Dyes and Pigments 1 (1980) 81–89

SPRAY DRYING WATER SOLUBLE ORGANIC DYES: EFFECT OF MORPHOLOGY AND CRYSTAL HABIT ON PROCESS AND PRODUCT PROPERTIES

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SUMMARY

Water soluble reactive dyes for cellulose are spray dried from high solids brine slurries and are commercially available in granular form The physical form, size and structure of the grains directly affects the bulk density, friability and solubility parameters and may be significantly influenced by the parent dye morphology and habit Isolated dye paste solids and the rheological behaviour of the slurry prior to drying are also affected.

The interactions, control and influence of dye morphology and habit on the process, drying and resultant grain properties are discussed

1 INTRODUCTION

Water soluble reactive dyes for cellulose are commercially available as powders or grains. Powders are inherently dusty requiring after-treatments of liquid dedusting additives which restrict the powder flow properties. A grain form may be generally defined as containing a major particle size fraction between 100 and 300 μm and is desirable for its good flow properties and environmentally acceptable low dust characteristics

Transition from powder to grain, however, may also introduce problems specific to the process technology requirements involved in producing a larger spherical particle Physical form of the final product is now largely dependent on control of the particle size and structure. Bulk densities of larger cenospheres are likely to be lower than for similar powder forms and to be significantly more variable Grains produced must be robust and capable of

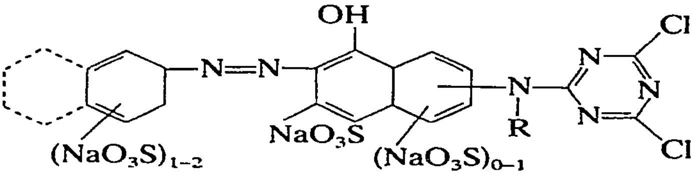
Dyes and Pigments 0143-7208/80/0001–0081/\$02·25—© Applied Science Publishers Ltd England, 1980
Printed in Northern Ireland

remaining intact when subjected to protracted transport vibration. Dye solubility which is primarily measured as rate of solution under application conditions, may be adversely affected due to a reduction in overall surface area.

All the physical parameters mentioned may be affected by the parent dye morphology. This paper is concerned only with the influence and effect of product feedstock and process variables: spray drying parameters are considered to be optimised and remain constant.

2. DYE CRYSTALLISATION

Soluble reactive dyes may be crystallised from the aqueous reaction solution by addition of sodium chloride to give the sodium salt. Such reactive dyes for cellulose of bright orange and red shades are of the general structure:



of which one member of this group is known to exhibit gross differences in crystal morphology Four isolated physical forms have been experienced by X-ray powder pattern diffraction and identified as A, B, C and D. The polymorphism is illustrated in Fig. 1 for forms A and B. Forms C and D are extremely metastable transferring to A and B rapidly in the liquid phase. Forms A and B only need therefore be considered In this particular dye structure it is significant that crystal habit corresponds with form, i.e. all form B material has the corresponding needle shape. Differential gravimetric analysis of both forms is given in Fig. 2. The peaks at around 80°C are attributed to physically bound water and the additional peak at 120°C for form A is chemically bound water. Form B, it may be concluded, is anhydrous whilst

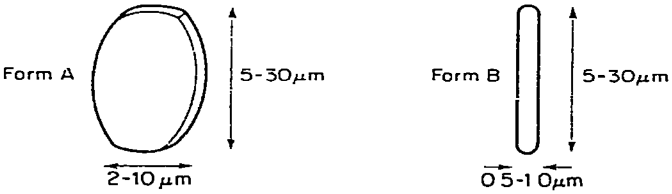


Fig 1 Crystal habit of dye forms A and B

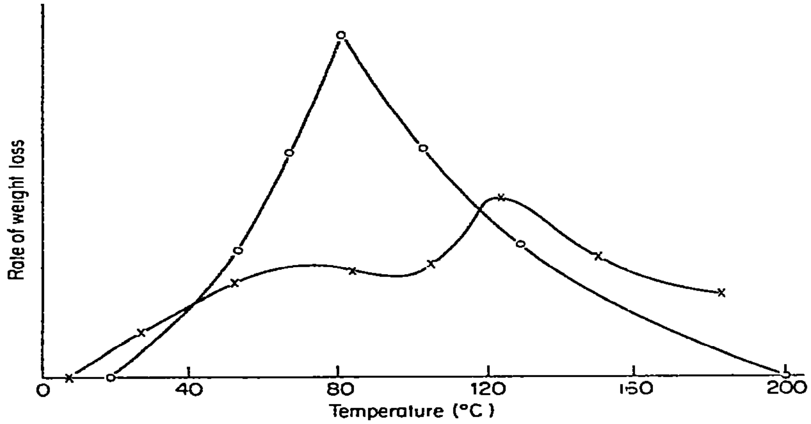


Fig 2 Differential gravimetric analysis for dye forms A and B ×——× dye form A, O——O dye form B

form A is a hydrate. The relevance of relationship of form to habit may now be clearer, the dye existing more correctly in an anhydrous or a hydrated form

Since the dye is dried from an aqueous suspension in brine and subsequently applied to cellulose from solution, the relative solubility differences are important, and are given in Table 1.

TABLE 1
RELATIVE SOLUBILITY DIFFERENCE BETWEEN DYE FORMS A AND B

Dye form	*Solubility of dye in saturated brine at* 22°C(kg m^{-3})
A	0.64
B	0.27

3. SEPARATION AND MIXING

The isolated dye suspension is separated by filtration and at this stage the form differences influence dye crystal packing and the total colour solids obtainable in the resulting paste. The inter-particle friction of the needles forms a more open structure with higher retention of the aqueous phase than the structured barrels. (Solids for form A = 68% and for form B = 50%.)

The separated dye paste is mixed with brine to adjust and control the solids concentration to spray drying requirements. At this slurry stage prior to drying the dyestuff is almost entirely precipitated, suspension rheology now being influenced by the particle size and, more significantly, the shape of the dye crystals.

4. SPRAY DRYING PASTE RHEOLOGY

During the mixing stage the dye paste may be subjected to a low shear rate over a protracted period with rapid increase in applied shear rate at the spray atomiser head (10^4–$10^5\,s^{-1}$). At the high solids required for commercially economic drying, the dye in form A exhibits shear thinning characteristics with increasing shear rate to $9 \times 10^3\,s^{-1}$ and then a significant rise in viscosity with subsequent increase in shear rate, therefore giving no rheological problems Rheology of needle shaped form B at high solids is more complicated than the classical thixotropy associated with needle paste systems where shear thinning

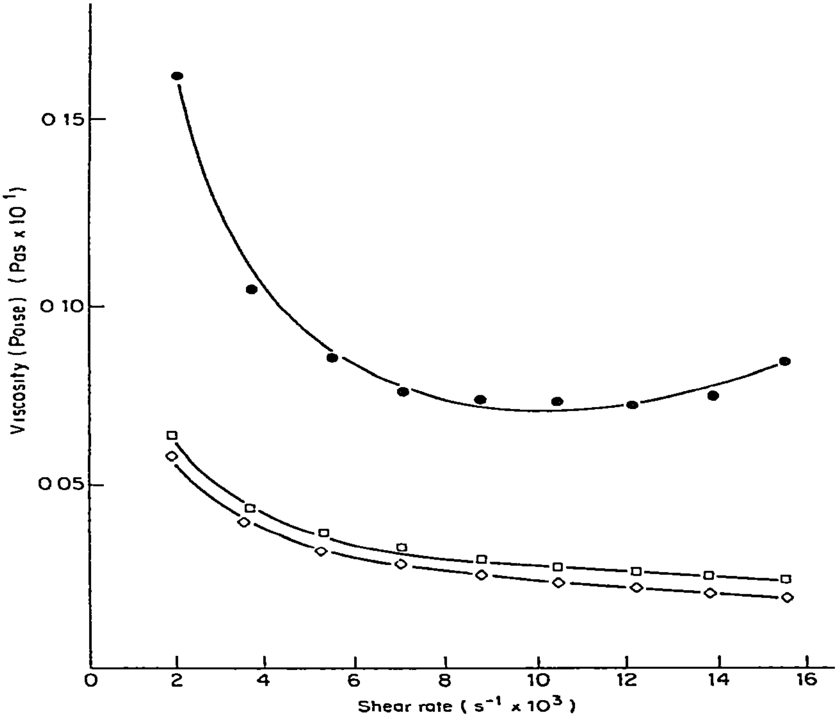


Fig 3 Rheology of dye paste suspensions ●——● dye form A—barrels, □——□ dye form B—large needles (30 μm). ◇——◇ dye form B—small needles (10 μm)

occurs as shear rate increases and is time dependent. The close packing of needles at high solids causes the paste to 'set-up' in a dilatent manner requiring dilution to facilitate further processing. Figure 3 illustrates the differences with form B diluted paste now exhibiting the expected shear thinning behaviour. Needle crystal size influences marginally shear thinning behaviour as can be seen from the two samples indicated.

5. GRAINS—PHYSICAL PROPERTIES

When spray dried as grains the major apparent difference between the two dye physical forms is one of bulk density (Table 2).

To examine the structural and geometric differences likely to contribute to this difference grain size distributions and pore size and volumes were determined. The samples were structurally examined using a scanning electron microscope (S.E.M.).

Information on pore size distribution was obtained from the mercury penetration porosimeter. Mercury, as a non-wetting liquid, is forced under pressure into voids and pores. The pore size and volume relationships are displayed in Fig. 4.

Grain size distributions were measured by a sieve separation technique and are given in Fig. 5. Assessment of grain stability during normal vibrations experienced in transport was obtained by subjecting the two products to gentle rotational tumbling action. Whilst the grain from dye form B remained essentially intact some structural breakdown occurred with dye form A and is indicated by the additional curve.

From S.E.Ms of mechanically ruptured grain spheres the structures of grains from the two forms were assessed. Barrel shaped crystals of form A are poor 'building blocks' and gave rise to thin walled (20–30 μm) friable cenospheres while the observed interlaced needle packing of form B gave a stable structured sphere, the complex packing possible giving rise to an aero structure with no specific central cavity (Fig. 6).

TABLE 2
BULK DENSITY SPRAY DRIED GRAINS FROM DYE FORMS A AND B

Dye form	*Bulk density grains* (kg m^{-3})
A	$0{\cdot}25 \times 10^{+3}$
B	$0{\cdot}57 \times 10^{+3}$

Breakdown of spheres from form A material is, therefore, not surprising and the increase of particles in the region below 70 μm would contribute to dust and environmental problems.

Mercury porosimetry measurements while showing little difference in pore size distribution indicated a specific, almost constant, difference in pore volume between the two forms. This is probably associated with the thicker walled 'aero' structure of the needle form B where many spherical cavities of radius 20 μm are present and will be filled at very low pressures. Cavities of hollow spheres of form A are of radius >100 μm. Open cavities of pore radius in excess of 70 μm will be filled at atmospheric pressure.

The grain size distribution measurements are not significantly different between the two dye forms. Such differences as do occur are related to the

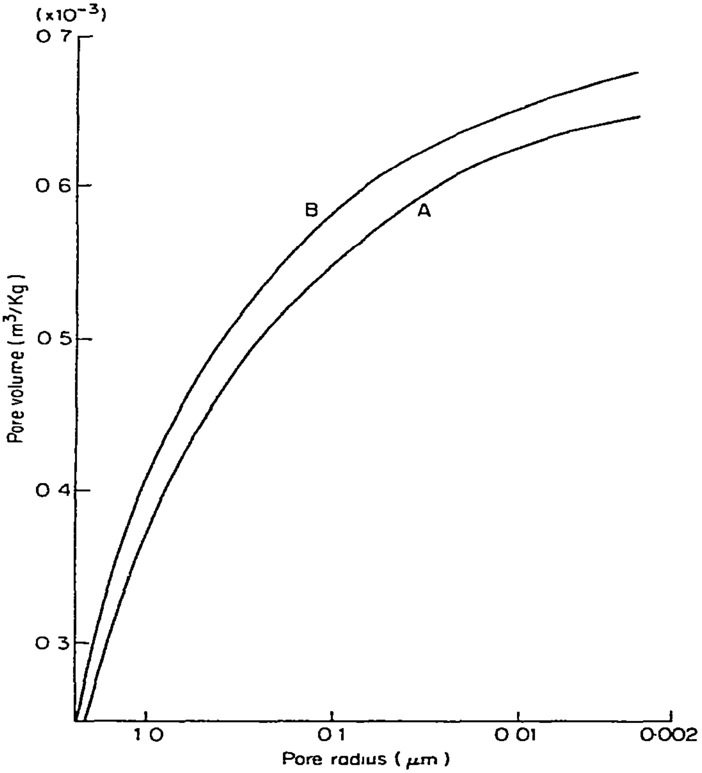


Fig. 4 Spray dried grains—pore size–volume relationship A, dye form A—bulk density 0.25 × 10^3 kg m^{-3}, B, dye form B—bulk density 0.57 × 10^3 kg m^{-3}

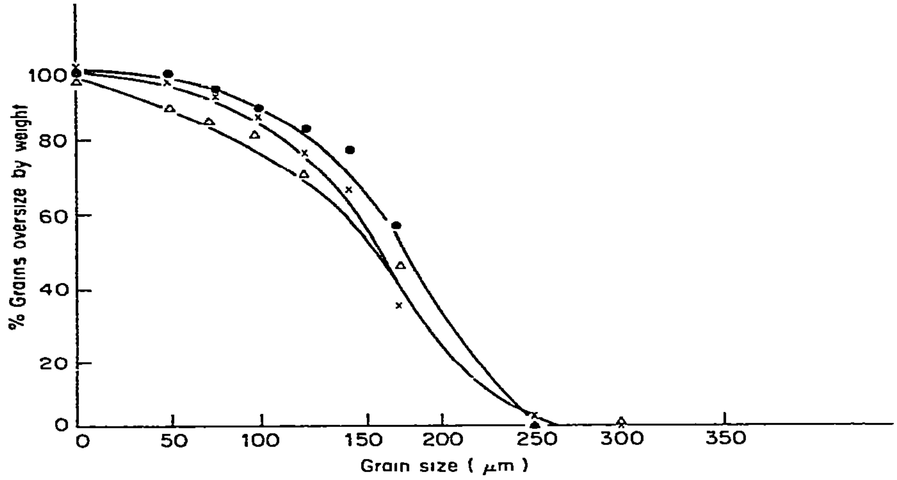


Fig 5 Spray dried grains—size distribution ●——● dye form A—bulk density 0·25 × 10^3 kg m^{-3}, △——△ dye form A—bulk density 0·25 × 10^3 kg m^{-3} (after tumbling), dye form B—bulk density 0·57 × 10^3 kg m^{-3}

viscosity differences of the two suspensions at high shear rate, particle size increasing with increasing viscosity.[1]

Bulk density changes of such magnitude must relate therefore to the closely packed, interlaced, almost solid grain structure obtained from form B, as opposed to the friable thin-walled cenospheres from form A.

6. DISCUSSION

It would be ideal if the desirable physical characteristics required were manifested in one specific physical form. Unfortunately this is not the case.

A model system would give high total colour solids when separated from the isolated suspension (form A), the desired rheological properties (form A), a robust spray dried grain of high bulk density (form B) and maximum dye solubility characteristics to fulfil dyeing application requirements (form A).

It is possible by controlling the parameters affecting dye crystallisation to isolate in form A and to convert the spray drying dye feedstock suspension to form B. However, this introduces rheology problems which may require paste dilution to feed to a spray head. Form conversion from hydrate to anhydrous dye may be possible during drying but control would be difficult. Affecting interparticle friction by addition of selected surface active materials with specificity for the dye structure may be an alternative. In this case the lower

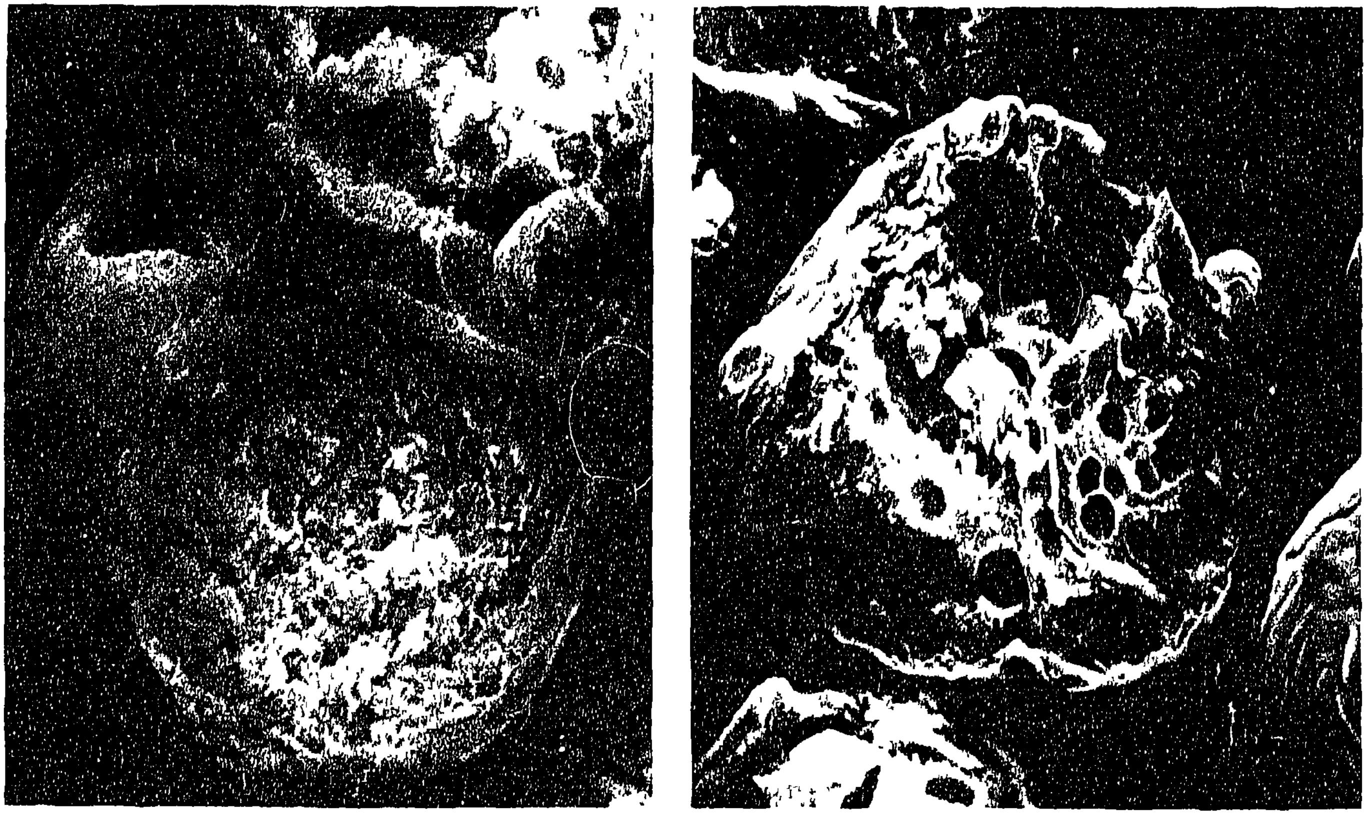


Fig 6 Scanning electron micrographs of sectioned grains Magnification ×200 Left dye form A, right, dye form B

finite solubility of form B must be accepted to give the more important robust grain structure and high bulk density

REFERENCE

1 K. MASTERS *Spray drying* (Chemical and Process Engineering Series) pp 172–3 London Leonard Hill Books (1972)