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OPTIMIZATION OF PIGMENT PERFORMANCE IN PAPER

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ABSTRACT

The apparent light-scattering coefficient of a given pigment in filled papers depends on the state of pigment dispersion and the beating level of fibers. This effect is seen on handsheets containing pigments deliberately introduced either as individual particles or as aggregates; well dispersed TiO_2 is optically superior and its contribution to the total light scattering increases with fiber beating. In order to achieve retention of dispersed pigment particles and to avoid their flocculation caused by polymeric retention aid, the pigment, prior to its addition to the fiber suspension, can be treated with a cationic polyelectrolyte. Since pigment introduction results in tensile strength loss, which is most pronounced with dispersed particles, a plot of optical properties versus tensile strength provides a means for evaluating the pigment effectiveness and for comparing different pigments.

INTRODUCTION

When expensive pigments are used to improve the optical properties of paper it is desirable to achieve the required effect with the least amount of pigment. This means that the conditions must be established under which the pigment potential is fully utilized. With respect to TiO_2, the first requirement is to optimize its opacifying efficiency, because the improvement is often less than expected. The second requirement is high pigment retention, which can only be achieved by pigment deposition on fibers if the particle size is too small to be mechanically entrapped in the forming sheet. Due to the limited time available, the deposition must be fast and the tenacity of particle attachment to fibers must be sufficient to withstand turbulence. The third requirement is to minimize any adverse effects that the introduction of a pigment may have on sheet properties. Often a compromise between optical and mechanical properties must be accepted, but their mutual relation provides a basis for evaluating the effectiveness of pigments.

While focussing mainly on TiO_2, this paper presents evidence that the light-scattering efficiency of pigments depends on the state of particle dispersion and on the level of fiber beating. For this purpose the pigment is deliberately introduced into handsheets either as individual particles or as aggregates. The method employed, which depends on pretreating the pigment with cationic polymer, offers the possiblity of optimizing the pigment performance.

LIGHT SCATTERING AND PIGMENT DISPERSION

The opacity of white pigments is directly related to their ability to scatter light, which is a function of pigment size and its refractive index. Fig. 1 shows how the specific light-scattering coefficient of a model pigment, represented by monodispersed polystyrene latex particles, depends on particle size. The optimum size of these particles is around 0.4 µm in diameter and the efficiency drops sharply with decreasing size. For TiO_2 the optimum size is 0.2-0.3 µm which is the average size of commercially available products. Nevertheless, the papermaker knows from experience that despite this the contribution of a given amount of pigment to the total light scattering of paper may fluctuate. This means that the scattering effect of the pigment is not a constant, as noted in several investigations (1-4), particularly in connection with the use of a variety of retention aids.

The effect of two different retention aids, polyethylenimine and polyacrylamide, on the light scattering of handsheets filled with a given TiO_2 is shown in Fig. 2. The polymeric retention aids, being essentially flocculating agents, are thought to cause aggregation of dispersed pigment particles and thus to decreas their ability to scatter light. This

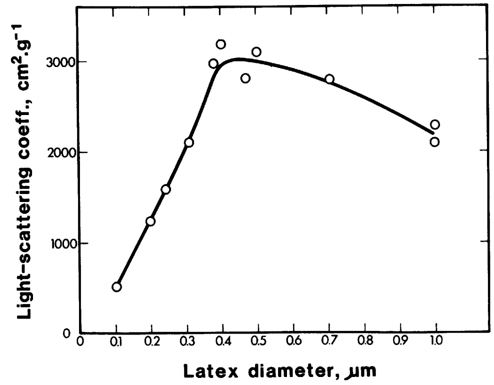


Fig. 1 Light-scattering coefficient (LSC) of polystyrene latex particles as a function of their size.

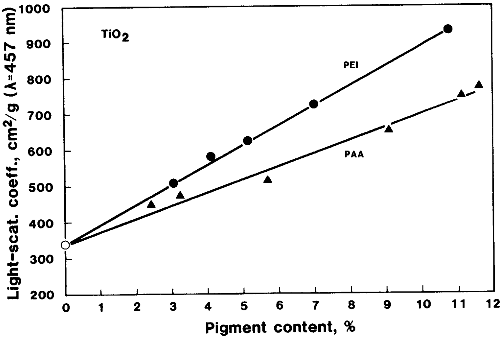


Fig. 2 LSC of handsheets as a function of TiO_2 content using polyethylenimine or polyacrylamide as a retention aid.

assumption was tested by introducing well-dispersed and deliberately flocculated TiO_2 pigments into handsheets. Before its addition to the pulp suspension, the pigment was treated with two types of cationic polymers, thus providing the particles with a positive charge and encouraging their deposition of negatively charged fibers. One of the polymers, highly charged polyethylenimine of low molar mass, is non-flocculating, the other is a cationic starch which flocculates the pigment.

The results in Fig. 3 on the electrophoretic mobility of treated pigments, measured as a function of pH, reveals that they bear a positive charge up to pH 7-8. This means that at pH 6, to which the system had been adjusted, the pigment would deposit on the negatively charged fibers due to a mutual attraction. The state of dispersion can be detected by the light transmittance measurement shown in Fig. 4. The well-dispersed untreated pigment and the polyethylenimine treated pigment have similar slopes of light transmittance versus pigment concentration, while the lesser slope of cationic starch treated pigments indicates larger scattering species, i.e. aggregates. A microscopic observation of particles deposited on fibers, shown in Fig. 5, reveals that the polyethylenimine treated pigment indeed covers the fiber surface as individual particles, while the flocculated pigment deposits in a form of aggregates. The light-scattering coefficient of handsheets containing the dispersed and the aggregated TiO_2, shown in Fig. 6, clearly indicate the superior performance of the dispersed pigment. The same behavior is observed with clay pigments and shown in Fig. 7.

LIGHT-SCATTERING AND FIBER BEATING

The contribution of pigments to the total light-scattering of filled paper is also affected by the beating level of fibers (5). The presence of pigments, however, reverses the trend normally observed in unfilled paper, i.e. a decreased light-scattering coefficient with increased beating. This effect occurs because of the loss of fiber-air interface due to the enlarged interfiber bonded area. Increased beating of fibers enhances the efficiency of pigments incorporated in the sheet. Fig. 8 shows the light-scattering as a function of TiO_2content of handsheets formed from fibers beaten to four levels. In order to avoid any effect of pigment aggregation caused by retention aids, a cationic TiO_2 was used. For a better illustration, in Fig. 9 the apparent light-scattering

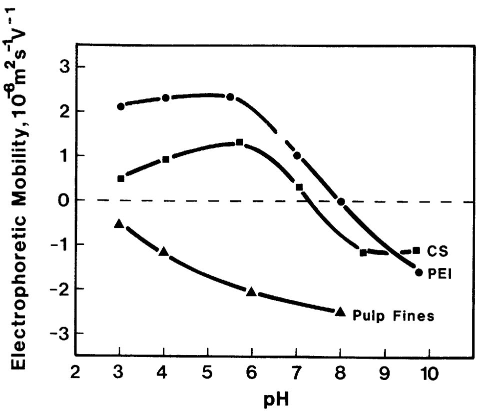


Fig. 3 Electrophoretic mobility of TiO_2 treated with polyethylenimine or cationic starch measured as a function of pH. Included are data for fiber fines, assumed to represent fibers.

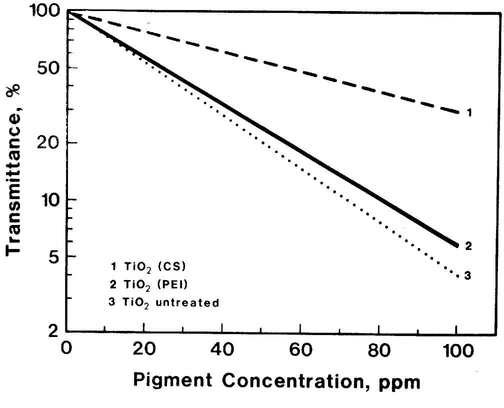


Fig. 4 Transmittance of TiO_2 suspension as a function of pigment concentration for untreated pigment and treated with polyethylenimine or cationic starch.

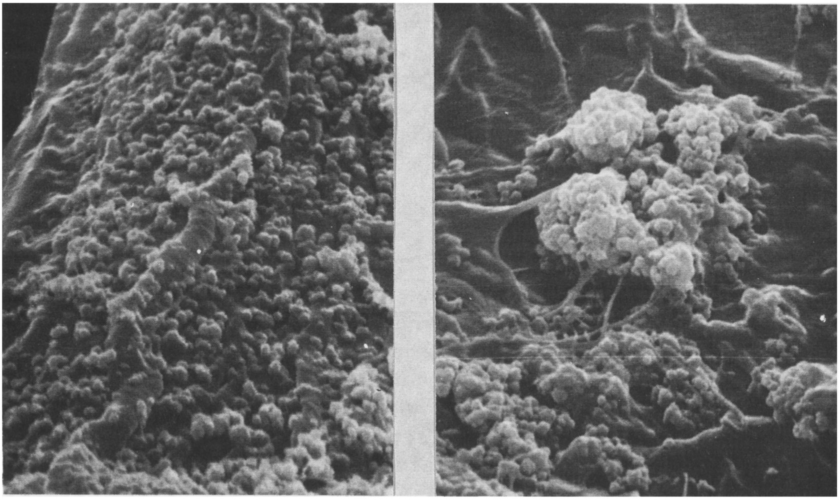


Fig. 5 Deposition of TiO_2 treated with polyethylenimine (left) or cationic starch (right).

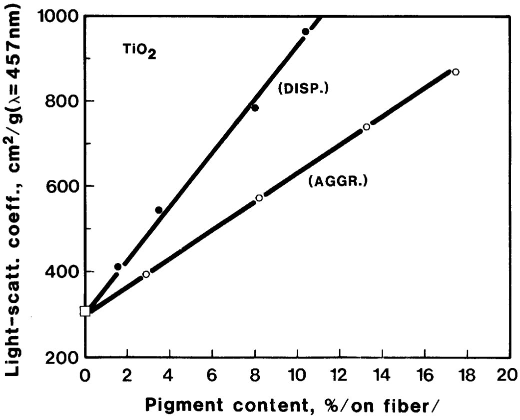


Fig. 6 LSC of handsheets containing TiO_2 treated with polyethylenimine (disp) or cationic starch (aggr).

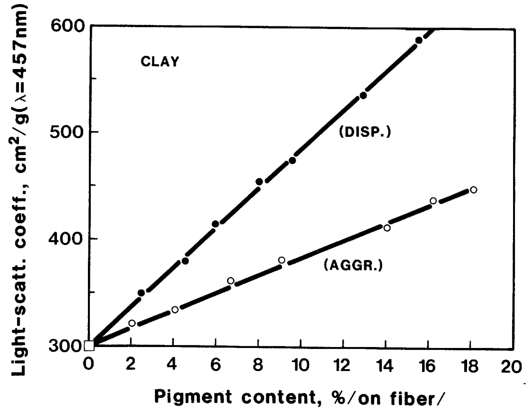


Fig. 7 LSC of handsheets containing clay treated with polyethylenimine (disp) or cationic starch (aggr).

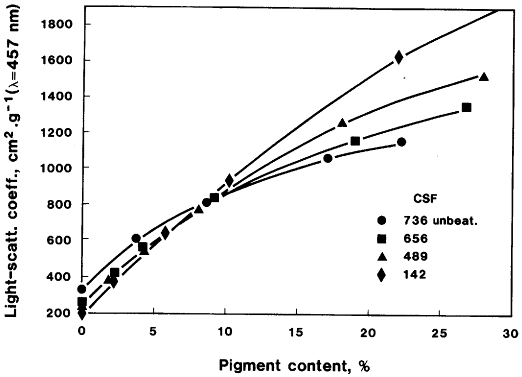


Fig. 8 LSC of handsheets formed from fibers of four beating levels as a function of TiO_2 content.

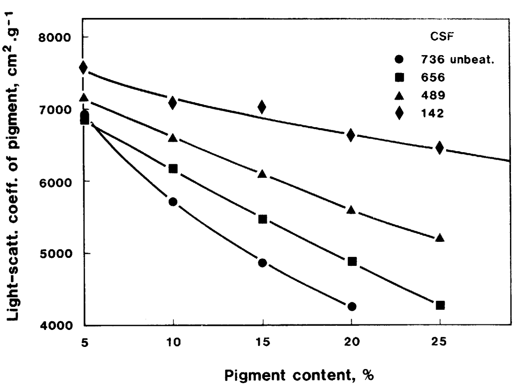


Fig. 9 Apparent LSC representing the contribution of TiO_2.

coefficient of pigment alone was calculated from the rule of mixtures, in which it is assumed that the contribution of fiber and pigment is independent and proportional.

$$S_{total} = S_{fiber}(1 - W) + S_{pig}.W \tag{1}$$

where S_{total} is the light-scattering coefficient of filled paper, S_{fiber} that of unfilled paper, and W is the mass fraction of pigment.

The general trend of decreasing efficiency with increasing pigment content is a rather common phenomenon, likely related to the crowding of pigment particles. The decrease becomes less pronounced, however, as beating increases. A suggestion (5), supported by a microscopic observation (6), provides an explanation. First, the S_{fiber} is not constant because the presence of pigment particles prevents fiber-fiber bonding and a new air-fiber interface is created above that which exists in the unfilled sheet. Second, owing to the presence of pigment particles, fibrils and fines generated by beating cannot collapse completely onto the fiber upon drying and thus an additional interface is formed. As beating progresses, and more particles are present, the additional light scattering interface increases. Consequently the S_{total} of filled sheets should include all the contributions:

$$S_{total} = S_{fiber}(1 - W) + \\ + (\Delta S_{fiber} + S_{fibrils} + S_{fines} + S_{pig.})W \qquad (2)$$

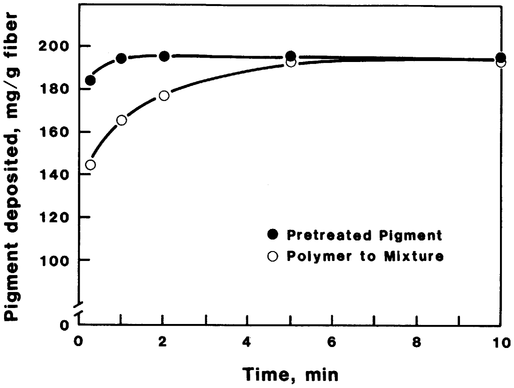
where ΔS_{fiber} is the additional source from unbonded fiber surface due to pigment, $S_{fibrils}$ and S_{fines} are the contributions from fibrils and fines prevented by the pigment from collapsing onto fiber surfaces, and $S_{pigment}$ is the light scattering of the pigment alone. The contribution from the unbonded fibers, fibrils and fines can be substantial (7) and it has actually been suggested that in the case of pigments of low refractive index (clay, $CaCO_3$) the increase is due only to fibers (5).

The effect of fiber beating on the apparent light-scattering efficiency of pigmnents was investigated under conditions where pigment particles were dispersed. Although no data are available for handsheets containing aggregated particles, it can be assumed that all the contributions due to the pigment will diminish.

PIGMENT RETENTION

Since fibers and common pigments are both negatively charged in an aqueous suspension and repel each other, achieving effective pigment retention in the sheet presents a problem. Mechanical entrapment of submicron particles in a forming sheet is negligible (8) and therefore two options are available: (i) to flocculate pigment particles into large aggregates to be filtered out, or (ii) to encourage their attraction to fibers by surface modification. Water soluble polymers used as retention aids may perform both functions - homoflocculation of pigment particles and heteroflocculation between pigment and fiber. When the retention aids are positively charged, an additional effect of charge reversal due to polymer adsorption may promote electrostatic interaction between fibers and pigment particles. The actual mechanism by which retention aids operate is not yet well understood and may differ depending on the polymer characteristic, namely molar mass, charge density and type of charge. Nevertheless, one general statement, based on experience, seems to be justified - the efficiency of a retention aid increases with its flocculating ability. This means, of course, that the optical efficiency of pigments will deteriorate due to pigment aggregation and, also, formation may suffer due to possible fiber flocculation. Therefore it may be advantageous to use the method employed for handsheet preparation, i.e. to treat a pigment with cationic polymer prior its addition to a fiber suspension. A cationic polymer adsorbed on pigment particles reverses their charge and thus promotes particle deposition on negatively charged fibers. In addition, when a non-flocculating polymer is used, the particles will remain dispersed because of their mutual repulsion, and thus will deposit as individual particles.

The pretreatment of pigment can also benefit the rate of pigment deposition. As shown in Fig. 10, the deposition of pretreated particles on fibers proceeds at a faster rate than when the same polymer is added to the suspension of fibers and untreated pigment. The reason is presumably that the polymer must first adsorb before interaction between the fiber and pigment takes place. Since polymer adsorption is not instantaneous, pigment pretreatment can eliminate the rate-limiting step.



Fib. 10 Deposition of clay particles on fibers as a function of time. Polyethylenimine in the amount of 0.5 mg/g fibers was added either to the mixture of clay and fibers or to the clay only. Clay addition 0.2 g/g fibers.

The concept of pretreatment by cationic polymer is not restricted to the pigment. The same effect can be obtained by treating the fibers before introducing a pigment, but this procedure can be less convenient and probably more polymer will be required for reversing the fiber charge. Under certain circumstances, however, the pretreatment of fibers may be advisable, for example when the system contains a soluble anionic substance which may adsorb on the cationic pigment and thus destroy its positive charge. Then it will be necessary to add polymer to the fiber suspension in an amount sufficient to neutralize the anionics and reverse the fiber charge.

The deposition of dispersed particles onto fibers may present other advantages, in addition to the effect on optical properties: (i) the distribution of pigments throughout the sheets will likely be uniform; (ii) the individual particles may be less sensitive to their removal from a fiber surface when exposed to hydrodynamic forces during paper formation.

TENSILE STRENGTH AND PIGMENT DISPERSION

The negative effect of pigment introduction is a loss in tensile strength. A dispersed and optically superior pigment is naturally more effective in preventing interfiber bonding, as shown in Fig. 11. The results in Fig. 11 were obtained on the same samples presented in Fig. 6, where the light- scattering efficiency of dispersed and aggregated TiO_2 were compared. A plot of tensile strength versus light-scattering coefficient gives approximately the same relation for both dispersed and aggregated pigments, as shown in Fig. 12. This observation may lead to the conclusion that, because for a given improvement in light-scattering there is a corresponding loss in tensile strength, controlling the state of pigment dispersion does not permit optimization of strength-opacity ratio.

However, the significance of pigment dispersion is evident if we consider the amount of pigment present at a given combined values of light scattering and tensile strength. The content of TiO_2 at selected values, given in the Table, clearly shows that when expensive pigment is used, a significant saving can be realized by controlling pigment dispersion.

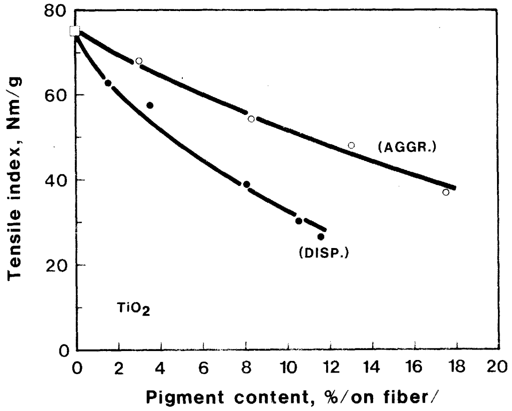


Fig. 11 Tensile index of handsheets containing TiO_2 treated with polyethylenimine (disp) or cationic starch (aggr).

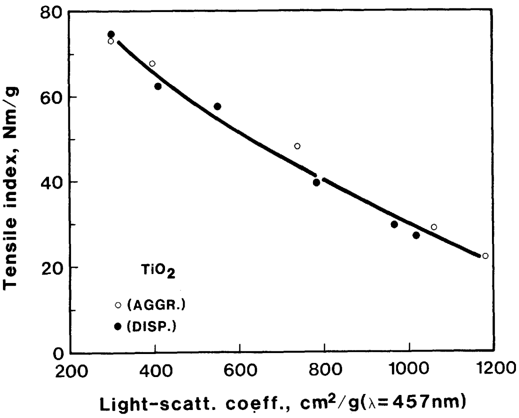


Fig. 12 Tensile index vs. LSC of handsheets containing TiO_2 treated with polyethylenimine (disp) or cationic starch (aggr).

TiO_2 content at selected combined values of scattering coefficient and tensile index

Scattering coefficient, cm^2/g	Tensile index, N . m/g	TiO_2 required, %	
		Aggregated	Dispersed
400	65	3.0	1.5
600	50	9.0	5.0
800	40	15.0	8.0

CONCLUSIONS

Light-scattering efficiency is enhanced when dispersed pigment particles are introduced into paper. Although it is conceivable that separated particles are more effective than aggregates, the improvement does not come from the pigment alone. A significant contribution to the total light-scattering is due to the effect of the particles on decreasing the contact between fibers and preventing fibrils and fines from collapsing onto fiber surfaces upon drying.

In order to ensure retention of dispersed particles, the pigment, before its addition to fiber suspensions, can be pretreated with a cationic non-flocculating polyelectrolyte. Since the dispersed pigment is also most effective in decreasing tensile strength, the plot of light-scattering versus tensile strength provides a basis for evaluating the pigment performance and for comparing different pigments.

When TiO_2 is introduced for optical improvement, its state of dispersion is the most important factor for optimization. Because it is used in small amounts, the contribution of fibrils and fines is rather small and the loss of tensile strength is of lesser concern. When, for reasons other than optical, the paper is to be loaded heavily with a cheaper filler it may be advantageous to preflocculate it before its addition to fibers. This procedure will improve retention by mechanical entrapment and minimize the negative effect on tensile strength.

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Transcription of Discussion

OPTIMISATION OF PIGMENT PERFORMANCE IN PAPER

Dr. B. Alince

Dr. M. Bruce Lyne, International Paper Company

I would suggest that you have not optimised the filler in fine paper unless it is retained during printing or copying. Can you comment on whether an aggregated or a dispersed system would lead to the least dusting during printing?

Dr. B. Alince

My title may have been too ambitious, because I was only dealing with optical properties, so I cannot answer your question.

I.K. Kartovaara, The Finnish Pulp & Paper Research Institute

You are presenting the average when you calculate the apparent light scattering co-efficient, i.e. the scattering of the total amount of pigment. If you calculated the marginal light scattering efficiency of added pigment, you would have a much more drastic change in that marginal efficiency, which would be practically zero. Do you have a comment on that?

Dr. B. Alince

No.

Prof. J. Silvy, EFPG

The control of the light scattering co-efficient is done to create brightness and opacity in the paper. Did you notice at the same time a variation of the absorption co-efficient of the sheet in respect of this better dispersion of the fines by beating the pulp in the presence of filler?

Dr. B. Alince

No, we did not notice any particular difference in the brightness. At least, for these samples, the absorbtion co-efficient remained the same.