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The effect of moisture on the structure of magnesium stearate

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Abstract

The effects of moisture on the structure of two commercial (batch A and batch B) and one pure grade (batch C) of magnesium stearate have been examined by using differential scanning calorimetry (DSC), thermogravimetry (TG), X-ray powder diffractometry (XRD) and thermomicroscopy (HSM). The results suggest that the role of water is different in both of the commercial batches. Powder A showed a two-stage mass loss at temperatures between 25°C and 100°C indicating that the water present was tightly bound. The scans from batch B exhibited a continual mass decrease indicating that the moisture present was more loosely bound. With high purity magnesium stearate (batch C) water was bound in the ratio of two molecules to every one of the fatty acid salt. During storage to hydrate at 76% RH and 93% RH, powder A became more crystalline while powder B remained amorphous. Magnesium stearate dihydrate exhibited no tendency to form a trihydrate or higher hydrated forms. A short review of previous studies on magnesium stearate is given in the Introduction.

Keywords: DSC; HSM; Magnesium stearate; TG; Water; XRD

1. Introduction

Magnesium stearate is widely used as a powder lubricant in pharmaceutical tablet and capsule formulations, due mainly to its ability to decrease friction between the surface of tablets and the die wall during the ejection process [1]. Magnesium

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stearate is classified as being non-hygroscopic [2], although the compound apparently will sorb moisture when stored under relative humidities greater than approximately 85% [2–4]. Commercially available batches vary in both chemical and physical character and have an unpredictable effect on formulations. Previous studies have suggested that many physical parameters, such as crystal structure, particle size, specific surface area or moisture content affect the lubricity of magnesium stearate. Analysis of pure grade materials has shown that magnesium stearate can exist as four different pseudopolymorphs: a needle-like trihydrate, a lamellar dihydrate, a monohydrate and an anhydrous form, each of which may have different lubrication properties. The dihydrate has been shown to be the best lubricant [5]. Frattini and Simioni [6] evaluated the lubricant properties of several magnesium stearate samples differing in their specific surface area and reported a good correlation between the magnitude of the specific surface area and the lubricant efficacy of the various samples. A recent study [7] examined two commercial-grade batches of magnesium stearate. Their crystal structures and moisture contents were similar, their chemical compositions differed only slightly, but their particle size distributions and specific surface areas differed significantly. The batch with smaller particle size and larger specific surface area had considerably better lubricity. The effects of tensile strength and particle morphology have also been reported [8].

Pure magnesium stearate may be prepared by precipitation from an aqueous medium according to the reaction

$$2CH_3(CH_2)_{16}COOX + MgCl_2 \rightarrow [CH_3(CH_2)_{16}COO]_2Mg + 2XCl$$

where X is a cation such as NH_4^+ or Na^+. Both plate-shaped dihydrate and needle-shaped trihydrate forms of magnesium stearate have been prepared by this method, the hydration state being a function of the pH of the precipitation medium and the cooling rate [9,10]. The hydrates have different crystal habits and, more importantly, belong to different crystal systems [11]. The effect of manufacturing conditions on the particle morphology of magnesium stearate powders has also been studied by Miller and York [10]. Larger batches made in an acidic environment produced thin, regular, plate-like particles whereas alkaline conditions produced particles with a more irregular structure. For smaller batch preparation in alkaline conditions the particles produced were needle-like in shape. It was also possible to produce dendritic structures. The surface area of the irregular forms was larger than that for the regular plate-like particles. Thus for equivalent processes, an alkaline manufacturing condition produced material with a higher specific surface. Data on moisture content showed that the samples including plate-like particles had two molecules of water present for every magnesium fatty salt molecule whereas the irregular particles contained less moisture from a molar consideration. Thus the shape, surface area and moisture content of magnesium stearate appeared to be clearly influenced by manufacturing conditions. However, in the study of Ertel and Carstenseen [1] the crystal habit was not sensitive to either the pH of the precipitation medium or the cooling rate, as all samples consisted of plate-shaped crystals. The needle-shaped crystals could not be isolated under any conditions. The pH of the precipitation medium did have an effect on the amount of moisture bound within the magnesium stearate crystals. Heating magnesium stearate at 105°C not only resulted in a loss of water of hydration from the crystals, but also a disruption of the three-dimensional lattice structure of the crystals. Both of these effects could be reversed by storing the dried crystals under appropriate relative humidity conditions. Müller et al. [12] studied the influence of physical properties of highly purified magnesium stearates on lubrication. The lubrication capabilities of highly purified magnesium stearates with different physical properties were tested with lactose and granulatum simplex. The magnesium stearates used were different in crystal habit (needle-shaped or plate-like), crystal structure (different water content, particle diameter) and bulk density. Measured data included residual and ejection forces, plastic and elastic deformation energies and tablet hardness. The best results were obtained with magnesium stearates with more than 5% water of crystallization, particle diameters between 3 and 15 μm and bulk densities of more than 6 ml g^{-1}. The crystal habit was less important using magnesium stearates with these properties.

However, the hydration state of commercial batches is still poorly understood, despite the clear importance of this factor to lubrication. Steffens et al. [13] have reported studies on commercial magnesium stearate products. The efficiency of three commercially-available batches as a tablet lubricant was determined using lactose as a model excipient. Two of the batches were additionally tested in a formulation containing nitrofurantoin, sulfadiazine, lactose, Avicel and Aerosil. Moreover the physical properties, such as particle size, water content, crystallinity or thermoanalytical behavior were determined. It was shown that the relationship between physical properties and lubricity, found for pure grade magnesium stearate [12], was also valid for commercial products. The best lubricity was found for a magnesium stearate containing a large amount of water of crystallization. Ertel and Carstenseen [14] characterized three batches of commercial magnesium stearate in terms of their fatty acid composition, moisture content, and specific surface area. None of these variables appeared to have any effect on the lubricant activity of the samples. The lubricant properties of the compound were further examined using three hydrates of laboratory-prepared (pure) magnesium stearate. Based on the results obtained from the pure samples, it appeared that differences in the lubricant properties of magnesium stearate correlated with differences in moisture content and crystalline structure.

Miller and York [15] have presented a frictional assessment of magnesium stearate and magnesium palmitate powders. Powders with a well-ordered crystal structure and particle shape had a lower initial maximum coefficient of friction μ_a (maximum static friction coefficient). The difference between μ_a and μ_b, the equilibrium dynamic friction coefficient (kinetic friction coefficient), gave an indication of lubricant film-forming propensity. The initial frictional properties of a magnesium stearate or palmitate powder varied according to their physicochemical characteristics. In theory, dihydrate with plate-like particles had superior initial lubricant properties. The equilibrium frictional properties of magnesium stearate or magnesium palmitate powder are less influenced by physicochemical characteristics.

As noted above, several possible reasons for batch-to-batch variation in the lubricant properties of commercial magnesium stearate have been proposed. However, a common denominator in most of the reports seems to be moisture content and crystalline structure. The purpose of this study was to compare physical characteristics and hydration behavior of two commercial magnesium stearate batches by means of thermal analysis. In addition, a pure grade magnesium stearate was studied.

2. Experimental

2.1. Material used

Samples from two different batches (A and B) of commercial magnesium stearate (Chemische Werke Otto Bärlocher GmbH, Munich, Germany) and one batch of pure magnesium stearate (batch C) were used as received. The three batches were the same as used previously; batches A, B and C corresponding to batches 2, 1 and 3, respectively as described by Leinonen et al. [7].

To examine the hydration behavior of magnesium stearate, desiccators containing saturated solutions of the following salts were prepared: NaCl (76% RH) and KNO_3 (93% RH). The desiccators were stored at 20°C to maintain the relative humidities shown in parentheses. In addition, a desiccator containing silica gel was prepared to produce a dry atmosphere.

2.2. Methods

Thermal analyses

Differential scanning calorimetric analyses were carried out in punched aluminum pans using a Perkin-Elmer DSC-7 with nitrogen supply. Thermogravimetric analyses were performed with a Perkin-Elmer TGA-7 thermogravimetric analyzer. About 2 mg samples, accurately weighed, were heated at a rate of 10°C min^{-1}.

X-ray diffraction studies

Powder X-ray diffraction patterns were obtained on a Philips PW1820, APD1700 automated powder diffractometer system with the following conditions: tube type Cu $K\alpha_{1,2}$; wavelengths 0.154060, 0.154439 nm; generator 50 kV, 40 mA; automatic divergence slit (irradiated sample length 12.5 mm); receiving slit 0.1 mm; fixed scatter slit (1°); proportional detector; step size, sample time 0.015°, 1.00 s, 0.015 deg s^{-1}; peak angle range 6.000–30.000°. Measured raw data were analyzed using the Philips APD1700 software package.

Thermomicroscopy

An Olympus optical microscope (model BH-2) together with a Mettler FP82 hot stage assembly were used for the study. The heating rate was 5°C min^{-1}.

3. Results and discussion

The crystal structures of the two commercial magnesium stearates A and B were confirmed by X-ray powder diffraction. Both of the batches appeared amorphous (Fig. 1). However, of particular interest is the region near $2\theta = 21°$. Batch C, representing high purity magnesium stearate, was crystalline (Fig. 2). The d values and the relative intensities I/I_{max} expressed as percentages of the strongest line in the pattern for the form C are given in Table 1.

The commercial batch A of magnesium stearate showed three thermal events when analyzed by DSC (Fig. 3, curve a). Endotherm peak temperatures were 72°C, 87°C, and 110°C. Scans of the commercial batch B showed two endotherms at 75°C and 105°C (Fig. 3, curve b). Samples from powder C also showed two endotherms in their DSC profiles. These occurred at 97°C and 123°C (Fig. 3, curve c). Only the latter was present when dried samples of the batch C were analyzed (Fig. 4). Previous workers have assigned the low temperature endotherms to the loss of bound water from the crystals and the high temperature endotherm to a melting phenomenon [10,11,16]. Hence, the first two endotherms of the sample A, and the first endotherms of samples B and C were due to the loss of bound moisture. The evidence for this was the mass losses observed using TG for undried samples at temperatures corresponding to these endotherms (Fig. 5). The remaining thermal events are associated with melting. Although the moisture contents of the commercial batches A and B are almost equal ($\Delta m \approx -3$ wt.% from 25°C to 100°C), sample A incurred a two-stage mass loss at temperatures corresponding to the first

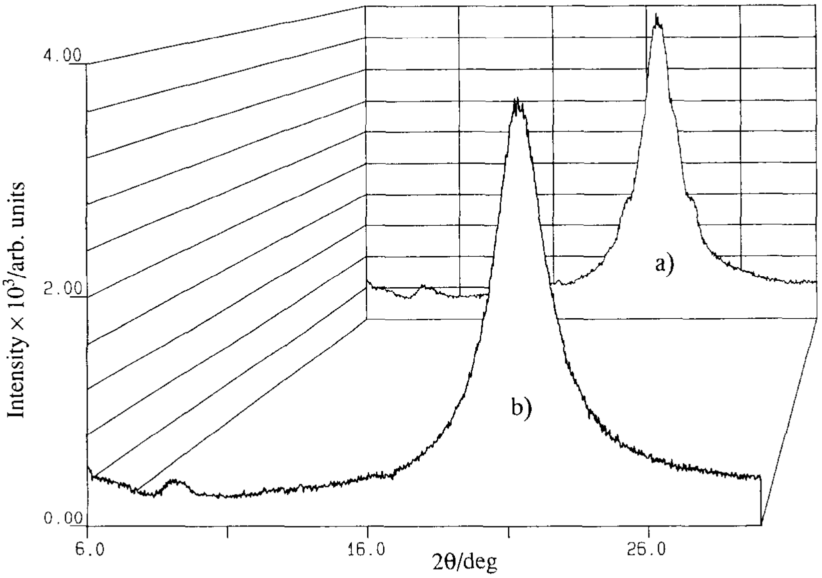

Fig. 1. X-ray powder diffraction patterns of commercial magnesium stearates: curve (a) batch A; curve (b) batch B. Cu Kα, 50 kV and 40 mA.

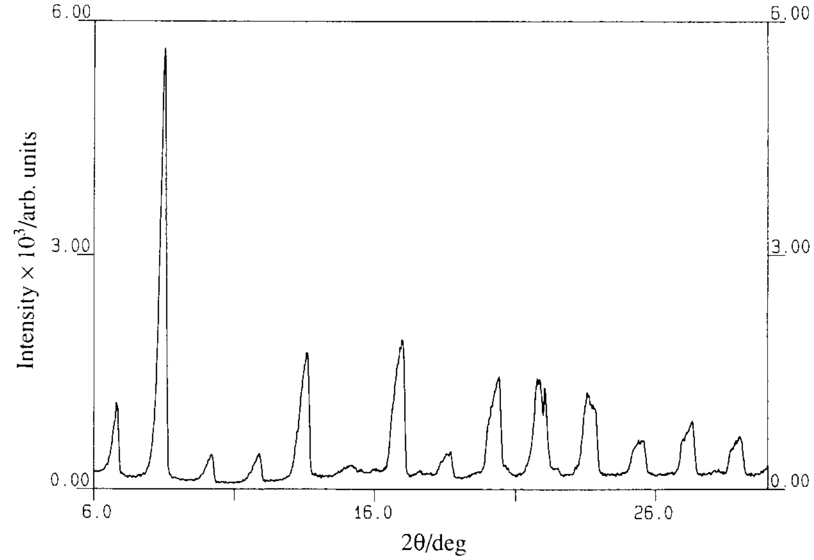

Fig. 2. X-ray powder diffraction pattern of pure grade magnesium stearate (batch C). Cu Kα, 50 kV and 40 mA.

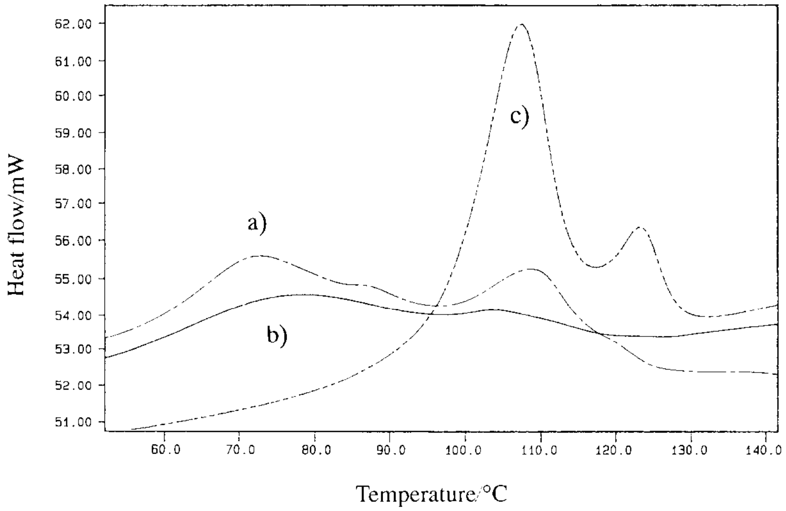

Fig. 3. DSC profiles of two commercial and one pure grade magnesium stearate: curve (a) batch A; curve (b) batch B; curve (c) batch C. Heating rate 10 C min^{-1}.

two endotherms shown by DSC (Figs. 3, curve a and 5, curve a). This indicates that the moisture was held in two different ways. Powder B contained only one type of bound moisture (Fig. 5, curve b). In the high purity magnesium stearate, it seems that water was bound in the ratio of two molecules to every one of the fatty acid salt. The bound nature of the moisture is indicated by the sharpness of the

Table 1
X-ray powder diffraction data for pure grade magnesium stearate (batch C) using Cu Kα 50 kV and 40 mA

2θ/deg [a]	d_{spac}/nm [b]	I/I_{max}/% [c]
6.83	1.293	15
8.52	1.037	100
10.20	0.867	6
11.90	0.743	7
13.60	0.651	31
15.97	0.554	2
16.59	0.534	15
16.75	0.529	27
17.00	0.521	32
17.59	0.504	1
18.31	0.484	3
18.51	0.479	6
18.69	0.474	5
19.98	0.444	12
20.42	0.435	22
21.72	0.409	23
21.84	0.407	23
22.05	0.403	19
22.49	0.395	2
23.49	0.378	20
23.85	0.373	16
25.16	0.354	6
25.56	0.348	9
26.90	0.331	8
27.28	0.327	14
28.13	0.317	1
28.64	0.311	6
29.04	0.307	9

[a] Twice the angle of incidence or reflection.
[b] Interplanar spacing.
[c] Percentage relative intensity (based on maximum intensity of 100; Cu Kα, 50 kV and 40 mA).

respective DSC endotherm (Fig. 3, curve c) and the TG sample mass loss over a small temperature range (Fig. 5, curve c). The observed mass loss in powder C from 25°C to 125°C was about 5.8 wt.%.

The effect of moisture loss on powder particle morphology and refractive behavior was studied by hot stage microscopy. This appeared to be most pronounced for regular plates such as sample C. The loss of moisture from this sample was accompanied by the appearance of diagonal striations in the particles at about 95°C. The loss of moisture resulted also in darkening of the appearance of the crystals when viewed under crossed polarized light, indicating a loss of their anisotropic property, as has been described previously [10]. The plate-shaped appearance of the original dihydrate was retained until melting at about 125°C. The smaller, irregular particles of powders A and B did not show anisotropic behavior.

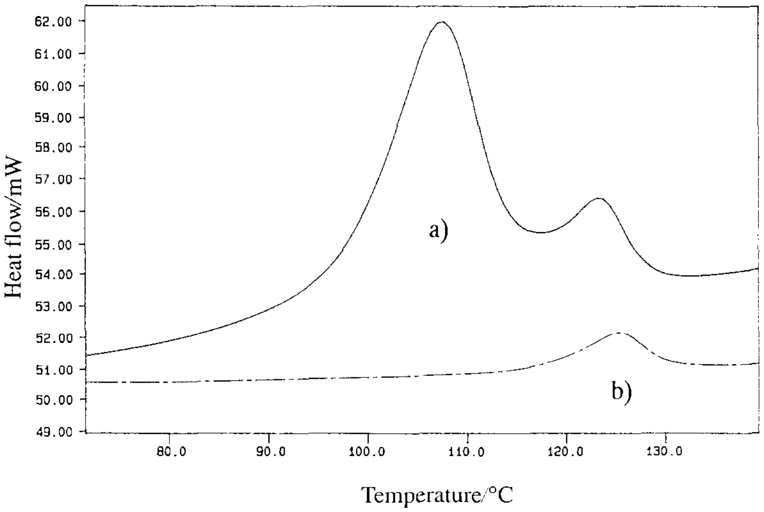

Fig. 4. DSC profiles of pure grade magnesium stearate: curve (a) dihydrate; curve (b) anhydrate. Heating rate 10°C $\min^{-1}$.

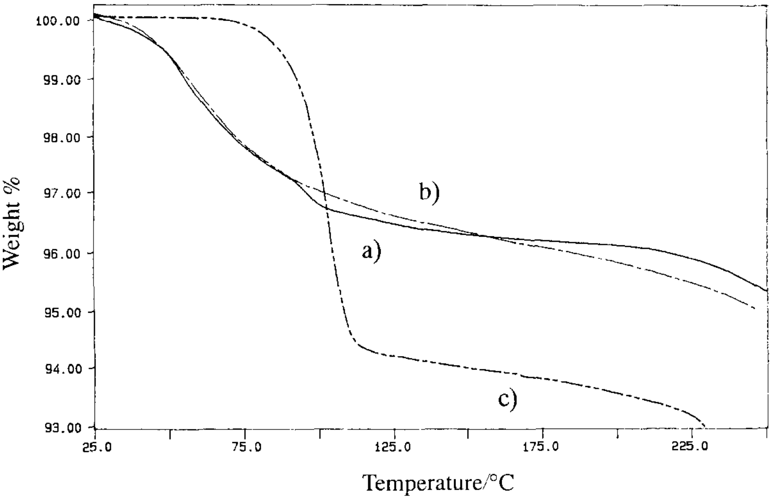

Fig. 5. TG curves for two commercial and one pure grade magnesium stearates: curve (a) batch A; curve (b) batch B; curve (c) batch C. Heating rate 10°C $\min^{-1}$.

Only slight particle changes were visible over the temperature range where those powders lost moisture.

Samples from the two commercial magnesium stearate batches were stored over the saturated salt solutions described in the methodology for 3 days. Table 2 summarizes the results from the TG analysis (Figs. 6 and 7) and the respective

Table 2
Percentage weight losses of commercial magnesium stearates observed by TG after hydrating or drying for 3 days

Sample	Batch A/wt%	Batch B/wt%
Dried	−2.5	−2.7
As received	−3.2	−3.0
76% RH	−3.4	−3.4
93% RH	−4.5	−3.4

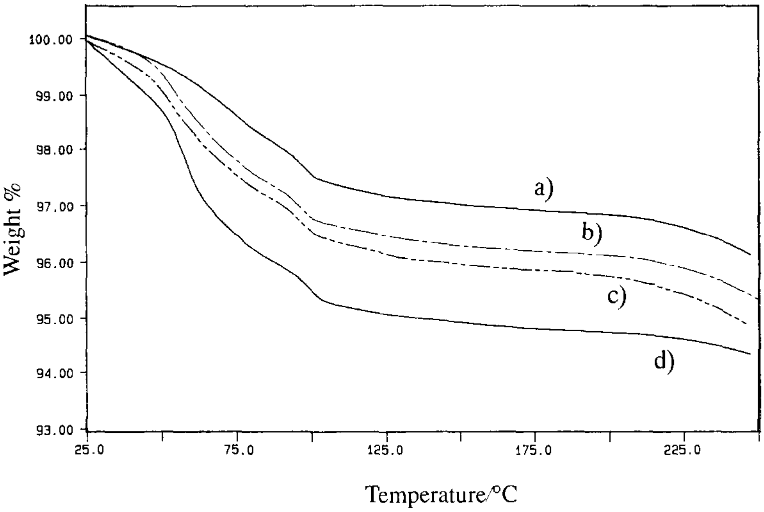

Fig. 6. TG curves of batch A magnesium stearate: curve (a) dried; curve (b) as received; curve (c) 75% RH; curve (d) 93% RH. Heating rate 10°C min^{-1}.

XRD profiles are presented in Figs. 8 and 9. It is proposed that the mechanism of water sorption is different between the two batches A and B. Powder A absorbed moisture willingly when the relative humidity exceeded 76%; this was not apparent with powder B. Furthermore, as the ambient relative humidity became high enough it resulted in structural changes in batch A towards a more crystalline form (Fig. 8, curve d). With powder B, the percentage mass loss from the 93% RH sample was lower than in the case of batch A, and no structural changes were detected by powder XRD.

Magnesium stearate dihydrate (batch C) exhibited no tendency to form a trihydrae or higher hydrated forms when stored over the saturated salt solutions for three days (Fig. 10, curves c,d). This is not surprising, since magnesium stearate is classified as being non-hygroscopic [2]. Furthermore, the dihydrate exhibited no tendency to lose water of crystallization when stored over silica gel (Fig. 10, curve a).

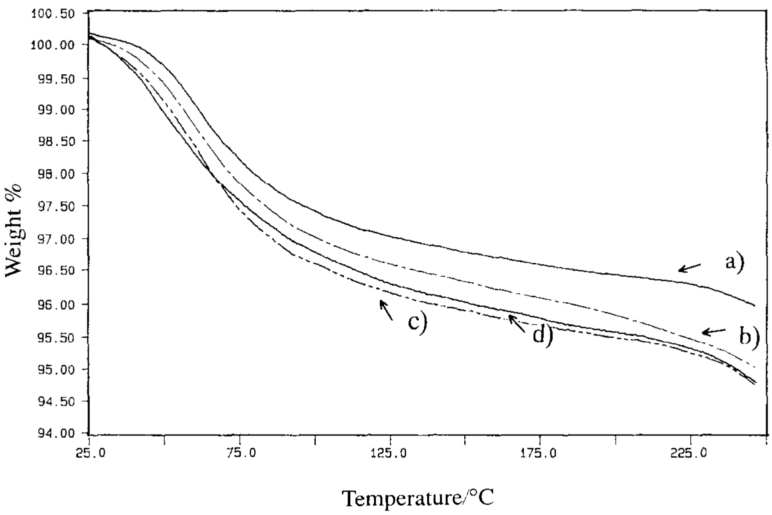

Fig. 7. TG curves of batch B magnesium stearate: curve (a) dried; curve (b) as received; curve (c) 75% RH; curve (d) 93% RH. Heating rate 10°C min^{-1}.

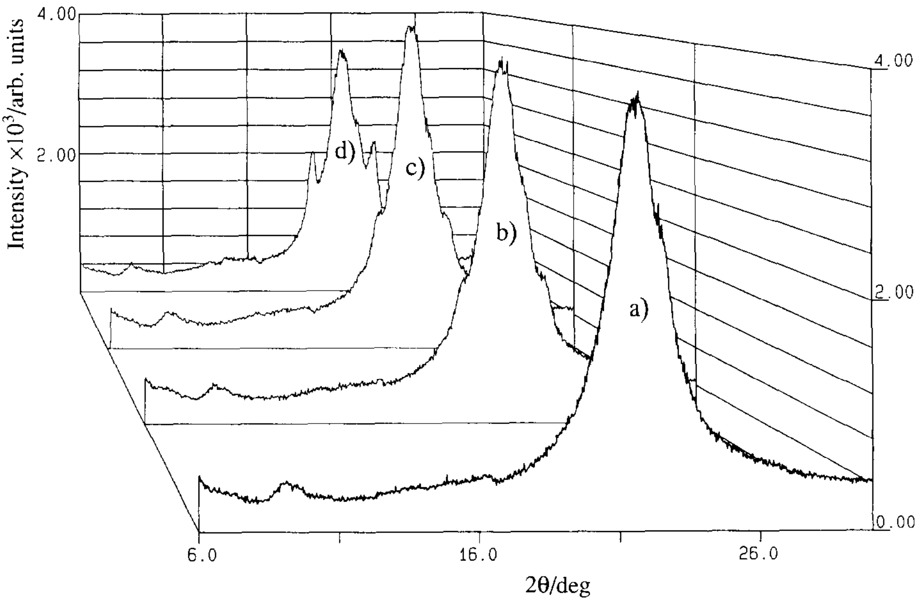

Fig. 8. X-ray powder diffraction patterns of batch A magnesium stearate: curve (a) dried; curve (b) as received; curve (c) 75% RH; curve (d) 93% RH. Cu Kα, 50 kV and 40 mA.

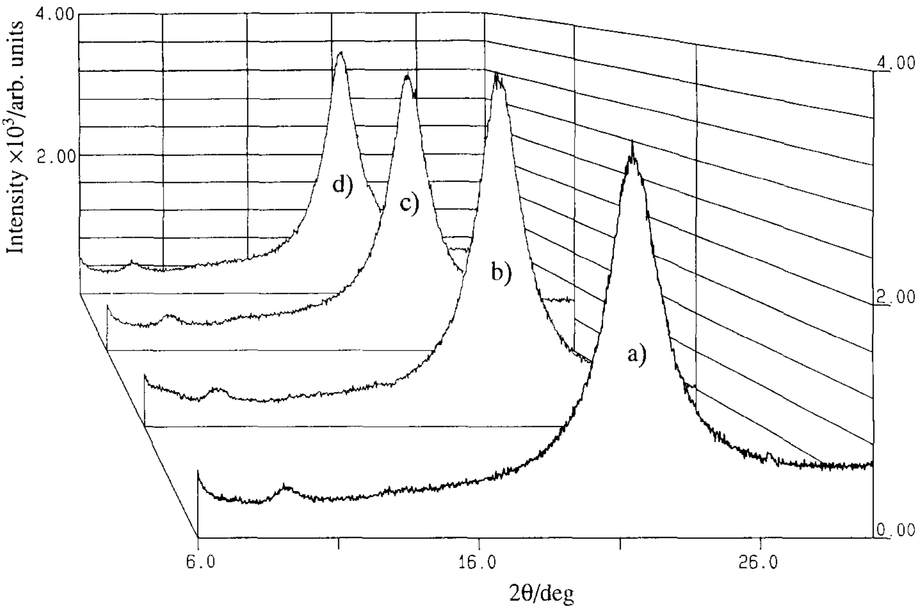

Fig. 9. X-ray powder diffraction patterns of batch B magnesium stearate: curve (a) dried; curve (b) as received; curve (c) 75% RH; curve (d) 93% RH. Cu Kα, 50 kV and 40 mA.

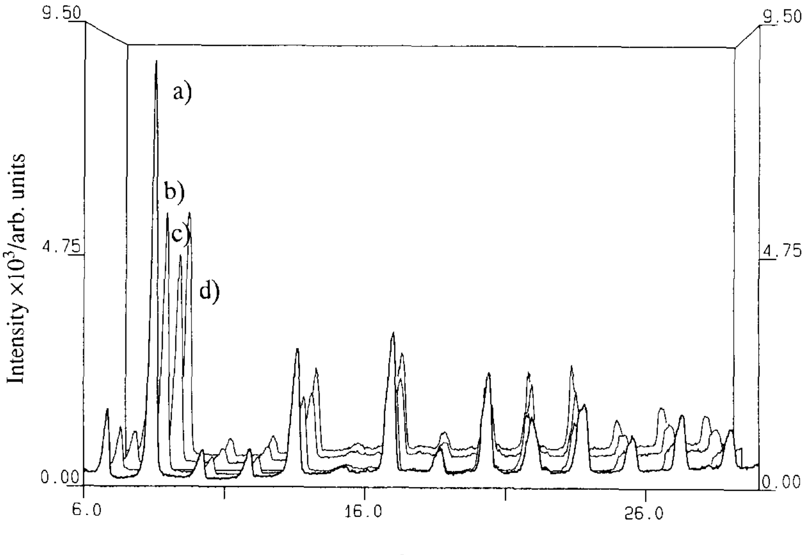

Fig. 10. X-ray powder diffraction patterns of batch C magnesium stearate: curve (a) dried; curve (b) as received; curve (c) 75% RH; curve (d) 93% RH. Cu Kα, 50 kV and 40 mA.

According to Ertel and Carstenseen [1] an anhydrous form of magnesium stearate, which can be prepared by drying the dihydrate to constant mass at 105°C, exhibited a tendency to sorb moisture. This moisture was present as adsorbed surface moisture when the relative humidity was less than 50%. When the relative humidity exceeded 50%, however, the anhydrate rehydrated to form a trihydrate. Once formed, the trihydrate was stable at 25°C when stored under relative humidity conditions less than those required for its formation. The anhydrate could be regenerated by drying the trihydrate at 105°C.

4. Conclusions

The two batches of commercial magnesium stearate examined in the present work did not differ significantly in terms of their fatty acid composition, and these batches exhibited only slight differences in their moisture contents. However, the nature of the moisture differed in the samples. The TG scans generated from batch B exhibited a continual mass loss as the temperature was increased, indicating that the moisture present was loosely bound (adsorbed), while scans from batch A exhibited a two stage mass loss indicating that the moisture was more tightly bound. Apparently the differences in the hydration behavior between batches A and B were notable only at the extreme conditions of high relative humidity and did not account for the batch-to-batch variation in lubrication activity found previously [7]. The results strongly support findings [7] that the lubrication properties of the commercial batches A and B correlated with particle size distribution and specific surface area.

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