Zusammenfassung

In der Arbeit wird eine Theorie des dielektrischen Verhaltens der amorphen Polymeren entwickelt. Sie geht von der Annahme aus, daß ein aus 5 bis 10 Monomereinheiten bestehendes Segment der polymeren Kette unter Einwirkung des elektrischen Feldes eine Rotation um die Segmentachse sowie Umlagerungen der Monomereinheiten durchführen kann. Dabei wird die Rotation im wesentlichen nur vom freien Volumen beeinflußt, während die Umlagerungen in einem äußeren Potentialfeld die Überwindung einer Potentialschranke erfordern.

Das Modell beschreibt das charakteristische Relaxationsverhalten, wobei im einzelnen die Temperaturabhängigkeit der Maximumfrequenz $\nu_m$ der Intensität $\Delta E$ und des Seitenparameters $\beta$ vom Haupt- und Nebenrelaxationsgebiet diskutiert werden.

Schlußbemerkungen


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Kolloide und natürliche Makromoleküle

The Action of Surface-Active Agents in Aqueous Milling Processes, Especially at Low Concentrations
By H. R. Harper and D. Seaman

With 4 figures in 10 details and 5 tables

(Received March 2, 1965)

Introduction

Published work on comminution processes is confined mainly to inorganic materials in the presence or absence of surface-active substances, as in the work of Rehbinder et al. (1). An aspect of comminution processes which has rarely received attention concerns the milling of insoluble organic materials in aqueous solutions of surface-active agents. This subject, which is of importance in the preparation of dispersions of dyestuffs, pigments, medicinals, and agricultural chemicals, has been discussed in general terms by Moilliet (2) and by Moilliet, Collie and Black (3).

In this work, we have investigated the effect of surface-active agent concentration in aqueous millings of the well known vat dyestuff, 16.17 dimethoxyviolanthrone (4), the surface-active agent in question being the sodium salt of a condensate of naphthalene-2-sulphonic acid with formaldehyde (5). In further experiments we have followed the progress of the milling of this dyestuff in a solution of the same agent and of copper phthalocyanine in a solution of sodium dibenzylsulphanilate (6).

Experimental

Materials

The 16.17 dimethoxyviolanthrone used was an aqueous filter cake made by washing Caledon Jade Green XBN (I.C.I.Ltd.) (4) press cake well with water.

The sodium salt of the condensate of naphthalene-2-sulphonic acid with formaldehyde was freed from uncondensed sodium naphthalene-2-sulphonate by Soxhlet extraction with ethanol for 8 days. Such condensates are a mixture of low polymers in the approximate molecular weight range 500–2300 (corresponding to a naphthalene nucleus content of 2–9 per molecule) (7). This
material was found by titration (see below) to contain 84.5% by weight of active agent, the remainder being sodium sulphate, and is referred to hereafter as “Dispersing Agent A”.

The copper phthalocyanine used was low surface area material (4.7 m²/g; see below) in the β (stable)-crystal form obtained by the phthalic anhydride/urea/solvent process (see, for example, ref. 8).

The sodium dibenzylsulphinate was purified by recrystallisation from water several times, and is hereafter called “Dispersing Agent B”. Its active-agent content by titration (see below) was 93.5% by weight.

**Method of Milling**

The method of milling chosen was that in which the suspension is positively agitated with small hard grinding elements. The advantage of positive agitation over the cascading action of ball and pebbles mill has of course been known for many years (ref. 8). It is the basis of several well-known comminution devices including that known as the “sand-grinder” (see, for example, ref. 10). The mill consisted of a 3 inch diameter, 5 inch deep water-cooled stainless steel beaker, 3/4 inch thick and 2 1/2 inch diameter, mounted on a central stainless steel shaft which was driven at 1800 r.p.m. by a 0.5 HP engine’s drilling machine. The grinding elements used were No. 10 grade (0.25–0.30 mm.) glass Ballotini (English Glass Company). 125 gms. of the formulation was milled with 375 gms. of the glass beads and then separated from the beads by straining through printer’s cloth.

**Measurement of the Adsorption Isotherm of Dispersing Agent A on 16.17 Dimethoxyviolanthrone**

16.17 dimethoxyviolanthrone washed filter cake (unmilled) equivalent to 3.0 gms. dry material was made up to 500 mls. of suspension with agent solutions of various concentrations such that the initial agent concentrations before adsorption were 2 x 10⁻⁴ N, 10⁻³ N, 2 x 10⁻³ N, 4 x 10⁻³ N, 6 x 10⁻³ N, 10⁻² N with respect to active agent. A normal solution was taken as that concentration corresponding to one naphthalene unit of the molecule i.e. a gm. equivalent weight of 241 gms. 100% agent. The suspensions were stirred for 15 hours in a thermostat at 25.0 °C in closed vessels, and then centrifuged at 10,000 r.p.m. (5,000–9,000 g) for 1–2 hours using a Servall angle centrifuge. The clear supernatant was then titrated to obtain the agent concentration after adsorption, the method used being as follows: a xylene in water emulsion stabilised with an aliquot of supernatant was titrated with M/1000 cetyl pyridinium bromide until the emulsion broke. Where necessary, aliquots of a N/1000 solution of Dispersing Agent A were added to the initial xylene/water/supernatant mixtures to enable emulsion to be formed. The adsorption isotherm obtained is shown in fig. 1, where the quantity plotted as ordinate is percentage surface coverage (i.e. amount adsorbed X 100 / amount adsorbed at surface saturation) rather than the more conventional amount adsorbed per unit weight of adsorbent; apart from the fact that this method gives a better mental picture of the completeness of the stabilising layer, it is more meaningful when one considers millings where the specific surface area of the substrate is changing with time. Surface saturation corresponded to the adsorption of 2.8 x 10⁻³ equivalents agent per gm. adsorbent, and a plot of the quotient, concentration in solution/amount adsorbed per unit weight of adsorbent, against concentration in solution gave a straight line suggesting Langmuir behaviour.

**Results and Discussion**

**Millings of 16.17 Dimethoxyviolanthrone at Various Concentrations of Dispersing Agent A**

The suspension for milling contained 10% of 16.17 dimethoxyviolanthrone by weight in the agent solution. Experiments were carried out at 1%, 2 1/2%, 10%, 40% and 100% by weight active agent upon the dyestuff i.e. 0.1%, 0.25%, 1.0%, 4.0% and 10.0% in the formulation as a whole. Millings were of one hour’s duration. After milling, the dispersions were analysed for particle size distribution using a centrifugal sedimentation method (11). This method furnishes size data in terms of Stokes diameter and does not distinguish single crystals from aggregates; any loose floccules are, however, dispersed during the preparation of the sample for the centrifuge, the 10% suspensions being diluted to 0.2% by addition to a 1% solution of the dispersing agent. The results shown in table 1 were read from smoothed curves drawn through the experimental points, the root mean square deviation of the latter from the smoothed curve being 1.5%.

Electron-micrographs were prepared from dilute suspensions and a selection is shown in fig. 2. These particle size distributions and electron micrographs show a marked effect of surface-active agent concentration on the milling of 16.17 dimethoxyviolanthrone in water, and two particularly striking features are the coarseness of the dispersion milled with 1% agent on dyestuff, even compared with the starting material, and the continued...