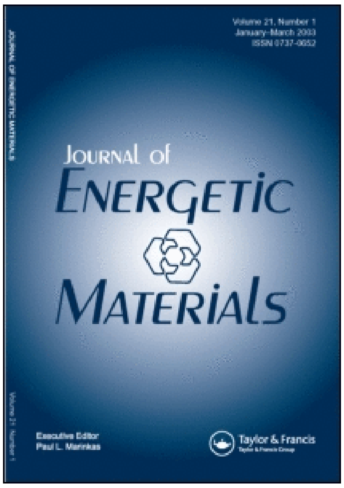

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Analysis of Slurry-Coating Effectiveness of CL-20 Using Grazing Incidence X-ray Diffraction

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A grazing incidence X-ray diffraction technique was developed to characterize the effectiveness of the coating of the solid particles by the binder in energetic formulations and was used in conjunction with scanning electron microscopy, traditional wide-angle X-ray diffraction, and specific gravity measurements to probe the microstructure of PAX-12 granules. The grazing incidence X-ray technique was applied to granules formed upon slurry coating and indicated different X-ray scattering characteristics for high- and low-sensitivity granules, suggesting significant differences in the distribution of the binder at the surface of the

This paper is dedicated to the memories of our friends and colleagues Dr. Rahmi Yazici of Stevens and Dr. Alan G. Allred of ATK Thiokol Propulsion.

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granules. The granules were made by slurry-coating crystals of epsilon CL-20 with cellulose acetate butyrate, a binder, and bis-(2,2 dinitropropyl acetal/formal), a plasticizer. Granules with high sensitivity to impact and friction were shown to have an interior that was relatively porous and that consisted of uncoated CL-20 crystals. Their surface had regions with a thick layer of coating material and other regions of uncoated crystals. Granules that showed a low sensitivity to impact and friction had coated CL-20 crystals throughout their interior and on the surface.

Keywords: slurry coating, X-ray diffraction, grazing incidence, CL-20, hexanitrohexaazaisowurtzitane

Introduction

Tests currently used to measure the sensitivity of energetic granules to impact and friction have a subjective aspect. Furthermore, various factors, including the effectiveness of the coating of the energetic particles, can currently be only qualitatively analyzed. The aim of this study is to develop a structure analysis technique that is quantitative and that can be correlated to granule sensitivity. Such a technique might supplement tests currently used to assess sensitivity. The techniques developed are demonstrated using a CL-20–based formulation designated as PAX-12. This energetic formulation was processed by CL-20 crystallites being slurry coated with cellulose acetate butyrate, a binder, and bis-(2,2 dinitropropyl acetal/formal), an energetic nitroplasticizer (this combination is abbreviated as CAB: BDNPA/F). The sensitivity of these energetic granules varies considerably and depends upon the conditions used in the slurry coating process.

A preexisting picture of the PAX-12 granule structure [1] suggested that granules that exhibit relatively low sensitivity to impact and friction had a uniform thin layer of coating material surrounding all CL-20 crystallites, whereas granules that exhibited higher sensitivity to impact and friction had a uniform thick outer shell of coating material surrounding uncoated and agglomerated CL-20 crystallites within the granules. Based on this picture an X-ray technique was developed that has an increased sensitivity to the surface region of the granules. The technique, grazing incidence X-ray diffraction (GIXRD), enhances scattering from the granule surface region as compared to its interior. A detailed description of the apparatus, methods, and procedures used for this technique has been given previously [1].

Initial examination of the PAX-12 granules by scanning electron microscopy (SEM) indicated that an important aspect of the initial structural picture was inaccurate. Granules that exhibited relatively high sensitivity to impact and friction did not have a uniform thick layer of coating material on their surface. Instead, images of their surface showed fissures, regions of uncoated CL-20 crystallites, and other regions with "puddles" of coating material. It thus appeared that an improved picture of granule structure was needed before the relationship between granule structure and properties could be elucidated. In the following the techniques that were developed are discussed along with typical results obtained on the PAX-12 formulation.

Experimental

Samples

Six lots of PAX-12 made with three different lots of CL-20 were slurry-processed for this study. The details of the slurry-processing operation are provided in Table 1. These six lots of PAX-12 were subjected to a series of ABL impact, ABL friction, and BOE impact tests for sensitivity analysis. On the basis of these sensitivity tests, lot -28 was determined to be the most sensitive and was designated as the worst performing lot, whereas lot -29 showed intermediate sensitivity performance, and lots -24, -25, -26, and -27 were found to be the least sensitive to impact and friction. Table 1 summarizes the information collected on sample performance and the formulation and provides a summary of the results obtained in the present work. The objective of the study was to determine what structural factors were at play to generate the significant differences in sensitivity observed with these samples. For structural analysis SEM, traditional wide-angle X-ray diffraction, GIXRD, and specific gravity measurements were made.

SEM: Experimental Procedures and Results

A series of SEM micrographs of the six PAX-12 lots were obtained. Granules were fractured while submerged in liquid nitrogen to reveal their interiors. Images were obtained using a LEO 982 digital scanning electron microscope operated at 1 kV, and samples were sputter coated with gold. The interiors of lots -28 and -29 have a spongy appearance with many large voids. At higher magnications the fractured surface is seen to consist of uncoated crystals (Figure 1). These crystals display well-defined faces, edges, and growth morphology. The interior of lot-24 (produced using the same 2 μm CL-20 that was used for lots-28 and

Table 1
Information describing six lots of PAX-12 and results of experiments described in this paper

	PAX-12 lot					
	1855-28	1855-29	1855-24	1855-25	1855-26	1855-27
Characterization	Ugly/poor	Bad/moderate	Good	Good	Good	Good
w % CL-20	90	90	90	90	90	90
CL-20 size (μm)	2	2	2	18	26	$2 + 26$
CL-20 lot number	2190150	2180150	2180150	PCL-0109	2180149	2180149 & 2180150
Ratio water/CL-20	5.6	4.8	4.0	4.0	4.0	4.0
Impeller rate (rpm)	500–525	450–500	400–450	400–450	400–450	400–450
ABL impact (cm)	1.8	6.9	11	17	51	26
ABL friction (psi@8ft/s)	130	240	320	320	320	180
BOE impact (@4in)	Fail	Fail	Pass	Pass	Pass	Pass
DSC (onset, °C)	230	230	231	229	228	228
Grazing incidence XRD amorphous/crystalline scattering × 1000	37.3 ± 3.2	44.2 ± 3.2	55.8 ± 8.6	—	71.9 ± 11.9	74.5 ± 6.2
Wide-angle XRD amorphous/crystalline scattering × 1000	87.0 ± 5.0	83.3 ± 3.0	76.4 ± 5.0	—	74.4 ± 11.0	74.8 ± 13.0
Weight % CL-20 by XRD	96.0 ± 1.2	92.3 ± 1.2	94.0 ± 0.9	—	95.4 ± 1.0	94.7 ± 0.9
Specific gravity (g/cm^3)	$1.20 - 1.54$	$1.35 - 1.54$	$1.60 - 1.64$	$1.62 - 1.63$	$1.66 - 1.67$	$1.68 - 1.70$

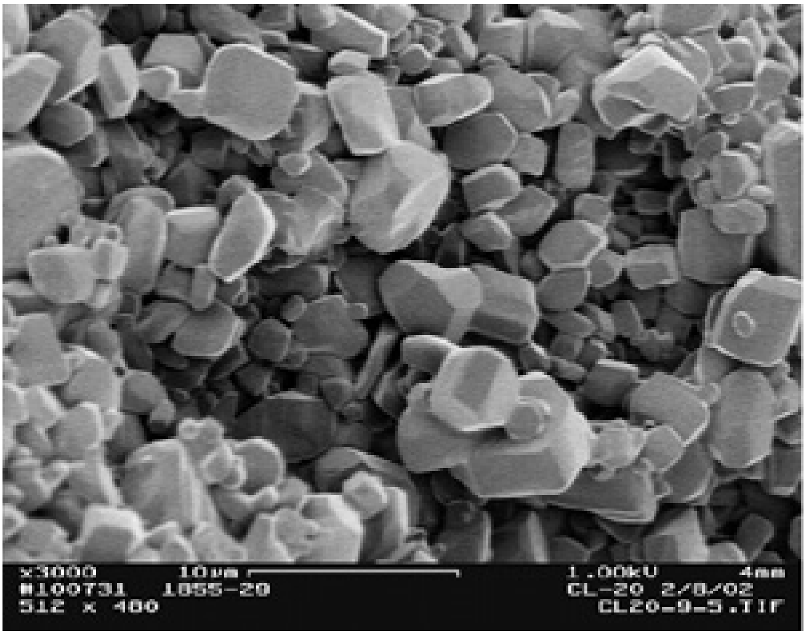

Figure 1. Interior of PAX-12 granule (lot 29) showing uncoated CL-20 crystals.

-29) has fewer and smaller voids. The CL-20 crystals are coated, and the coating material is seen to form bridges between particles (Figure 2). None of the crystal faces, edges, and well-defined growth morphology seen in -28 and -29 are evident in lot -24. The interiors of lots -25, -26, and -27 (similar to lot -24) show a relatively low number of voids, and their CL-20 crystallites appear to be well coated. Overall the presence of voids in the granules should decrease their specific gravity. The morphology of the CL-20 crystals in these lots is more evident because of their larger size.

Figure 3 shows the surface structure of lot -29. Low-magnification images reveal a surface with pores and crevices. At higher magnification some areas of the surface are seen to be covered with a thick layer of coating material containing few crystals, whereas other areas consist of apparently uncoated CL-20 crystals. Clearly a model predicting a thick uniform layer of coating material at the surface of these granules does not apply. Figure 4 shows the surface of a granule in lot -24. In this lot, as in -25, -26, and -27, surfaces appear to consist of a layer

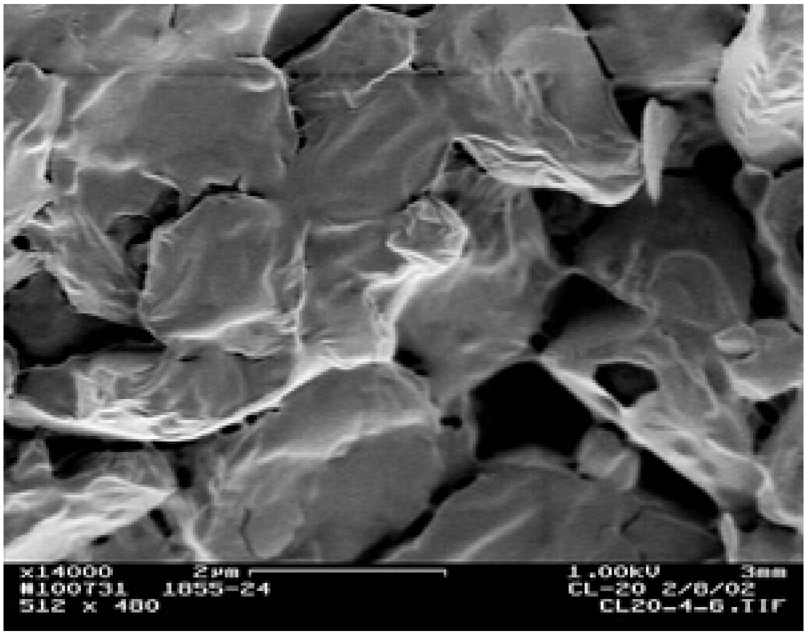

Figure 2. Interior of PAX-12 granule (lot 24) showing coated CL-20 crystals.

of coating material covering underlying crystals. In some regions coating material appears to be present in a thicker layer than in others. Although such SEM measurements are very valuable and convey much information on the causes of the sensitivity differences, they cannot be easily converted into quantitative data and are not amenable to on-line process and product quality control. Thus, there was a need to develop X-ray techniques that furnish quantitative data and are amenable for use as nondestructive methods of on-line product quality control.

XRD: Procedures and Results

Phase Identification. Diffractograms of the three lots of CL-20 were obtained using a Rigaku Miniflex X-ray diffractometer with copper K-alpha radiation. Data matched both in-house and JCPDS [2] reference patterns for ε-CL-20 (JCPDS reference pattern 50-2045 for hexanitrohexaazaisowurtzitane, $C_6H_6N_{12}O_{12}$). Data from CL-20 lot PCL-0109,

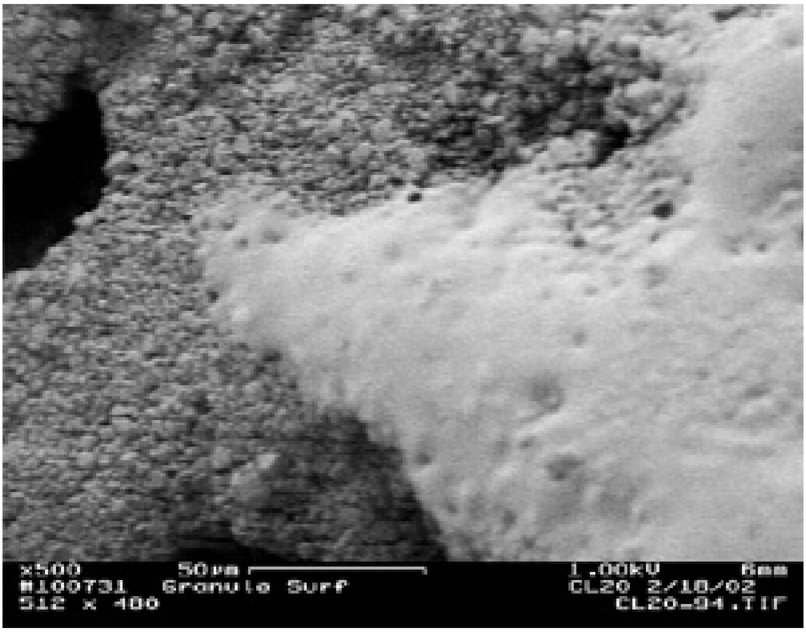

Figure 3. Surface of PAX-12 granule (lot 29) showing regions of uncoated CL-20 crystals and other regions with a thick layer of binder material.

used to make PAX-12 lot -25, contained a small amount of additional scattering that may be due in part to the alpha polymorph of CL-20. This additional scattering would have required us to modify our procedures for this lot. Therefore, to be consistent this lot (lot -25) was not subjected to further X-ray measurements.

GIXRD. Samples for each of the GIXRD experiments consisted of a number of PAX-12 granules that were mounted on a 12 mm × 12 mm glass slide covered with about a 1 mm thick layer of soft red wax. The granules were partially pressed into the wax so that their upper surface (the one irradiated by the X-ray beam) was flat. Data were collected using a Bruker D8 Advance X-ray diffractometer with a Gobels mirror in the incident beam. This mirror produces a parallel monochromatic X-ray beam, which is incident on the sample. Soller slits in the diffracted beam path are used to define the two-theta angle. Data obtained by GIXRD are presented in Figure 5 and Table 2.

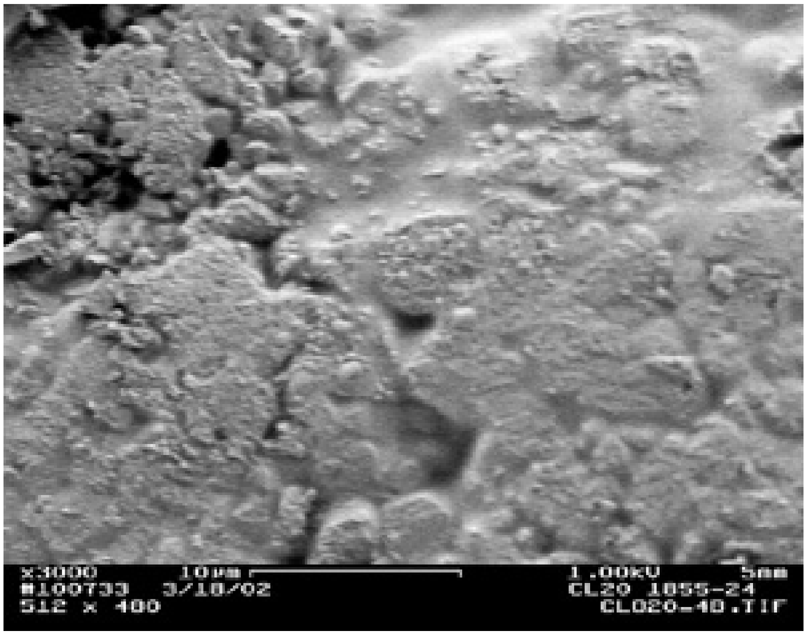

Figure 4. Surface of PAX-12 granule (lot 24) showing complete coverage of surface by binder material.

The graph shows the ratio of amorphous (A) to crystalline (C) scattering for the five lots studied. Amorphous scattering arises from the coating material, that is, the binder, whereas the crystalline scattering arises from the CL-20 particles. Calculations indicate that in the GIXRD case about 90% of the scattering arises from the upper 100 µm of the sample. Thus, the A/C ratio is directly correlated to the ratio of binder to CL-20 in this surface region. Eight samples from each lot were prepared, analyzed, and are reported. In these experiments the X-ray beam incident on the sample was maintained at either 2° or 3° to the sample surface, while a scintillation detector was scanned from a 2θ of 5°–45°. Data in the 2θ range of 11.3°–26.7° were separated into amorphous and crystalline scattering and used to determine the A/C, indicative of the binder to CL-20 ratio.

These results show a significantly reduced A/C ratio (reduced binder to CL-20 ratio) for the lot with the highest sensitivity to impact and friction, that is, lot -28, in comparison to the other lots

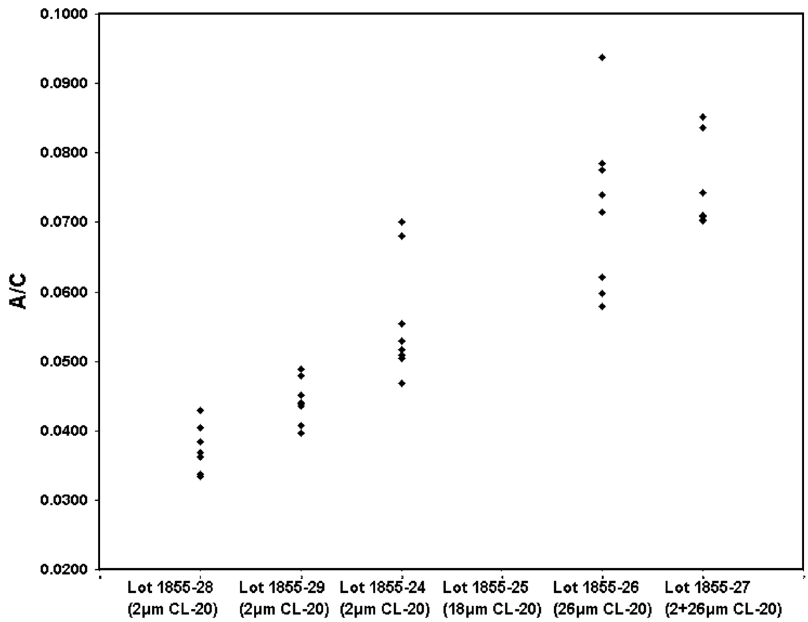

Figure 5. Ratio of Amorphous/Crystalline scattering by grazing incidence XRD for PAX-12 lots studied.

with lower sensitivity to impact and friction, that is, lots -24, -26, and -27. On the other hand, an intermediate value of the A/C ratio (intermediate binder to CL-20 ratio) was observed for the lot with

Table 2
Ratio of amorphous/crystalline scattering (A/C) for different CL-20 lots obtained by GIXRD

Lot number	Average $A/C \times 1000$	Standard dev. of $A/C \times 1000$	Coefficient of variation
1855-28	37.3	3.2	8.66%
1855-29	44.2	3.2	7.14
1855-24	55.8	8.6	15.34
1855-25	—	—	—
1855-26	71.9	11.9	16.57
1855-27	74.5	6.2	8.34

intermediate sensitivity to impact and friction, that is lot -29. The lower values of the binder to CL-20 for lots -28 and -29 are clearly associated with the surface structures of these granules, which are characterized by fissures, pores, and a very uneven distribution of binder material on the surface. This surface structure together with the presence of uncoated CL-20 crystals on the surface and within lots -28 and -29 should be responsible for the increased sensitivity of these lots to impact and friction as shown in Table 1. The results also indicate a larger value of the binder to CL-20 ratio (A/C ratio) for the PAX-12 lots made with 26 µm CL-20 (lots -26 and 27) in comparison to the PAX-12 lot made with the 2 µm CL-20 (lot -24). Bearing in mind that these three lots consist of similar weight percentages of coating material, a thicker layer of coating material is expected to develop on the larger crystallites in lots -26 and -27 because of the reduced surface area available in these lots. Such quantitative data emanating from the grazing incidence X-ray diffraction technique can be used for detailed descriptions of the distributions of the coating of the CL-20 particles.

Wide Angle X-ray Diffraction. A series of experiments were also performed to determine the goodness of mixing of the binder and CL-20 in each of the PAX-12 lots. Eight 25–50 mg samples from each lot were

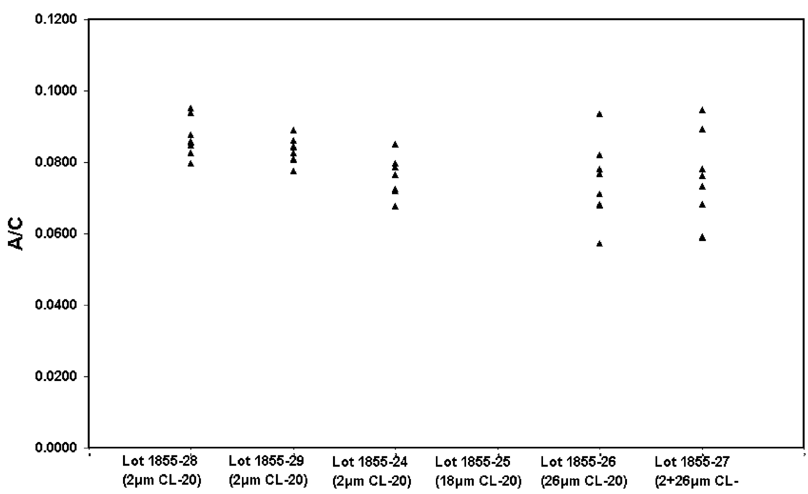

Figure 6. Ratio of Amorphous/Crystalline scattering by wide angle XRD for PAX-12 lots studied.

Table 3
Ratio of amorphous/crystalline (A/C) scattering for different CL-20 lots obtained by wide-angle X-ray diffraction, WXRD, and specific gravity ranges

Lot number	Average A/C × 1000	Standard deviation of A/C × 1000	Coefficient of variation std. dev./average	Specific gravity range
1855-28	87.0	5.0	6.1%	1.20–1.54
1855-29	83.3	3.0	4.2	1.35–1.54
1855-24	76.4	5.0	7.0	1.60–1.64
1855-25	—	—	—	1.62–1.63
1855-26	74.4	11.0	14.6	1.66–1.67
1855-27	74.8	13.0	17.2	1.68–1.70

prepared by crushing granules to form a powder that was placed in an off-cut, single crystal, quartz sample holder and examined by standard wide-angle XRD. The data were analyzed using the same procedure used for the GIRXD data. Granule size varied from lot to lot and required the crushing of two or three granules in some lots and 20–30 in others. Results from these experiments are shown in Figure 6 and Table 3.

The smaller values of the standard deviation for the three PAX-12 lots made with 2 μm CL-20 suggest that they exhibit a greater granule to granule compositional uniformity than exists in the lots made with the larger CL-20 crystallites. This uniformity in composition does not hold true within granules as was shown in the SEM data for these lots. It is interesting to note that the binder to CL-20 ratio (as indicated by the amorphous over crystalline scattering, A/C ratio) is higher for lots -28 and -29 than for the others, although this difference is not statistically conclusive. This may be due to the presence of larger binder-rich regions in these samples. Such regions would enhance micro-absorption effects in -28 and -29 and increase the binder to CL-20 scattering ratio (A/C ratio) because of the lower linear absorption coefficient of the binder. Compositional lot-to-lot uniformity is suggested by the observation that the overall binder to CL-20 scattering ratios (A/C ratios) are similar for different lots (within typical experimental confidence levels).

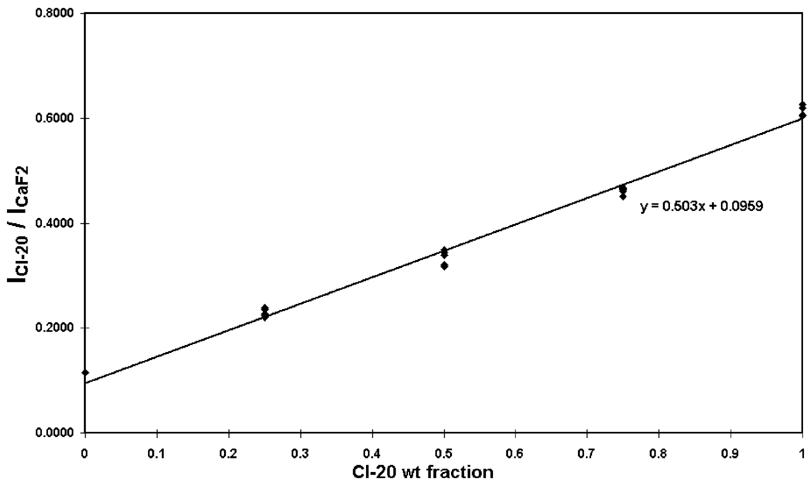

Figure 7. Ratio of (Intensity of scattering from CL-20 + other)/(Intensity of scattering from 10-weight% CaF_2) versus weight fraction of CL-20.

Quantitative Phase Analysis, QPA. To further check for compositional uniformity, quantitative phase analysis (QPA) was performed on the five PAX-12 lots made from CL-20 lots 2180149 and 2180150. To perform the QPA a calibration curve of the ratio of X-ray intensity scattered by CL-20 to that scattered by CaF_2, $\mathbf{I}_{\text{CL-20}}/\mathbf{I}_{\text{CaF2}}$ versus weight% CL-20 was established and is shown in Figure 7. Each of the samples used to establish the calibration curve contained 10-weight% CaF_2 and 40% petroleum jelly. The remaining 50% of each sample was a mixture of CL-20 and amorphous silica. For each composition on the calibration curve (except 0% CL-20) five samples were characterized. The calibration curve has a y-intercept of 0.0959, instead of the expected zero value. This is because in the regions where the CL-20 peaks were measured there was a small peak associated with CuK-beta radiation scattering from the CaF_2 (111) and a small peak due to the petroleum jelly.

Samples for analysis contained 50-weight% PAX-12, 10-weight% CaF_2, and 40-weight% petroleum jelly. The QPA results, which are given in Table 4, indicate that lots -24, -26, -27, -28, and -29 contain between 92.3 and 96.0 weight% CL-20. These values are higher than the nominal 90-weight% specified during formulation and may indicate a loss of some binder (presumably to be entrained out of the

Table 4
Weight percentage of CL-20 in different PAX-12 lots by quantitative phase analysis

Lot number	Weight percentage	Standard deviation	Coefficient of variation
1855-28	96.0%	1.2	0.012
1855-29	92.3	1.2	0.013
1855-24	94.0	0.9	0.010
1855-25	—	—	—
1855-26	95.4	1.0	0.010
1855-27	94.7	0.9	0.010

mixer with the solvent phase) during the slurry-coating operation. This loss of the binder during the slurry-coating process may have an additional effect on the sensitivity results since the sensitivity to impact and friction should increase with the decreasing concentration of the binder in the granules.

Specific Gravity Measurements. Specific gravity measurements were made to gain further validation of the observed structure of the PAX-12 granules. The calculated specific gravity of void free PAX-12 containing 90% CL-20 and 10% CAB: BDNPA/F is 1.90 g/cm^3. Results of specific gravity measurements on the six lots of PAX-12 of interest are given in Table 3. Between 200 and 450 mg of granules were weighed, and the volume associated with this weight of material was determined using a 2 ml pycnometer and distilled water. The specific gravity values of various granules are in the range 1.2–1.70, which are significantly smaller than the theoretical specific gravity of 1.9, suggesting that the void fraction of the granules is indeed significant. A greater void fraction is suggested for the PAX-12 lots -28 and -29 which exhibit higher sensitivity to impact and friction (as evidenced by their lower specific gravity values).

Conclusions

In this study we introduced the use of GIXRD to study the distributions of the binder to CL-20 ratios in slurry-coated granules. The coating materials, that is, the binder, CAB: BDNPA/F, gives rise to amorphous scattering, **A**, and the energetic CL-20 gives rise to crystalline scattering, **C**. Using GIXRD, we have demonstrated that the ratio of A/C (ratio of binder to CL-20) is signicantly lower for granules, which are more sensitive to impact and friction in comparison to granules, which are less sensitive to impact and friction. By comparing PAX-12 samples made from the same lot of CL-20 but processed in different ways, we determined the A/C ratio to be the highest for granules that are least sensitive to impact and friction, and the A/C ratio to be the smallest for granules that were the most sensitive to impact and friction, suggesting that the diminished availability of the binder at various sections of the surface of the granules increases the sensitivity of the granules. We confirmed that indeed those granules that are more sensitive to impact and friction contain uncoated CL-20 crystallites both on their surface and interior while in less sensitive granules all crystallites observed appear to be coated.

An improved picture of granular structure was obtained from SEM examination. The interior of "poor" high-sensitivity material was relatively porous and contained an agglomeration of uncoated CL-20 crystals. The surface of these granules was fissured and porous and showed both regions of uncoated crystals and regions of thick coating material. In contrast, granules that exhibited lower sensitivity to impact and friction consisted of coated crystal both within and on the surface of granules. Specific gravity measurements supported these observations by yielding lower values for the granules that were more sensitive to impact and friction.

The techniques that are developed here should be applicable to other coated granular materials and can be used as on-line product quality control tools. While we have demonstrated a quantitative technique that for PAX-12 may provide a direct correlation between A/C from GIXRD and sensitivity, direct sensitivity testing is still of primary importance at this stage of technique development.

Acknowledgments

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