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Physical and chemical characteristics of some high purity magnesium stearate and palmitate powders

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Summary

High purity magnesium stearate and palmitate powders have been prepared at two batch sizes under different pH environments. Larger batch products were analyzed for chemical and physical character using gas chromatography, atomic absorption, surface area estimation, scanning electron microscopy, thermal analysis (moisture evolution analysis, DSC, TGA, hot stage microscopy), infra-red and X-ray diffraction techniques. Powder particles produced under acid conditions had a thin, regular, plate-like appearance whilst those manufactured from alkaline conditions had more irregular structure. Acid-manufactured powders were found to be associated with two molecules of water and had a small degree of structure which was disrupted on drying. Materials precipitated from alkaline conditions appeared to consist of two species, the major one being one molecule of magnesium stearate or palmitate associated with two molecules of water, and the second minor component probably associated with equimolar proportions of water. Estimates of activation energy (E_a) associated with the major thermal transitions confirmed the low level molecular structure in prepared materials.

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Introduction

Magnesium stearate is used extensively as a powder lubricant in tablet formulations. Commercially available batches vary in both chemical (Pilpel, 1971; Mroso et al., 1982; Hölzer, 1983) and physical character (Butcher and Jones, 1972) and have an unpredictable effect on formulations (Billany, 1981; Moody et al., 1979). However, in many studies involving magnesium stearate, little or no description of the physical and chemical nature is given.

Commercial magnesium stearate has been shown to inhibit granule (Lerk et al., 1977) and tablet dissolution (Levy and Gumtow, 1963) and reduce tablet strength (De Boer et al., 1978). This material generally contains a significant proportion of magnesium palmitate. Both magnesium stearate and palmitate, in the pure state, have been reported to exist in different forms and hydrates (Müller, 1977a; Steffens, 1978).

The failure to establish connections between the physical properties of commercial batches of magnesium stearate and their lubricant performance (Hanssen et al., 1970) shows the need for more fundamental characterization of the materials involved. A number of batches of high purity magnesium stearate and palmitate have been made under different controlled conditions. Four larger batches were chosen for more precise physicochemical characterization and compared with a pharmaceutical grade material. This is of basic relevance to the eventual understanding and optimization of lubrication by magnesium fatty salts in the pharmaceutical field.

Materials and Methods

All reagents were of analytical grade unless otherwise stated.

Large batch lubricant manufacture

Two batches of magnesium stearate (A and B) and two batches of magnesium palmitate (C and D) were prepared by precipitation from aqueous dispersion at 90°C, using a method adapted from the general preparation for pharmaceutical grade magnesium stearate (Pilpel, 1963; Müller, 1977b). A and C were prepared, after forming the sodium salt of the fatty acid as an intermediate dispersion in the presence of excess sodium hydroxide. The manufacture of B and D was carried out via the ammonium salt, adding an excess of ammonium chloride to the mixture. All batches were prepared from 0.5 mole of the respective fatty acid (specially pure, > 99% by gas chromatography, B.D.H., Poole). Precipitation was from 20 litres of deionized, double-distilled water from an all-glass still. Stirrer speed with an 8 cm marine propeller was 2850 rpm, stirrer position was standardized and pH was monitored during manufacture. The preparations were cooled at $10°C \cdot h^{-1}$, filtered off and cleaned in a Soxhlet apparatus with deionized, double-distilled water and then acetone, each for 20 h. The powders were then dried for 24 h at 50–54°C below 0.1 torr and stored at 20°C below 45% relative humidity for at least one month prior to use.

Small batch magnesium stearate manufacture

Three batches (1, 2 and 3) of magnesium stearate were prepared each from 0.05 mole stearic acid (specially pure > 99% by gas chromatography, B.D.H., Poole) with precipitation from 3 litres of deionized double-distilled water stirred at approximately 600 rpm. Batch 1 was prepared in a similar manner to larger batches A and C. Batch 2 was prepared from an ammonium salt intermediate, a small excess of ammonia creating a slightly alkaline environment. The preparation of magnesium stearate batch 3 was similar to that for batch 2 but prior to cooling this batch was maintained at 90°C for 6 days.

Chemical determination

The stearate and palmitate content of powders A–D were determined by gas chromatography of methyl derivatives using a Pye Model 104 instrument (Pye Unicam, Cambridge, U.K.). The 5-foot glass column was 10% w/w polyethylene glycol 20 M on chromosorb W (Phase Separations, Queensferry, U.K.) at 170°C and nitrogen flow 60 ml · min^{-1}.

Samples were boiled in acetic acid and the liberated fatty acids extracted into chloroform. The solvent was removed under vacuum at 55°C. The solid was dried at 50–52°C below 0.1 torr for 24 h. Approximately 20 mg, accurately weighed, was methylated by refluxing in a solution of 14% boron trifluoride in methanol (Sigma Chemicals, Poole, U.K.) for 5 min (Darbre, 1979). The methyl esters, in heptane solution, were compared with reference standards (Pierce and Warriner, Chester, U.K.). At least twenty 5-μl injections were assessed from 2 or 3 separate reactions.

The aqueous solution remaining after reaction of the powder samples with acetic acid was diluted and magnesium ion content analysed using a Pye-Unicam SP 1950 atomic absorption spectrophotometer. Readings were taken for 20 s and results represent a mean of ten readings from at least two separate reaction mixtures.

A further aqueous solution was obtained by boiling about 2.5 g powder, accurately weighed, with 30 ml of 2 M acetic acid. The resultant solution was diluted to 50 ml and analysed for chloride using an Orion 94-17 specific electrode (M.S.E. Scientific Instr., Crawley, U.K.), calibrated with sodium chloride solutions.

Moisture content

A DuPont Model 903 moisture evolution analyzer was used to measure the moisture evolved from 20–50 mg of powders at 100°C for 1 h. This time interval was sufficient to record all the available moisture. The instrument was calibrated with a 2-μl dip tube of distilled water.

Surface area

The B.E.T. (Brunauer, Emmett, Teller) surface area was measured by nitrogen adsorption at liquid nitrogen temperature using an Orr surface area pore volume analyzer (Model 2100, Micromeritics, Luton, U.K.) and calibrated using a National Physics Laboratory carbon standard (Standard M11-01, London, U.K.). Powders were dried for 16 h at 78°C below 0.1 torr and outgassed on the instrument for 22–24 h at 23°C. Results represent an average of two determinations.

Electron microscopy

Powders were observed using a Stereoscan 600 electron microscope (Cambridge Instr., U.K.) with backscattered electron detector (K.E. Inst., Cambridge, U.K.) to give an indication of particle shape, size and surface morphology.

Thermal analysis

Samples weighing up to 10 mg were analyzed using a DuPont Model 910 differential scanning calorimeter linked to a Model 1090 thermal analyzer (DuPont, Stevenage, U.K.). Open aluminium pans were used at 2°C · min^{-1} heating rate. Thermogravimetric analysis (TGA) was performed on 10–20 mg samples using a Model 950 thermogravimetric analyser (DuPont, Stevenage, U.K.) at a heating rate of 2°C · min^{-1}. Both differential scanning calorimetry (DSC) and TGA were carried out on samples previously equilibrated at 20°C below 45% relative humidity, and DSC on samples dried at 90°C below 0.1 torr for 18–24 h. Further DSC analyses were performed at heating rates of 5, 10, 20 and 50°C · min^{-1}. Data from these were used to calculate the activation energies for moisture loss and melting, using the method of Kissinger (1957). DSC calibration was achieved with an indium standard at 156.6°C and TGA with a thermocouple positioned adjacent to the instrument thermocouple and cold junction, connected to a sensitive millivoltmeter.

Thermal microscopy

A Watson microscope (London, U.K.) and hot stage unit (Stanton Redcroft, London, U.K.), calibrated with a phenacetin standard at 135°C, were used to observe the powders in normal transmitted, and polarised light, up to 150°C. The heating rate was 2°C · min^{-1} corresponding to that for DSC and TGA.

Infra-red spectroscopy

Infra-red spectra of powders A–D were obtained using a Perkin Elmer 297 Model spectrophotometer (Beaconsfield, U.K.) scanning from 4000 to 600 cm^{-1}. 1.0 ± 0.1% w/w of undried powder sample was ground with dry potassium bromide, compressed to a transparent disc and scanned for 3 min.

X-Ray diffraction

X-Ray diffraction patterns were obtained of powder samples, mounted on adhesive tape, using an XDC-700 Guinier-Hägg camera (Junger Instr., Stockholm, Sweden). Irradiation was for 1 h from a copper source.

Results and Discussion

Fig. 1 illustrates the effect of manufacturing conditions on the particle morphology of magnesium stearate and palmitate powders. Larger batches B and D made in an acidic environment produced thin, regular, plate-like particles, where alkaline conditions produced particles with a more irregular structure for batches A and C. For the smaller batch preparation in alkaline conditions the particles produced were needle-like in shape. It was also possible to produce dendritic structures (batch 2) probably because of reduced agitation (Mullin, 1972). The larger particles observed in batch 3 resulted when the precipitation media was held at 90°C for 144 h prior to cooling. The evaporation of ammonia during this manufacture left the pH slightly acidic, hence particles of batch 3 are plate-like.

Fatty acid and magnesium ion analyses were combined to give values for magnesium salt and excess magnesium present in the original powders A–D (Table 1). All laboratory-made powders contain only one fatty acid species. The presence of excess magnesium ions indicates the possibility of a small amount of inorganic impurity but the small values of chloride content show the absence of appreciable magnesium chloride residue from the manufacture.

The surface area of the irregular forms of magnesium stearate and palmitate (A and C) is larger than that for regular plate-like particles (B and D). Thus for

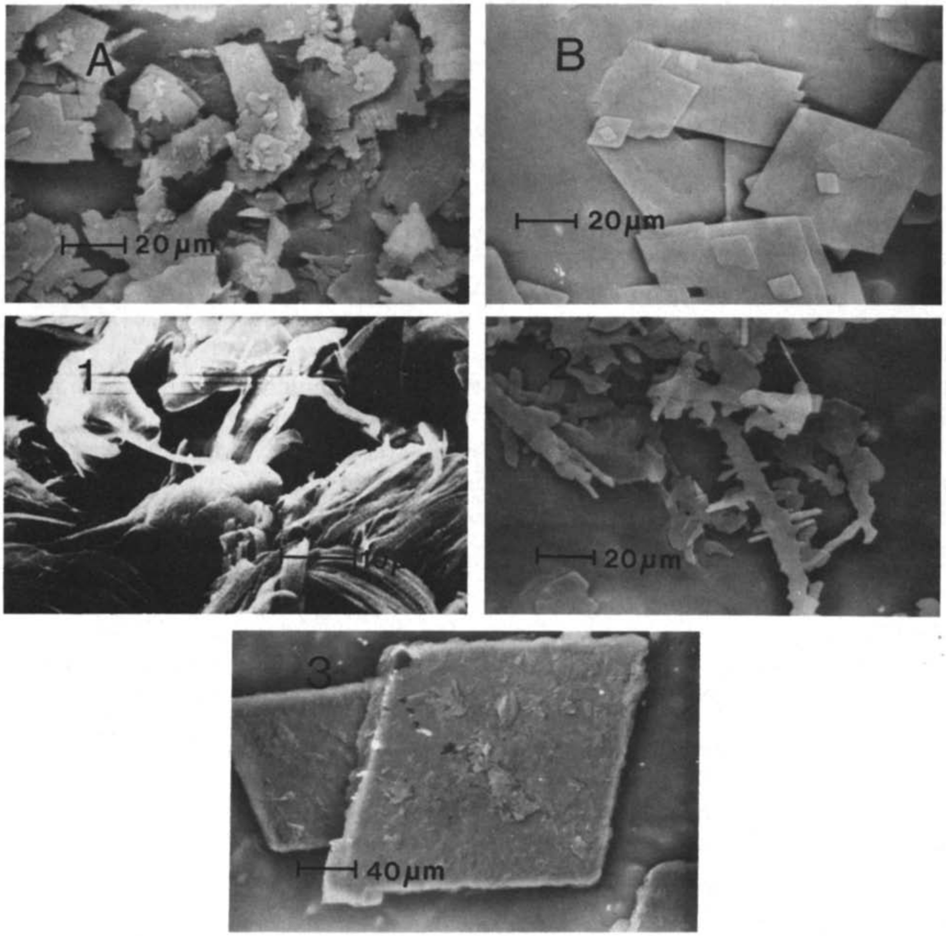

Fig. 1. Electron micrographs of magnesium stearate prepared in 100 g (A and B) and 10 g (1, 2 and 3) batches.

TABLE 1

SOME PHYSICOCHEMICAL CHARACTERISTICS OF PREPARED MAGNESIUM STEARATE AND PALMITATE

Sample		pH of prep.	Particle form	% mg salt of fatty acid	Excess mg %	Excess Cl %	Surface area m^2/g
Mag. stear.	A	10.1–6.9	irregular	92.58(5.15)[a]	1.27	0.002	4.17
	B	6.5–5.1	plate	93.45(2.78)	1.39	0.006	1.57
Mag. pal.	C	9.7–6.9	irregular	90.82(4.95)	1.66	0.003	2.99
	D	6.6–5.7	plate	86.61(3.92)	0.980	0.003	1.43

[a] Standard deviation bracketed.

equivalent processes, an alkaline manufacturing condition produces material with more specific surface (Table 1). Literature values for the surface area of commercially manufactured samples are usually higher than those given here for high purity powders (Butcher, 1973; Lerk et al., 1977; Moody, 1981) with values from 0.95 to 29.0 $m^2 \cdot g^{-1}$ reported (Buehler, 1978). Measurements of particle size distributions were not attempted as the small particles tend to form cohesive agglomerates.

The moisture content data show that samples B and D have two molecules of water present for every magnesium fatty salt molecule whereas the irregular particles contain less moisture from a molar consideration (Table 2). This is discussed later with respect to thermal analysis results. Attempts to quantify moisture by infra-red spectroscopy were unsuccessful due to the poor solubility of the powders in all common solvents. Karl Fischer moisture determinations gave widely variable results, possibly due to an interaction between stearate or palmitate and free iodine in the Fischer reagent.

Thus the shape, surface area and moisture content of magnesium stearate and palmitate are clearly influenced by manufacturing conditions. This is critical as these factors may play an important role in determining the lubricity of a particular powder batch.

TABLE 2

MOISTURE CONTENT OF MAGNESIUM STEARATE AND PALMITATE BY MOISTURE EVOLUTION ANALYSIS (M.E.A.) AND THERMOGRAVIMETRIC ANALYSIS (T.G.A.)

Sample	% w/w moisture		Molecular ratio water/fatty acid [a]
	M.E.A.	T.G.A.	
A	5.16 (0.12) [b]	4.67	1.79
B	5.83 (0.09)	5.59	2.03
C	6.20 (0.08)	5.99	1.96
D	6.32 (0.17)	5.99	2.01

[a] Ratio based on M.E.A. data.

[b] Standard deviation bracketed.

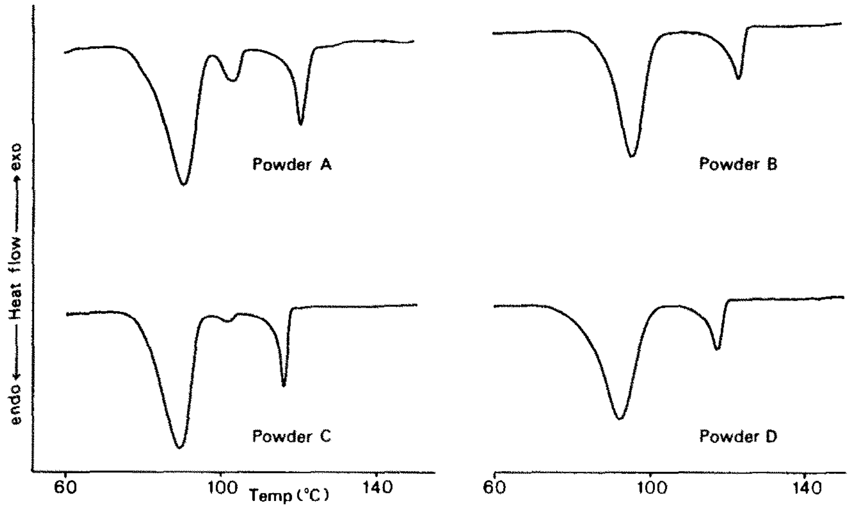

Fig. 2. Differential Thermograms at 2°C·min^{-1} of undried magnesium stearate (A and B) and magnesium palmitate (C and D).

Considering now the thermal analysis data, the irregular forms A and C each show four thermal events when analyzed by DSC. Three of these are readily discernible from scans of undried samples (Fig. 2). The small fourth endotherm is difficult to see with undried samples because the large events due to moisture loss cause a lack of scale sensitivity. Scans of dried A and C show the third and fourth endotherms only (Fig. 3). Endotherm peak temperatures are 90, 103, 121 and 132°C

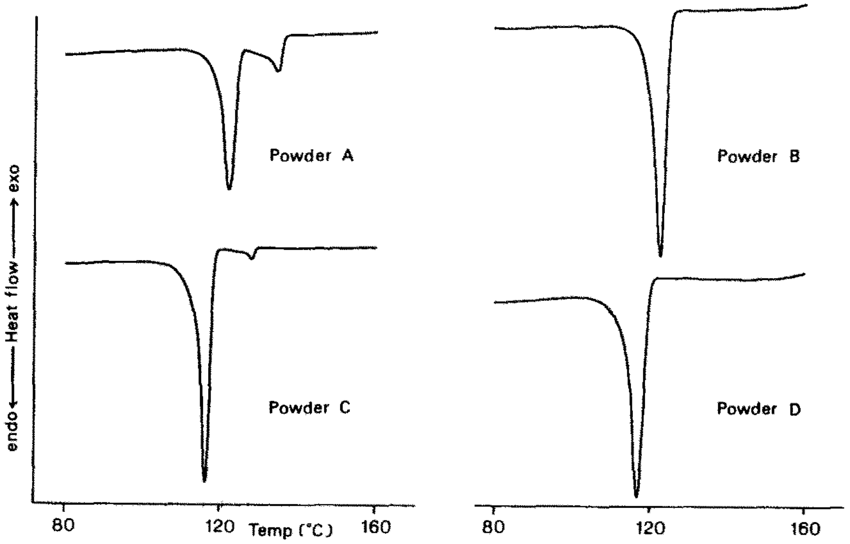

Fig. 3. Differential Thermograms at 2°C·min^{-1} of magnesium stearate (A and B) and magnesium palmitate (C and D) dried at 90°C under vacuum.

for magnesium stearate A and 89, 101, 116 and 126°C for magnesium palmitate C.

The plate-like samples from powders B and D each show two endotherms in their DSC thermal profiles. These occur at 96 and 123°C for magnesium stearate B and at 92 and 118°C for magnesium palmitate D (Fig. 2). Only the latter is present in each case when dried samples are analyzed (Fig. 3).

The first two endotherms of samples A and C, and the first of B and D are due to the loss of bound moisture. Evidence for this is the absence of these endotherms in dried samples and the weight losses observed, using TGA, for undried samples at temperatures corresponding to these endotherms (Fig. 4). The total percentage weight losses observed by TGA were lower than the figures for moisture evolution analysis, but followed the same rank order (Table 2).

Sample A and C incur a two-stage weight loss at temperatures corresponding to the first two endotherms shown by DSC (Figs. 2 and 4). This indicates moisture held in two different ways. It is possible that most of the water is bound in the ratio of two molecules to every one of fatty salt, with a small amount of water bound more strongly in a ratio of one molecule to each fatty acid molecule. This would explain the observed molar ratio water/magnesium fatty salt of less than 2 for A and C and of 2 for powders B and D which have only one type of bound moisture.

The bound nature of the moisture is indicated by the sharpness of the respective DSC endotherms and TGA sample weight loss over a small temperature range. Also, the infra-red spectra show a broad band from 3100 to 3700 cm^{-1}, the characteristic band of bound moisture (Williams and Fleming, 1966).

It was possible, by hot stage microscopy, to observe the effect of moisture loss on powder particle morphology and refractive behaviour. This appeared to be more

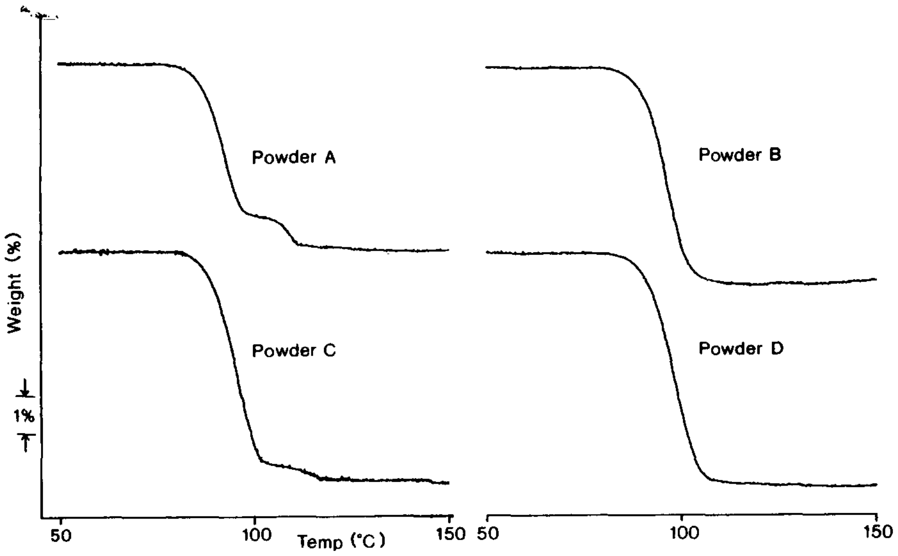

Fig. 4. Thermogravimetric Plots at 2°C·min^{-1} of undried magnesium stearate (A and B) and magnesium palmitate (C and D).

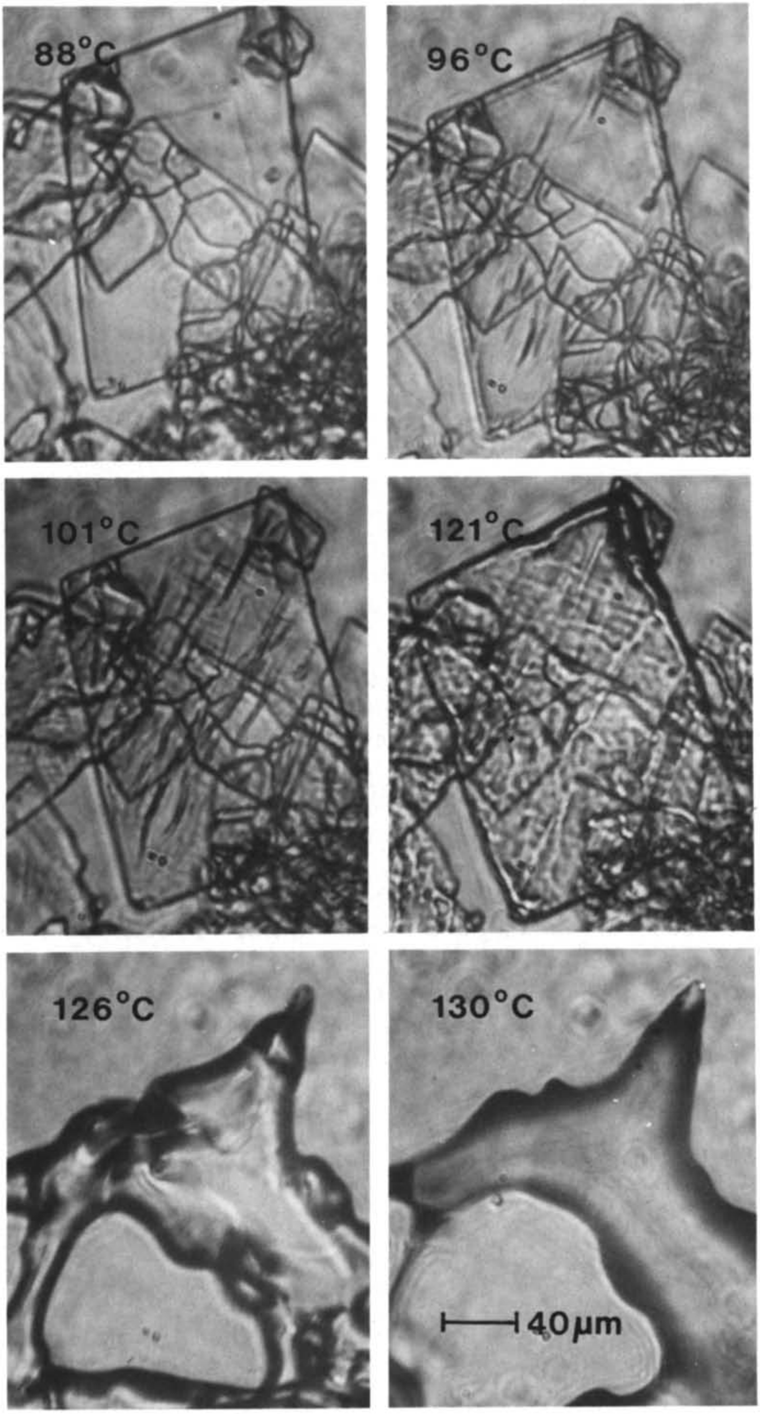

Fig. 5. Photomicrographs showing the thermal changes of magnesium stearate (B).

pronounced for regular plate-like samples B and D. The loss of moisture in these cases was accompanied by the appearance of diagonal striations on the particles, shown occurring for magnesium stearate B at 96°C (Fig. 5). The particles also lose their anisotropic property at this temperature. The smaller irregular particles of powders A and C did not show anisotropic behaviour. Only slight particle changes are visible over the two temperature ranges where these powders lose moisture.

The remaining thermal events, not due to the loss of bound moisture from the powders, are associated with melting. These endotherms are seen alone when dried samples are analyzed by DSC (Fig. 3). Powders A and C possess two such events whereas B and D have one only. However, magnesium stearate B does not become completely liquid until 130°C (Fig. 5) although the corresponding endotherm (Fig. 3) is complete at 126°C. Thus the final transition to complete liquid requires a small amount of energy which does not register as an appreciable heat flow difference on the DSC trace. A similar phenomenon occurs for all four powders, being more pronounced for irregular batches A and C. It is likely that the melting of the powders involves a two-stage phase transition, the first stage only registering as a DSC endotherm. Multiple transitions of this kind have been described in the literature for magnesium stearate and other metal soaps although the sample purity in those cases is questionable (Hattiangdi et al., 1949; Vold et al., 1941).

It seems likely that the additional small melting endotherms of powders A and C (Fig. 3) are due to a small amount of a different pseudo-polymorph of magnesium stearate and palmitate, respectively. It is this pseudo-polymorph which does not bind two molecules of water and thus causes the samples with irregular particles to have a lower molecular water content.

Table 3 gives the activation energies (E_a) of the two major thermal transitions calculated from the variation of endotherm peak temperature (T_m) with change in DSC heating rate (ϕ) (Kissinger, 1957). A plot of log (ϕ/T_m^2) against $1/T_m$ yields a straight line with slope $-E_a/2.303$ R. This is shown in Fig. 6 for the transition involving the major water loss from magnesium stearate sample A. Analysis of the transition for water loss gives relatively small activation energies (E_aw) corresponding to values of 238 kJ · mol^{-1} reported for the solid I–solid II transition of sulphathiazole (Shami et al., 1972). The activation energies associated with melting (E_am) are larger than E_aw values, but small enough, compared with 850 kJ · mol^{-1}

TABLE 3

ACTIVATION ENERGIES FOR THE MAJOR WATER LOSS (E_aw) AND MAJOR MELTING ENDOTHERM (E_am) CALCULATED ACCORDING TO KISSINGER (1957).

Sample	Activation Energy (kJ·mol^{-1})	
	E_aw	E_am
A	186	361
B	166	339
C	156	299
D	153	371

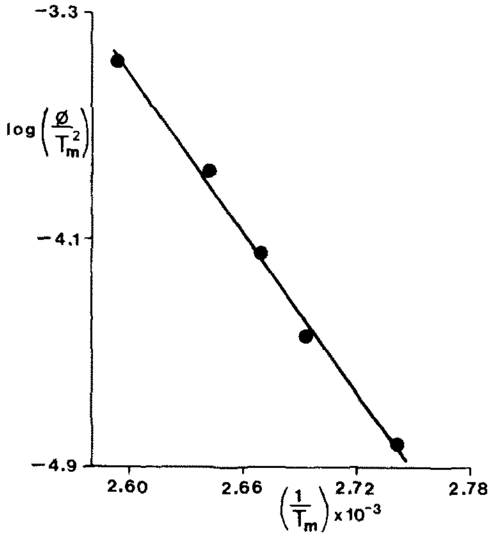

Fig. 6. Plot showing the relationship of heating rate and peak maximum temperature for the transition endotherm in determination of activation energy.

for the solid–liquid transition of phenylbutazone (Müller, 1978), to suggest a low level of structure in the stearate or palmitate powder prior to melting.

As these four samples of high purity show endotherms ranging from 89 to 132°C it is not surprising that commercial batches, which are a variable mixture of these and other compounds, have been reported to have melting points from 86°C to 145°C (Jacobson and Holmes, 1916; Levy, 1968; Katalog Pharmazeutischer Hilfsstoffe, 1974; Weast, 1978; Hölzer and Sjögren, 1981).

The X-ray powder diffraction patterns for powders A–D were poorly resolved confirming a small degree of crystallinity suggested by E_am figures. Slightly stronger diffraction lines for plate-like samples B and D indicate a greater degree of molecular order in these particles. This is emphasized by their anisotropic nature and the fact that they contain only one type of bound moisture. Samples A and C possess a small amount of a second pseudo-polymorph which may disrupt the small degree of molecular order causing the X-ray diffraction lines to be faint and anisotropy to be absent. X-Ray diffraction patterns for dried powders show no visible lines, indicating amorphous samples. This shows the importance of bound water in the low level structuring of magnesium stearate and palmitate molecules.

Conclusions

(1) Samples of high purity magnesium stearate and palmitate have been prepared and analyzed for physical and chemical character.

(2) The solid state characteristics of magnesium stearate and palmitate powders are influenced by manufacturing process variables such as pH, stirring rate and precipitation concentration.

(3) For equivalent manufacturing conditions, powders with plate-like particles have a lower surface area.

(4) The energy requirement for the final transition of these materials to complete liquid is so low as not to register as a DSC endotherm.

(5) Regular-plate like particles of acid-precipitated lubricant powders (B and D) consist of molecules of magnesium stearate or palmitate each associated with two water molecules. These units are structured to a small degree but this structure is disrupted when the powder is dried.

(6) Batches prepared over an alkaline pH range, such as powders A and C, consist of two species. Firstly dihydrate units proposed for acidic preparations B and D and secondly as association with equimolar or other proportion of moisture which disrupts the structuring of dihydrate units.

(7) X-Ray diffraction and activation energies for moisture loss and melting for these materials confirm a low degree of structure with anisotropy for plate-like materials suggesting that these possess slightly more molecular order.

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