiteners when added to paper absorb light in the ultra violet region and re-emit them in the visible range. The re-emitted light is in the blue end of the spectrum, thereby giving a bluish white tint to the paper that results in the optical compensation of the yellow cast. In this paper, we present a comprehensive review on the extensive work done in our laboratories, on the optimisation of the optical whitener dosage, and examine the implications of these results in the elucidation of the mechanism of action of optical whiteners.

The most common optical whiteners used in the paper industry are fluorescent compounds, which are mostly limited to *bis (1, 3, 5 - triazinyl)* derivates of *4. 4—diamino stilbene disulfonic acid*[1,2] (Fig. 1). Infrared spectral examination of the optical whiteners used in our work also, showed the presence of the sulfonic acid function in the molecules.

As the added optical, whitener offsets the natural yellow cast of the pulp, we explored the possibility of quantitative relationship between percentage of added optical whitener and the drop in yellowness[3,4]. Indeed, we found that there exists an excellent correlation between percent drop in yellowness and the added optical whitener dosage (Fig. 2).



TRIAZINYL DERIVATIVE OF 4, 4'-DIAMINOSTILBENE-2, 2'-DISULFONIC ACID

FIGURE-1

It is known that presence of diketone groups in the C-2 and C-3 carbon atoms in the glucose moieties of the cellulose causes reversible colour change (Yellow to colourless[5] (Fig. 3). The colour is similar to that of systems such as glyoxal, diacetyl, or benzil all of which are yellow in colour. The colourless form arises due to the hydration of the ketonic functions, and it is well established in literature that hydration of carbonyl compounds is general acid catalysed[6]. It is interesting also to refer to the fact that the corresponding alcohols of the above mentioned yellow ketones are colourless or white.

*The AP Paper Mills Ltd., Rajahmundry, A. P.

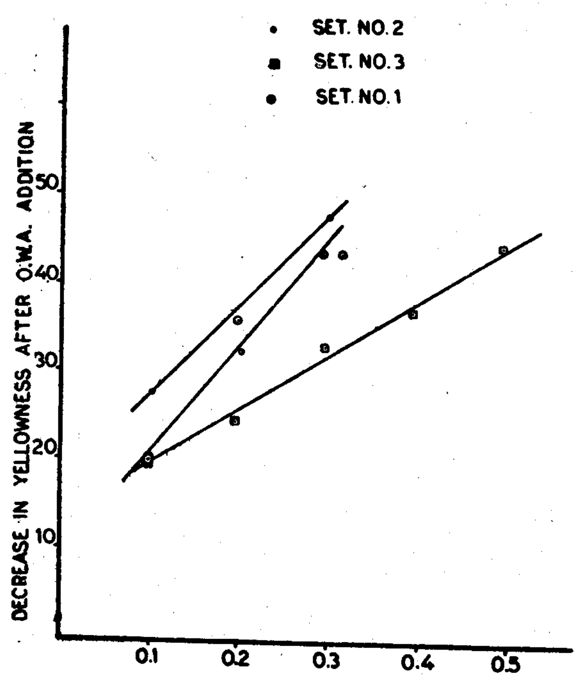


FIGURE_2

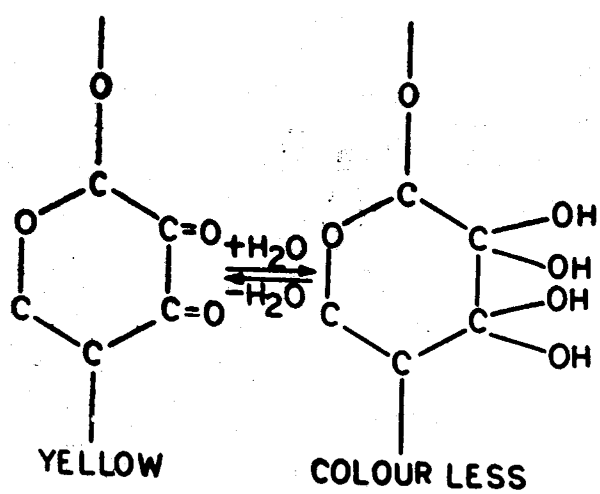


FIGURE_3

So, first our studies on the optimisation of optical whiteners were directed towards finding ou tsuitable reagents which will catalyse a better hydration of the ketonic functions as a result bringing down the yellowness and then the optical whitener dosage. In this context it is pertinent to refer to the various strategies suggested by Harkavy[7] on the optimisation of the use of these fluorescent optical whiteners which are relatively expensive. It should also be pointed out here that Harkavy's suggestions were more based on this experience and no quantitative data has been published to support these.

These strategies suggested by Harkavy are as follows :

1. Use of sulfuric acid with alum for sizing as aluminium ions dull or quench the brilliance of many optical whiteners.
2. Use of Polyphosphates or organic sequesterants.
3. Use of iron free alum or use of alum with low iron content.

With the basic idea of the hydration of ketonic functions catalysed by acids we have explored the possibility of replacing a part of the alum by sulfuric acid and thence the dosage of the optical whiteners[8]. The tristimulus reflectance photometry technique was used for the first time to monitor the dosage. The acid introduced will act as catalyst in the hydration reaction and thereby should bring down the yellowness.

In the alum blend used for sizing we have replaced alum by sulfuric acid upto 25% (weight basis) and the results of this study are presented in Table 1. It is evident from the results that on the replacement of alum by sulfuric acid, there is a marked drop in the yellowness and marked increase in the brightness.

As a logical follow up we also studied the possibility of reducing optical whitener dosage when sulfuric acid replaces—part of the alum in the blend. The results of this study are collected in Table II.

It can be seen that optical whiteners dosage can be cut down substantially to maintain the same yellowness level when sulfuric acid partly replaces the alum. An increase in the brightness at the same 'yellowness' level is also noticed.

The marked drop in yellowness is due to the cumulative effect of two factors :

a) Hydration of the ketonic functions of the cellu-

MECHANISM OF HYDRATION OF KETONES

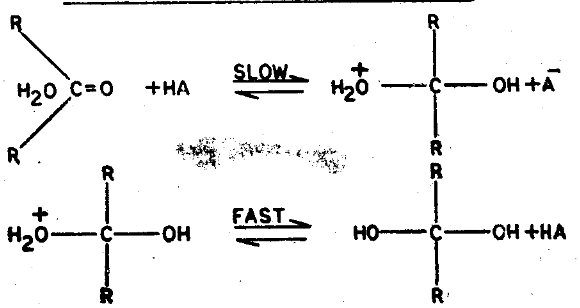


FIGURE.4

lose catalysed both by sulfuric acid as well as the sulfonic acid function present in OWA's.

b) deminution in the concentration of aluminium ions which have a dulling effect.

The effect of replacement of alum partly by sulfuric acid on the strength properties and sizing was also studied by us. It is found that we can successfully replace alum upto 20% by sulfuric acid without affecting the sizing or strentgth properties[8] (Table III.)

TABLE—I EFFECT OF REPLACEMENT OF ALUM BY SULFURIC ACID IN ALUM BLEND ON 'YELLOWNESS'

Particulars	Brightness %	Yellowness %
1. Pulp without beating	73.0	14.87
2. After beating but without addition of Rosin and Alum	68.3	14.6
3. Pulp after beating and addition of Rosin+Alum (100%)	62.0	17.84
4. Pulp + O. W. A. + Rosin + Alum		
a) 100% Alum	66.1	13.60
b) 95% Alum + 5% H_2SO_4	66.3	12.90
c) 90% Alum + 10% H_2SO_4	67.4	12.23
d) 85% Alum + 15% H_2SO_4	67.6	12.03
e) 80% Alum + 20% H_2SO_4	69.2	11.03
f) 75% Alum + 25% H_2SO_4	70.0	10.20

Final stock freeness = 40° SR, Stock pH = 5.0, Rosin : 0.8% Optical Whitener : 0.3%

TABLE—II EFFECT OF VARIATION OF WHITENING AGENT DOSAGE AND SULFURIC ACID CONTENT IN ALUM BLEND ON BRIGHTNESS AND "YELLOWNESS"

Particulars	Brightness %	Yellowness %
1. Pulp before beating	73.5	14.60
2. Pulp after beating without addition of Rosin Alum and W.A.	67.0	14.70
3. Pulp + Rosin + Alum (100%)	62.0	17.44
4. 0.30% W.A. + Rosin + 100% Alum	64.6	14.22
5. 0.25% W.A. + Rosin + 95% Alum + 5% H_2SO_4	65.0	14.13
6. 0.20% W.A. + Rosin + 90% Alum + 10% H_2SO_4	65.4	14.15
7. 0.15% W.A. + Rosin + 85% Alum + 15% H_2SO_4	65.7	14.07
8. 0.10% W.A. + Rosin + 80% Alum + 20% H_2SO_4	66.8	14.12

Stock pH = 5.0, Rosin = 0.8% W.A. : Whitening agent.

TABLE- III EFFECT OF REPLACEMENT OF ALUM BY SULFURIC ACID IN THE ALUM BLEND ON THE STRENGTH PROPERTIES OF PAPER & SIZING

Particulars	Sizing secs	Burst Index K Pa m^2/g.	Tear Index mN m^2/g	Breaking Length Km
1. Pulp + Rosin + 100% Alum	24	3.35	6.27	6.05
2. 95% Alum + 5% H_2SO_4	24	3.34	6.47	6.01
3. 90% Alum + 10% H_2SO_4	26	3.33	6.47	6.03
4. 85% Alum + 15% H_2SO_4	27	3.33	6.47	6.01
5. 80% Alum + 20% H_2SO_4	27	3.39	6 57	6.00
6. 75% Alum + 25% H_2SO_4	20	3.22	6 20	5.90

Rosin = 0.8%, Stock pH = 5.0, Final Freeness = 40°SR

To further assess the relative importance of two factors mentioned above in controlling the optical properties of paper, we have studied the addition of sulfamic acid on the optical properties of paper.
In table IV data is presented on the effect of added sulfamic acid on the optical properties of paper at a constant dosage of alum and optical whitener. The results showed that there is a small but perceptible drop in yellowness and marginal or no increase in brightness, by the addition of sulfamic acid[9].

In these experiments we noticed that addition of sulfamic acid resulted in the drop of pH of the stock. We have carried out another set of experiments in which pH was kept constant, as was done in our studies of sulfuric acid replacement[8]. At higher dosages of sulfamic acid, the amount of alum needed to maintain in same stock pH decreased. This set of experiments therefore gave us an opportunity to assess the importance of the demunition of aluminium ion concentration on the optical properties of paper.

The result of the study for one set are presented in TABLE V. It is observed that the reduction in yellowness and increase in brightness are almost of the same magnitude as in the previous set of experiments, when the alum dosage was kept constant. We had expected a greater effect on the optical properties, because the effect would be the sum of the effect of the addition of sulfamic acid (found to be marginal in earlier sets) and the decrease in the aluminium ion concentration, since the alum dosage was decreased to maintain the same stock pH. This was not observed.

TABLE – IV EFFECT OF SULFAMIC ACID ADDITION ON BRIGHTNESS AND YELLOWNESS OF PAPER

Sl. No.	Particulars		Brightness %	Yellowness %
1.	Pulp without beating		70.0	15.36
2.	Pulp after beating		67.9	14.94
3.	Beaten pulp after addition of alum and Rosin		60.1	19.14
4.	Pulp + Rosin + Alum + O.W.A		63.6	14.44
5.	**Pulp + Rosin + Alum + O.W.A. + Sulfamic Acid**			
	Sulfamic acid	0.1%	64.3	14.11
6.	Sulfamic acid	0.15%	64.44	13.69
7.	Sulfamic acid	0.20%	64.1	13.37
8.	Sulfamic acid	0.30%	64.2	12.90
9.	Sulfamic acid	0.40%	64.3	12.70

Alum = 5.0% (Same for all experiments)
Rosin = 0.8%
Optical whitners (OWA) = 0.3%

TABLE—V EFFECT OF SULFAMIC ACID ADDITION AT CONSTANT STOCK pH ON BRIGHTNESS AND YELLOWNESS OF PAPER AND ALUM DOSAGE

Sl. No.	Particulars	Alum dosage %	Brightness %	Yellowness %
1.	Pulp without beating	0.0	72.6	15.56
2.	Pulp after beating	0.0	70.5	15.49
3.	Beaten pulp + Rosin + Alum	5.9	64.8	19.77
4.	Beaten pulp + Rosin + Alum + Sulphamic Acid (0.467%)	4.67	66.6	19.01
5.	**Pulp + Rosin + Alum + Sulfamic Acid**			
	a) Sulfamic Acid (0.50%)	4.80	64.4	19.63
	b) Sulfamic Acid (0.75%)	4.60	64.9	19.31
	c) Sulfamic acid (1.0%)	4.40	66.0	18.79
	d) Sulfamic acid (1.5%)	3.67	67.5	17.40

Stock pH = 5.0 Rosin — 0.8%.

We do not contend that aluminium ions do not have dulling effect. It is quite possible that aluminium ion concentration has already attained the optimum level above which it does not have a perceptible effect. The observation that sizing was not affected by the decrease in alum dosage indicates this. Theoretically only 0.35 parts of alum are needed per part of rosin size for fixing the size[11], but in practice atleast 3-5 times are needed. Nevertheless at the same level of alum addition, and when stock pH and other conditions are kept constant, added sulfuric acid has a greater effect than the added sulfamic acid. The implications of these results in the elucidation of the mechanism of action of optical whiteners are discussed in another section.

We have also examined the applicability of second suggestion of Harkavy i.e. addition of polyphosphates or organic sequesterants in optimisation of optical whitner dosage.

It was felt by Harkavy that metallic ions like aluminium, calcium, magnesium and iron have quenching effect on optical whitners and adverse effect of these ions can be nullified by the use of sequesterants.

We have investigated the effect of added EDTA and Trisodium poly phosphate[10] and the results are presented, in tables VI & VII. It can be seen that while addition of Trisodium polyphosphate has a marginal beneficial effect on the optical properties, added EDTA does not result in any improvement. Hence this strategy will not result in any optimisation of optical whitener dosage.

We have also examined the third suggestion of Harkavy, viz. replacement of ferric alum by non ferric alum[12]. The results of this study are presented in Table VIII. It is obvious from the results that use of non ferric alum in place of ordinary alum does not improve the efficiency of optical whitner addition.

TABLE—VI EFFECT OF ADDITION OF E.D.T.A. ON OPTICAL PROPERTIES OF PAPER

Sl. No.	Particulars	Brightness, %		Yellowness %	
		Set I	Set II	Set I	Set II
1.	Pulp before beating	75.6	74.0	13 39	14.17
2.	Beaten Pulp + Rosin + Alum	64.6	60 0	18.71	19 15
3.	Beaten pulp + Rosin + Alum + O.W.A.	69.0	64.4	11.83	12.60
4.	Beaten pulp + Rosin + Alum + O.W.A. + E.D.T.A				
	a) EDTA 0.1%	68.7	64.5	11.65	12.57
	b) EDTA 0.2%	68.6	64.7	11 53	12.57
	c) EDTA 0.3%	68.4	63.8	11.50	12.63
	d) EDTA 0.4%	69.1	64.6	11.36	12.70
	e) EDTA 1.0%	69.0	64.8	11.07	12.24

Alum : 5.0%; Rosin — 0.8%, O.W.A : 0.3%; Stock pH 5.0

TABLE—VII EFFECT OF ADDITION OF TSP ON OPTICAL PROPERTIES

S. No.	Particulars (Sample a)		Set I		Set II	
			Brightness %	Yellowness %	Brightness %	Yellowness %
1.	Unbeaten pulp		72.1	17.09	72.9	13.55
2.	Beaten Pulp + Rosin + Alum		62.5	22.73	63.0	20.29
3.	Beaten Pulp + Rosin + OWA + Alum		65.3	17.76	66.0	15.25
4.	Beaten Pulp + Rosin + OWA + Alum + Tri Sodium Poly Phosphate					
	a. TSP	0.2%	67.4	16.86	67.3	14.47
	b. TSP	0.4%	67.3	16.73	67.4	14.43
	c. TSP	0.6%	68.5	16.25	67.9	14.21
	d. TSP	1.0%	68.6	15.91	67.9	13.73

a : In all cases : Rosin—0.8%; OWA—0.3%; Alum 6.33%;

TABLE—VIII EFFECT OF IRON FREE ALUM AND FERRIC ALUM ON THE OPTICAL PROPERTIES OF PAPER

Sl. No.	Sample	Brightness %		Yellowness %		Iron content %	
		Set I	Set II	Set I	Set II	Set I	Set II
1.	Raw pulp	72.2	70.2	21.0	17.3	0.01	0.011
2.	Beaten pulp	68.5	67.9	21.6	17.5	0.01	0.011
3.	Pulp + Rosin + OWA+						
	a) Ferric alum	64.8	65.6	20.6	15.4	0.021	0.021
	b) Iron free alum	64.9	65.5	20.6	15.4	0 013	0.013

Rosin — 0.8% OWA -- 0.3% Stock pH 5.0

IMPLICATIONS OF THESE RESULTS IN THE DELENEATION OF THE MECHANISM OF ACTION OF OPTICAL WHITNERS.

The implications of the results in the deleneation of the mechanism of action of optical whiteners are interesting.

From these results we postulate that the mechanism of action of optical whiteners also involves at least partly, the hydration of C-2 and C-3, ketonic functions of the cellulose mo ecules catalysed by the protons of the sulfonic acid function present in the optical whitener molecule (as pointed out in literature and as confirmed by our own infra red spectral measurements).

As stated earlier, it is well documented that the hydration of ketones is general acid cata ysed. The mechanism of hydration of these carbonyl compounds especially acetaldehyde[13] and dichloroacetone[14] has been studied in detail and it is found that they undergo hydration by a mechanism involving general acid catalysis, Excellent correlations have been obtained in the Bronsted plots, with a significant "Alpha" value 0.54 and 0.27 for these two compounds respectively.

The considerably reduced effect of sulfamic acid as compared to sulfuric acid can be traced to this mechanism Sulfuric acid with a considerably less pKa as compared to the sulfamic acid, is a much more efficient catalyst and therefore, gives better results. These results, also therefore, lend further support to our postulate about the importance of the hydration of the ketonic functions catalysed by the sulfonic acid function of O.W.A. molecule.

We have conducted further infra red spectral studies to conform this postulate. We have studied the I.R. Spectrum of a simple di-ketone benzal in the persence and in the absence of optical w hitener Only a nujal mull was studied and not a solution spectra as we did not have the facilities for studying the I.R. Spectra of aqueous solutions. It was found that by the addition of OWA, the carbonyl stretching frequency shifted to the lower frequency to the extent 5 to 10 cm^{-1} Further work in this direction using calcium fluoride cells for IR Spectral determinations in aqueous solutions is underway.

We venture to suggest therefore on the basis of these results that the efficiency of the optical whitner molecule can be further improved by having more electron attracting substituents built in the molecule which will increase the acidity of the sulfonic acid groupings present.

EXPERIMENTAL

The experimental procedures followed in these studies have been described in our earlier publications[3,4] Tristimulus reflectance photometry was used to determine the yellowness.

CONCLUSIONS

For effective utilisation of the Optical whiteners replacement of alum partly by sulfuric acid is suggested. The replacement can be done upto 20%, above which an adverse effect on sizing and strength properties is noticed. Use of sequestering agents like EDTA has practically no effect. Use of non-ferric alum in place of normal alum has also no beneficial effect.

From a thorough analysis of the results of these extensive studies, it is postulated that mechanism of action of optical whiteners also partly involves the hydration of ketonic functions by the sulfonic acid group, present in the optical whitener molecule. Since the mechanism of hydration of ketones, is known to be general acid catalysed, introduction of an electron with drawing substituent will decrease the pKa of the sulfonic acid function and thus lead to higher reduction of the yellowness and thence improve the action of the optical whiteners.

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