Effect of Four Anticaking Agents on the Bulk Characteristics of Ground Sugar

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ABSTRACT

Fine silicon oxide, sodium aluminum silcate, tricalcium phosphate and calcium stearate powders were admixed with dry ground sugar at four concentration levels between 0.1 to 2%. Appreciable increase in loose bulk density and decrease in compressibility were noticeable at 0.1% concentration in all four agents. The effect reached an apparent peak or a flat maximum at an agent concentration of about 0.5–1%. With the exception of silicon oxide treated powders, increase in density was accompanied by a corresponding decrease in compressibility. Bulk parameters (i.e., density and compressibility) were more sensitive indices to changes occurring in powders as compared to parameters determined in compacted specimens (i.e., yield in shear, internal friction and relaxation pattern). Results are explained in terms of possible bed arrays and their scatter by differences in particle size and shape distributions. Support for these explanations is presented in scanning electron micrographs of sugar treated and untreated particles.

INTRODUCTION

ACCORDING TO THE Code of Federal Regulations (1980) "anti-caking agents and free flowing agents" are "substances added to finely powdered or crystalline food powders to prevent caking, lumping or agglomeration." Commonly the anticaking agents are very fine powders (particle size in the order of few microns) of silicon oxide, silicates, insoluble phosphates and the bi or tri valent salts of stearic acid. They are commercially available in different types or grades that are distinct with respect to particle size, bulk density and absorptive capacity as well as other less important properties. Most of them are fairly inert substances and are classified as GRAS. Their legally permitted concentration is restricted to a proven, useful level as anticaking agents (Code of Federal Regulations, 1980) and in practice this level is usually in the order of 1% or less.

There is no established method for evaluating the effectiveness of anticaking agents. The main reason is that the major factors that regulate powders cohesion and caking tendency, namely moisture and temperature, are independent variables. Therefore, the term effectiveness has meaning only under a very specific range of composition and storage conditions. Under such conditions the anticaking agent effect can be quantified in terms of flowing time through a funnel (a commercial test), by flowability related physical parameters (Peleg and Mannheim, 1973; York, 1975), or by sieving and weighing of the lumps formed after exposure to moisture (Irani et al., 1959; Irani and Callis, 1960). For qualitative evaluation, the mere observation of whether lumps have been formed under controlled environmental conditions is a simple and convenient method (Peleg and Mannheim, 1969; Peleg and Mannheim 1977). This procedure is also commonly reported in the manufacturers technical publications. Its major shortcoming (and that of the sieving method as well) is that the hardness of the agglomerates is not taken into account.

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Powdered sugars are known to be fairly cohesive materials and with strong caking tendency. Because of being a frequent ingredient in the food and pharmaceutical industries the flowability and physical characteristics of these powders is of concern in a variety of processes. The effect of two types of anticaking agents (or flow conditioners) on the properties of sucrose was previously reported (Peleg and Mannheim, 1973). The results of this work indicated that at 1–3% concentration the effect of aluminum silicate and calcium stearate was practically independent of the conditioner concentration. The suggested explanation was that at 1% conditioner concentration the sucrose particles had already been effectively covered by the conditioner and therefore additional coverage could not produce any significant effect. York (1975) who worked with conditioned powdered crystalline lactose found that a saturation situation indeed existed and that beyond a certain critical concentration level (in his report about 1–2%) the flowability could not be further improved. It ought to be memtioned, however, that such a behavior cannot be assumed as typical to all conditioned powders and there are reports of an actual decline in flowability once a critical concentration has been exceeded (e.g. Kristensen and Jensen, 1969; Danish and Parrott, 1971).

In this work the concentration effect of four anticaking agents (conditioners) was studied in dry powdered sucrose. Unlike in the previous work on sucrose the selected concentration levels were such as to cover the range in which saturation or optimal conditions could be found. The study focussed on the induced modifications in the physical characteristics of the conditioned powders with special emphasis on their bulk density.

EXPERIMENTAL

COMMERCIAL SURCOSE was purchased at a local store and was pulverized by a laboratory mill prior to testing. The powder was sieved and the fraction between 50 and 300 micron was collected. This fraction was admixed with amorphous fumed silicon oxide, (CAB-O-SIL®, EH-5, Cabot Corp., Tuscola, IL) sodium aluminum silicate (ZEOLEX® 7, Huber Corp., MD), tricalcium phosphate (Stauffer Chemical Co., Westport, CT, and calcium stearate (Mallinckrodt® Co., St. Louis, MO) at agent concentrations of 0.1, 0.5, 1 and 2% on weight basis. In each series of experiments, part of the powdered sugar was tested untreated and the results were used as a reference. In each powder specimen (treated and untreated) the moisture content was determined by drying in a vacuum oven at 70°C for at least 48 hr.

Mechanical analysis

Loose bulk density was measured by weighing a cell with a known volume filled with a freely poured powder.

Compressibility was determined by compression of the powder in the cell by a piston mounted on the crosshead of an Instron Universal Testing Machine model TM. (For more details see Moreyra and Peleg, 1980). The force deformation curves were transformed to bulk density (ρ_B) vs normal stress (σ_N) relationships. As previously shown (e.g. Peleg and Mannheim, 1973; Moreyra and Peleg, 1980) the latter could be described by the equation:

$$\rho_B = a + b \log \sigma_N \tag{1}$$

where a and b are constants. The constant b depicting the change in bulk density as a result of loading is referred to as compressibility.

The stress relaxation curves of the compacted specimens were also recorded. The curves were normalized and linearized by (Peleg, 1977; Peleg and Moreyra, 1979; Moreyra and Peleg, 1980):

$$\frac{F(o)\,t}{F(o)-F(t)} = k_1 + k_2 t \qquad (2)$$

when F(o) is the initial force, F(t) the decaying force after time t and k_1 and k_2 constants. The constant k_2 representing the asymptotic portion of the stress that remains unrelaxed was used as a measure of short term solidity on a scale where $k_2 = 1$ represents liquid properties (the stress totally relaxes) and $k_2 \rightarrow \infty$ ideal elasticity (no relaxation at all).

Shear analysis was performed by the Jenike and Johanson Flow Factor Tester model ST-HT. Results are reported in terms of yield stress in shear under given consolidation load and as effective angle of internal friction (Jenike, 1964).

All the mechanical tests were performed in two to four replicates and their results are given as mean values.

Scanning electron microscopy

The dried powders were affixed to aluminum stubs with copper tape, coated with gold-palladium at 15 mA for 3 min (∿495A) and examined with an ISI Super III-A scanning electron microscope using a tilt angle of 40° and an accelerating voltage of 30V.

RESULTS & DISCUSSION

PHOTOMICROGRAPHS of fumed silica, aluminum silicate, tricalcium phosphate (TCP) and calcium stearate are shown in Fig. 1–4. These demonstrate that the particles of the first three agents have a porous structure while the calcium stearate particles have a distinct flaky or layerly shape. It is also evident from the photographs that because of the very fine size their particles tend to aggregate and form soft agglomerates with a very nonuniform size.

A photomicrograph of untreated sugar particles is shown in Fig. 5. It demonstrates that the particles have an active surface that attracts a significant number of smaller particles, in this case mostly fine sugar particles. This type of particle adherence is characteristic to many cohesive powders especially if composed of water soluble crystalline materials. In the powder technology literatue, such powders are termed and treated as "ordered mixtures" since the fines are found at the surface of the larger particles and therefore cannot be considered as randomly distributed in the strict sense of the expression (Yeung and Hersey, 1979; Lai et al., 1981).

The interaction between fines and the surface of the larger particles is not limited to particles of the same species. It is necessary, however, that chemical or physical compatibility will exist between the adhering particles so that the system will not segregate. Fig. 6 demonstrates that such compatibility indeed exists in the mixtures of sucrose and the tested anticaking agents. Confirmation of the presence of the agent particles at the surface of the sugar particles is crucial to the analysis of the bulk behavior. The reason is that the powder bed structure is strongly affected by interparticle forces, especially in the case of cohesive powders (e.g., Scoville and Peleg, 1981; Moreyra and Peleg, 1981). It is, therefore, important to know whether the agent activity is through surface modification, that alter the interparticle friction and the particles capacity to form bridges or through reducing the bed porosity by being merely a filler of the interparticle space. In our

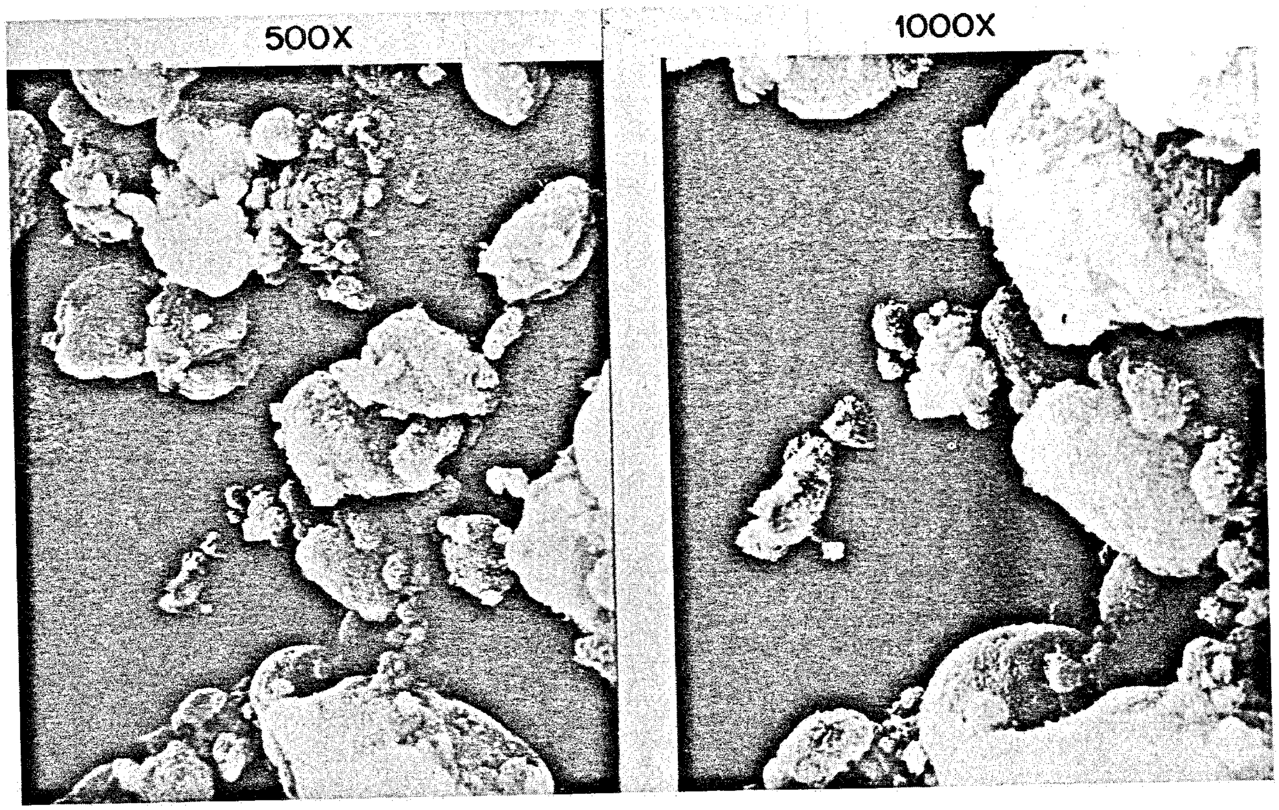

Fig. 1—Scanning electron micrographs of silicon oxide.

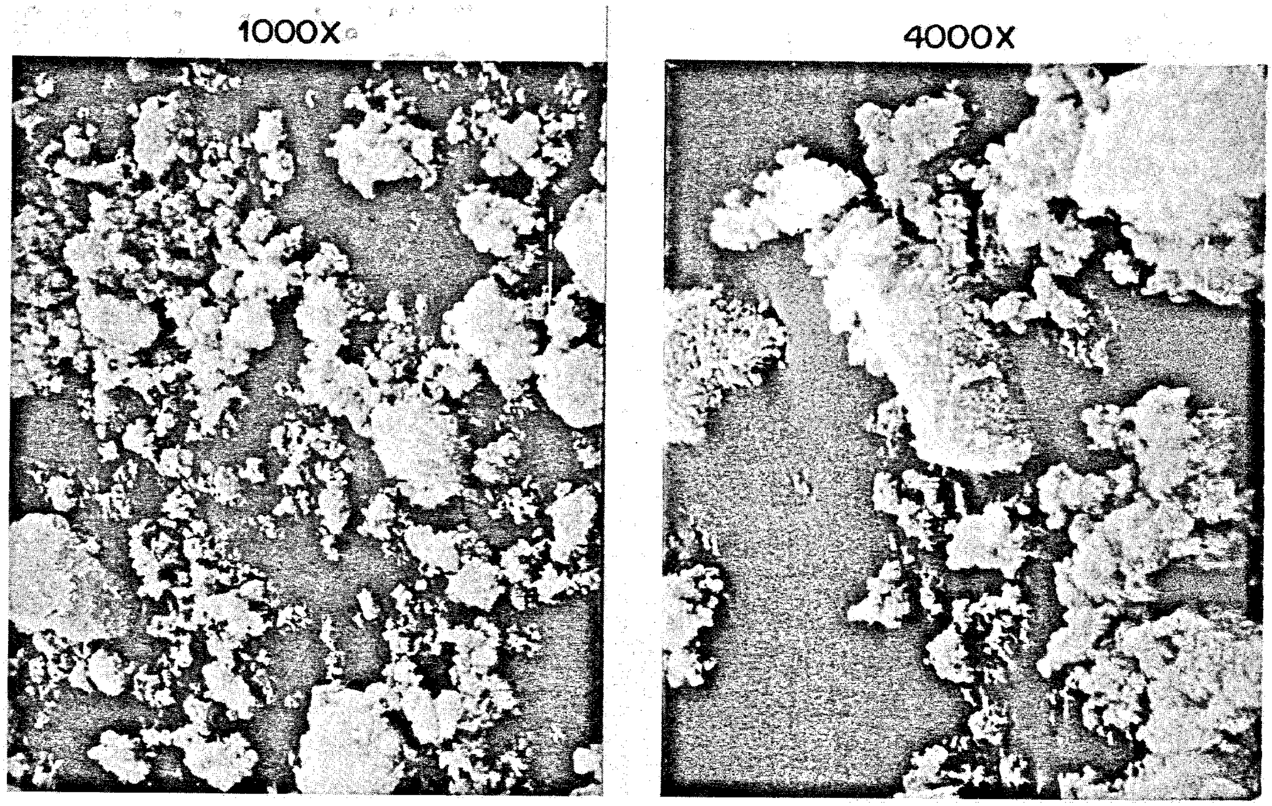

Fig. 2—Scanning electron micrographs of sodium aluminum silcate.

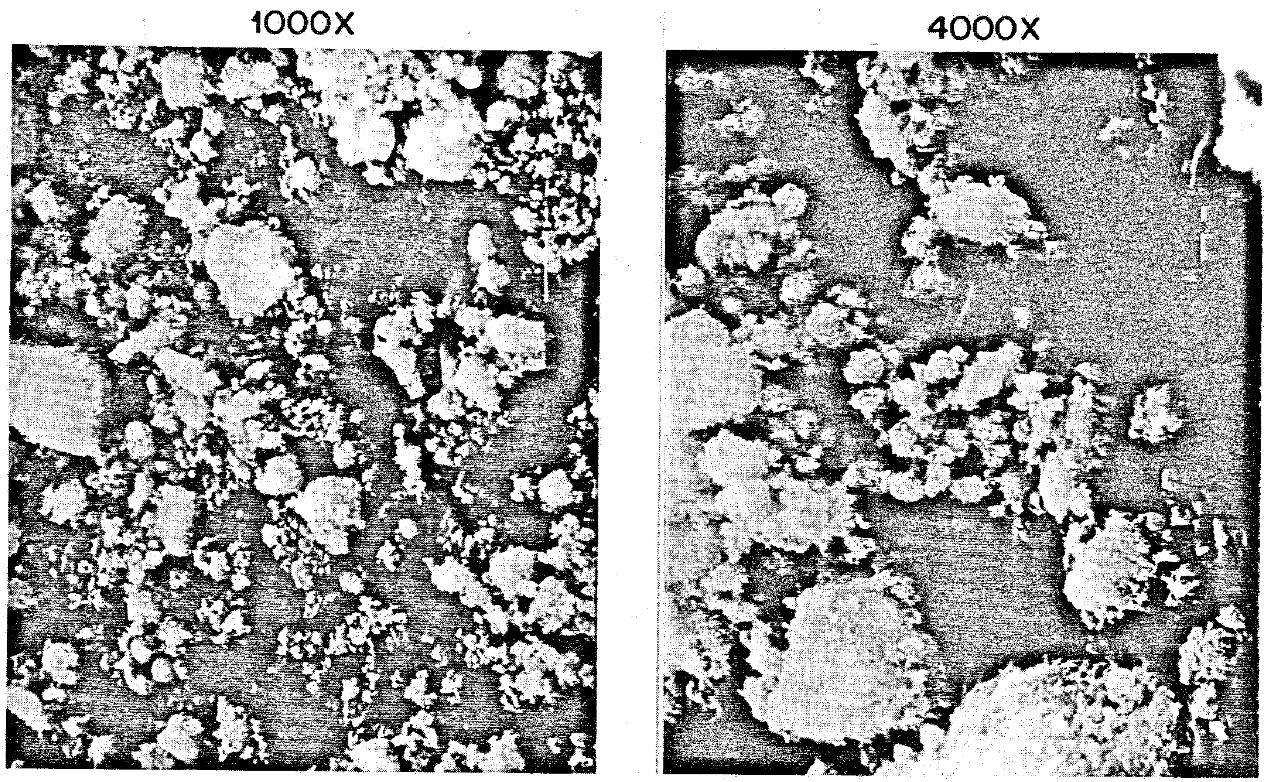

Fig. 3—Scanning electron micrographs of tricalcium phosphate (TCP).

case the fairly uniform distribution of the agents at the sugar particles surface suggests that the former mechanism is dominant. Further support for this hypothesis is provided by the kind of changes in bulk behavior which are reported and discussed below.

Bulk density and compressibility of conditioned powders

The effect of the four anticaking agents on the loose bulk density of ground sugar is shown in Fig. 7. The observed increases in loose bulk density were generally in the order of 5–25% depending on the agent and its concentration. (The exceptional case of silicon oxide will be discussed separately). If the admixture of the agents resulted in the filling of interparticle voids only, the bulk density of the conditioned powder ought to have been given by:

$$\rho_{BT} = \rho_{BU} \, (1 + X_A) \qquad (3)$$

where ρ_{BT} is the bulk density of the treated (conditioned) powder, ρ_{BU} is the bulk density of the untreated powder, and X_A the weight fraction of the agent.

By this equation the expected increases in loose bulk density would have been in the order of 0.1–2% independently of the agent type and density. It is clear, therefore, that the conditioners weight contribution ought to be excluded as a major reason for the increase in bulk density. A more plausible reason is that the presence of the conditioner at the particle's surface physically separates the particle, thus reducing its attractive interparticle forces. Their presence also interferes with the formation of liquid bridges between particles in cases where surface moisture is sufficient to produce such bridges (Peleg and Mannheim, 1973).

The reduction or elimination of interparticle forces also reduces the possibility of maintaining an open bed structure supported by these forces. The result, therefore, in contrast to the effect of added moisture for example (Scoville and Peleg, 1981; Moreyra and Peleg, 1981), is a higher bulk density in which the porosity is largely decided by the geometrical characteristics of the particles and the random voids that are created during the settlement of the particle in the measuring container. This denser structure, which is characteristic to noncohesive powders is also expected to show lower compressibility under relatively small loads. (Conditioners are not expected to modify the host powder particles rigidity.) It is possible, however, that some of them will facilitate interparticle sliding under high pressures (e.g., in tabletting) thus producing denser compacts. This range, however, is out of the scope of this work and will not be discussed here).

The observed decline in compressibility (Fig. 8) is in line with this explanation, and in all but two of the tested powders the increase in bulk density was also accompanied by a corresponding decrease in compressibility (See also Fig. 9).

The case of silicon oxide at 1 and 2% concentration was unique with respect to bulk density. Unlike in the other conditioned powders the density not only did not significantly increase but actually decreased slightly at an agent concentration of 2%. This seems to be an indication of the formation of a new kind of relatively stable bed structure as is clearly evident from low levels of these powders compressibility when compared to that of the untreated powder (Fig. 8).

Effects of agent concentration

Bulk density and compressibility of ground sugar treated with various levels of anticaking agents are shown in Fig. 7 and 8. These figures clearly show that all four agents had a noticeable effect on these physical bulk characteristics at

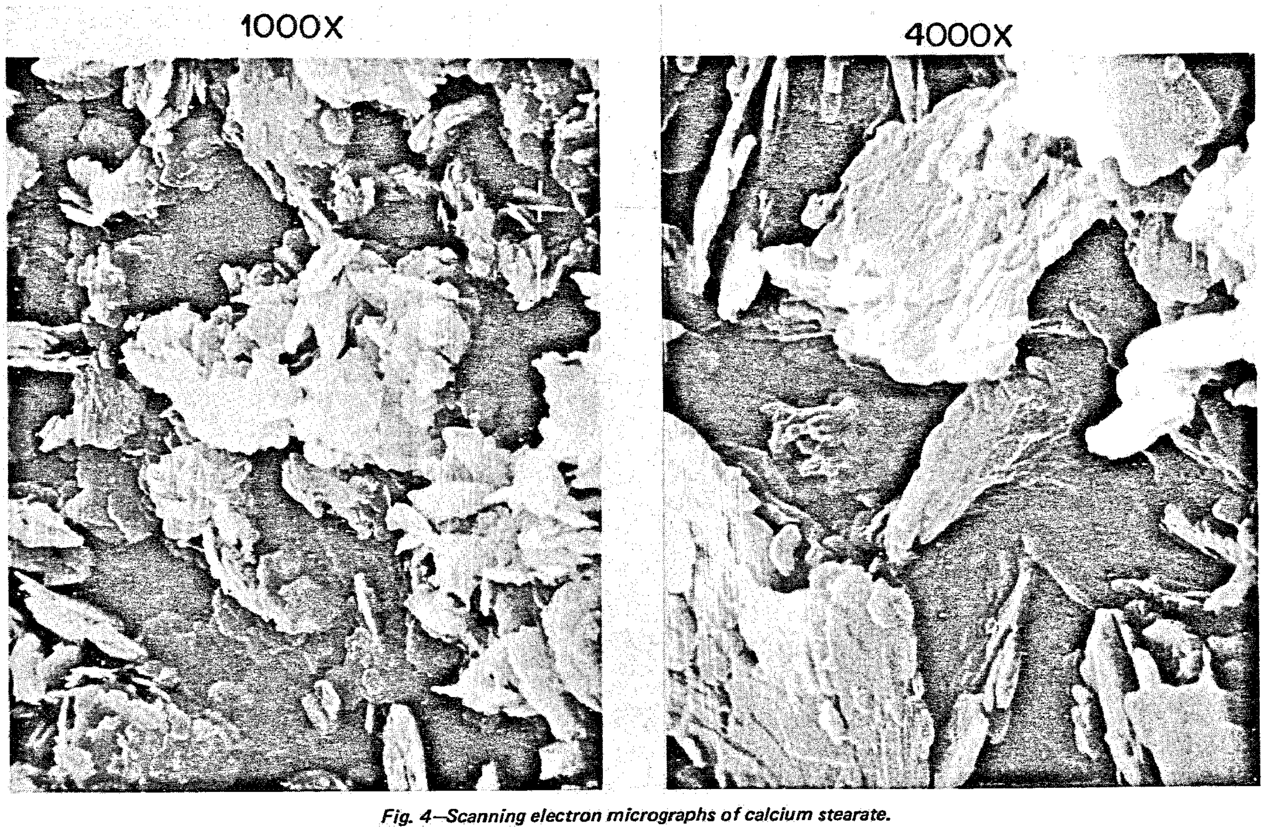

Fig. 4—Scanning electron micrographs of calcium stearate.

concentration as low as 0.1%. It is also evident that maximum effect was reached at agent concentration of about 0.5–1.0%. Beyond this level the effect remained practically the same or even declined. Although this general trend is clearly evident the relationships between the agent concentration and the bulk properties do not appear to be quite smooth. Deviations of this order could well be expected as a result of inevitable random differences in the particles size and shape distributions among the experimental powders (see Fig. 5 and 6) and perhaps in minor differences in moisture too. The total moisture content range was between 0.04–0.12% with almost all the powder falling between 0.05–0.08%. Analysis of the data with respect to a possible moisture effect showed that the latter had been only a minor factor.

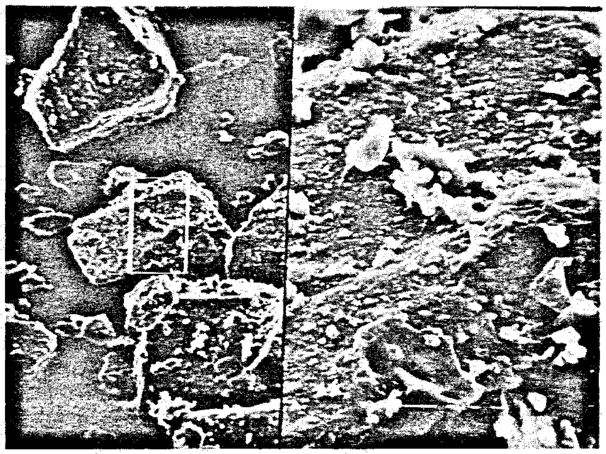

Fig. 5—Scanning electron micrographs of the surface of untreated sugar particles. (Note the adherence of fines).

The existence of a critical agent concentration at around 0.5–1% indicates that effective coverage of the particles surface is obtained at this level. This also helps to explain why in a previous work (Peleg and Mannheim, 1973) no significant differences could be found between the properties of sucrose powders treated at levels of 1–3%. It ought to be mentioned, however, that the critical concentration level is not necessarily fixed for a given anticaking agent and it may well be a function of the host powder chemical nature as well as its particle size and shape distributions.

The critical concentration may also be influenced by segregation of the agent particles in extremely dry host powders or by its uneven distribution in the case of cohesive host powders. The latter may also result in nonuniform bed structures which will be expressed in a large scatter in the measured bulk properties. It appears though that the reproducibility of the density and compressibility measurements was fairly high (deviations of and 0.5–6% from the mean) thus excluding insufficient mixing as a major factor in determining the critical concentration level in the systems that were tested in this work.

Evaluation of the other mechanical parameters

The mechanical characteristics of ground sugar treated with the four anticaking agents at 0.5% concentration are summarized in Table 1. The table presents two groups of mechanical parameters. The first (i.e., loose bulk density and compressibility) solely refers to the properties of the powders original bed structure and the second (i.e., yield stress in shear, angle of friction and the relaxation parameter) is to a large extent a representation of the compact properties. Although it is obvious that the two are interdependent (Jenike, 1964), they do not necessarily have the same sensitivity to changes that occur in the powder bed structure. This can be partly attributed to inherent experimental artifacts (e.g., there can be differences in density between the tested compacts), but it is also due to instrumental limitations (especially in a linear shear cell) and certain theoretical weaknesses of the methodology. (A

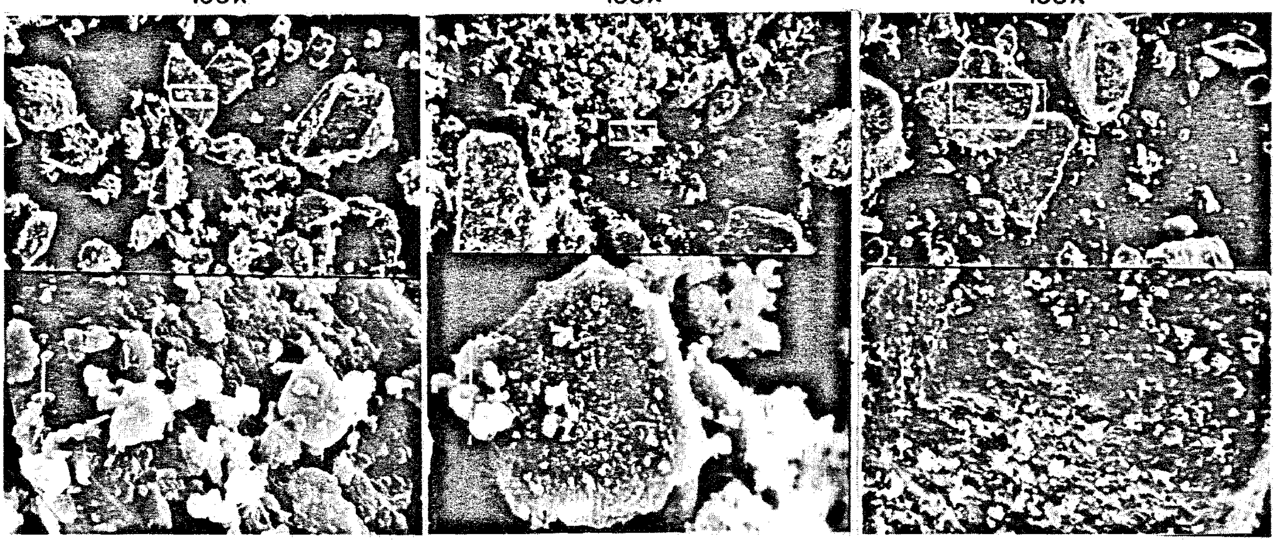

Fig. 6—Scanning electron micrographs of sugar particles coated with 2% calcium stearate (left), tricalcium phosphate (middle) and silicon oxide (right). (Note the adherence of the anticaking agents particles to the sugar surface.)

more detailed review of these aspects of powder testing and their relation to food powders has been published elsewhere (Peleg, 1977)).

The table demonstrates that as far as the powder's cohesiveness is concerned the changes in bulk density and compressibility, were much more sensitive and reliable indices than the compact related parameters. This, of course, does not mean that the compact properties were not affected by the anticaking agents presence. It means that the magnitude of such changes was not big enough to be revealed by a small number of experiments, especially where considerable variability (due to differences in size distribution for example) is an inherent characteristic of the system. It ought to be also added that the ground sugar used in this study was dry and therefore only moderately cohesive. In more moist and cohesive powder, the agents presence was significantly expressed in the compact properties as well as those of the loose powders (Peleg and Mannheim, 1973).

Regarding the relaxation pattern, the only significant effect was found in the silicon oxide treated powder. The expected effect was an increase in the value of k_2, (i.e., or reflecting a more solid compact) and indeed this was what has been found. In the other powders, the trend was unclear. As in the case of the parameters determined by shear the differences may not have been large enough to overcome small differences in moisture and perhaps in density too. It seems, however, that calcium stearate, because of its fatty anion may not only reduce friction by lubrication (Peleg and Mannheim, 1973) but also effect the relaxation pattern by allowing interparticle contacts to flow. However, since this effect is also produced by moisture, its significance can only be established by additional work.

CONCLUSIONS

IN THIS WORK, no effort has been made to compare the effectiveness of the four agents in preventing caking nor to evaluate their capacity to improve flowability. A previous report indicated that anticaking agents in powdered sugar also act like flow conditioners (Peleg and Mannheim, 1973).

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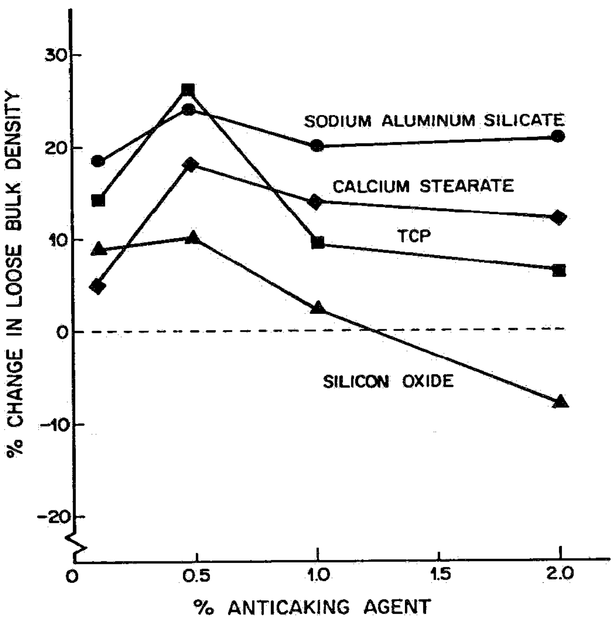

Fig. 7—Effect of the anticaking agent concentration on the bulk density of ground sugar.

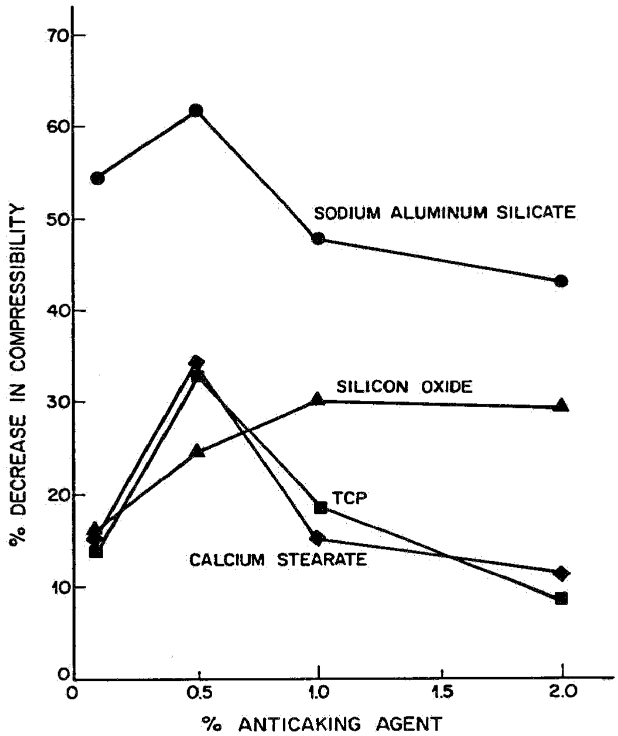

Fig. 8—Effect of the anticaking agent concentration on the compressibility of ground sugar.

Table 1—Some physical parameters of ground sugar conditioned with four anticaking agents at 0.5% concentration

Conditioner	Loose bulk density ($g \cdot cm^{-3}$)	Compressibility[a] (b in Eq. 1)	Yield stress in shear ($kg \cdot cm^2$) under consolidation stress of: 1.2 $kg \cdot cm^{-2}$	0.27 $kg \cdot cm^{-2}$	Angle of internal friction (deg)	Relaxation parameter[b] (k_2 in Eq. 2)
None	0.697	0.066	0.96	0.46	42	1.77
Silicon oxide	0.749**	0.052**	1.10	0.50	43	2.25*
Sodium aluminum silicate	0.872**	0.026**	1.05	0.48	42	1.63
Tricalcium phosphate	0.761*	0.044**	1.10	0.48	43	1.76
Calcium stearate	0.865**	0.039**	0.87	0.43	36	1.61

[a] The regression coefficients in fitting Eq. 1 were between r = 0.992 and r = 0.999 (significant at P = 0.001)
[b] The regression coefficients in fitting Eq. 2 were between r = 0.997 and r = 0.999 (significant at P = 0.001)
*Different from the corresponding value of the untreated powder at significance level of P = 0.05.
**Different from the corresponding value of the untreated powder at significance level of P = 0.01.

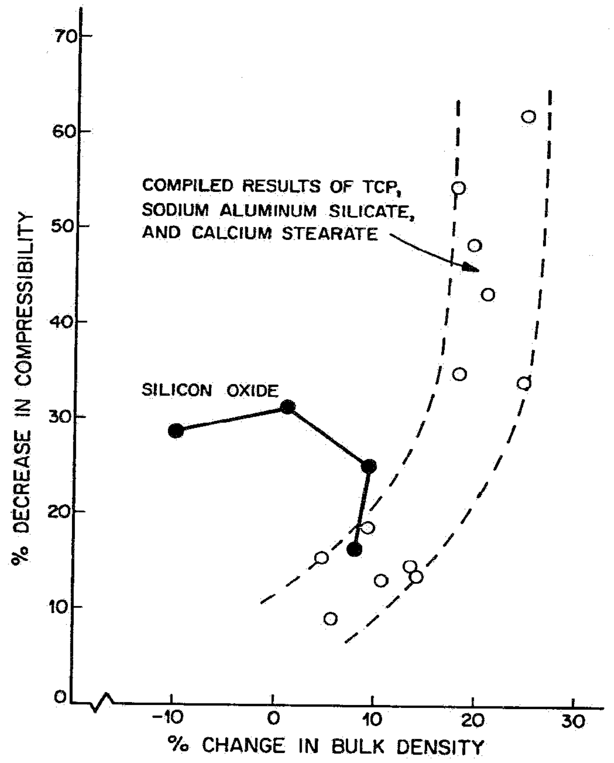

Fig. 9—The relationship between the changes in bulk, density and compressibility of ground sugar treated with anticaking agents constructed from the compiled data of Fig. 7 and 8. (Note the peculiar deviation of 1 an 2% mixtures of silicon oxide where the decrease in compressibility was not accompanied by a corresponding increase in bulk density.)

It is also known, however, that when hygroscopic powders are exposed to an atmosphere with high relative humidity, they cake despite the agents presence (Peleg and Mannheim, 1977). Therefore, the range of humidities in which such agents are effective is inherently limited. In that range or at lower humidity levels where the powder does not cake spontaneously, the addition of the anticaking agent is expected to modify the powder bulk peoperties to a much larger extent than can be assumed by their weight concentration. As shown in this work, the magnitude of such effects can vary according to the conditioner type and its concentration. Therefore, it seems adivsable that such consequences ought to be considered seriously before a powder is treated with an anticaking agent or when one agent is replaced by another.

It would also be worth mentioning that in all the tested powders affinity existed between the sugar surface and the agent particles and this was probably the source of these large effects on density. Such affinity, however, cannot be taken for granted and there are powders (e.g., soyflour treated with calcium stearate) where certain types of anticaking agents will have little or no effect because of segregation of the agent particles.

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