A STUDY ON GYPSUM PRODUCTS, PHOSPHATE DIE REFRACTORY MATERIALS AND PHOSPHATE INVESTMENTS BY IMPULSE EXCITATION OF SONIC VIBRATION.

Evaluation of GrindoSonic Analyzer for Characterization of our Chemical Products

Introduction:

Material manufacturing is associated with a large number of obstacles which continue to be the cause of failure in producing consistent and reliable finished products. Some of the most obvious problems are listed to be the inherent variations in raw materials, the aging that contributes heavily to the variability of the environmentally sensitive raw materials and finished products, the difficulties in controlling the associated processes, existing operational errors, and the lack of technically sound test methods that function reproducibly and dependably.

Reference to our own test methodology, the following observations illustrate some of the deficiencies: (1) we need to find a test method to incorporate the quantitative measure of the abrasion resistance of our Gypsum products, especially of die stones, resin-based stones, and model stones, (2) our existing test methods frequently fail to assure the consistent performance of our products that are being used for high temperature operations, (3) we have limited control over the processes on which our test results are being collected; because most of them are not quantitatively correlated to the factors and conditions associated with product performance in actual practice. Test methods that would be independent or less affected by such variables could provide better characterization of our products, and (4) all of our test methods are destructive ones. The use of non-destructive test methods to evaluate materials at conditions of practical application has been highly acclaimed in modern material science and technology. We have no access to any of them.

A series of publications by International Refractory Services ⁽²⁾ reported an attempted correlation between abrasion resistance and Modulus of Rupture of refractory materials. In engineering principles, the modulus of rupture is an approximation of the tensile strength of elastic material. The bulk modulus (K), a measure of the crushing strength determined by compression, is related to the Young's modulus (Y):

Y = 3K (1-2v)where v = Poisson's ratio

Since the GrindoSonic determines Young's Modulus (Modulus of Elasticity) and estimates the Poisson's ratio, it can determine the Bulk modulus as well. All the above led us to investigate sonic vibration as a tool to better characterize our materials, and provide more reliable and consistent data. During late 1991 and the first half of 1992, we conducted a preliminary investigation with a GrindoSonic instrument on sixteen Type IV and Type V die stones. Young's Modulus, crushing strength and Rockwell superficial surface hardness were measured. The project, however, had led to inconclusive results due to the limited study on the specimens, aged for 24 to 74 hours, and we could not collect data for verification of reproducibility, because the GrindSonic instrument was available only for a short period of time. Still a qualitative analysis of the data showed that the Young's Modulus (Modulus of Elasticity/E-MOD) correlated with the corresponding crushing strength and Rockwell surface hardness. No quantitative statistical analysis could be performed due to insufficient data collected under the same set of controllable variables. In addition, the lack of appropriate test methods for determining the abrasion resistance, had reduced the scope of this part of the study.

The leasing of the instrument from July 7 to September 6, 1996, provided the opportunity to conduct a more in-depth study and assess the potential benefits off the GrindSonic as an addition to our laboratory test methodology.

Principle, Technique and Instrumentation of Test Method:

The application of sonic vibration as an analytical test method is based on the principle and technique of determining the dynamic elastic properties of materials by utilizing the impulse excitation of sonic vibration as an analytical tool. During the last decade, the test method has emerged as a highly recognized analytical method in material science. The ability to characterize the dynamic elastic properties has contributed in the development and success of high technology materials, such as innovative ceramics, refractories, alloys and composites. A number of ASTM Standards⁽¹⁾ for this test method have been formulated in recent years. The application of this analytical tool, however, remains limited to the domain of dental and other associated biomaterial systems, if there is any.

The GrindoSonic instrument - designed, manufactured and marketed by J. W. Lemmens, Inc., is based on the principle of the impulse excitation technique to determine the dynamic properties of suitable materials, such as ceramics, refractories, metals, alloys, plastics and composites at ambient temperatures. Also as stated, the test method can be performed at cryogenic and high temperatures with suitable equipment modifications and appropriate modifications to perform calculations compensating for cryogenic shrinkage and thermal expansion⁽³⁾. For this versatility, the test method becomes a vital tool in the characterization of modern materials being used in high technology in industries such as the aerospace and ceramics.

Principally, the characteristic mechanical resonant frequency of a material and its mass and geometry are mathematically related to compute the elastic modulus. This leads to the determination of the dynamic elastic properties of the material: the Dynamic Young's Modulus (Modulus of Elasticity) is determined using the resonant frequency in the flexural mode of vibration, whereas the Dynamic Shear Modulus (Modulus of Rigidity) is obtained using the torsional resonant vibrations. The Dynamic Young's Modulus and the Dynamic Shear Modulus are used to compute the Poisson's ratio of the test material

The GrindoSonic instrument consists of several basic components, and is a simple device The components are: (1) a metallic impulser to generate excitation of sonic frequencies, (2) a piezo-electric transducer to pickup and convert the mechanical vibration into an electrical signal, (3) an assembly of electronic system consisting of a signal conditioner/amplifier, signal analyzer, and a frequency readout device, and (4) specimen support system made of foam with a flat surface to rest the specimen and isolate it from extraneous vibrations without restricting the desired mode of vibration.

Even if the instrument is based on complicated principles of material and engineering sciences, it is one of the simplest instruments that one can easily operate to collect multiple readings within seconds. The manufacturer has also listed the following advantages of the test method as follows:

1. The test method is a non-destructive which allows use of the same specimen again and again, and which can also be used for other testing to collect other data, such as of the abrasion resistance, surface hardness and compression/tensile strength.

2. The instrument does not require calibration, though the manufacturer provides a standard for checking its accuracy. Any operator can operate it with minimal personal and operational errors.

3. It can be operated under any kind of harsh industrial condition and environment. For high temperature operation it has a separate more expensive device for measurement.

4. It covers a wide range of materials. The dimension of test specimen can vary from a small metal test bar weighing less than 100 mg to a full size graphite electrode weighing more than a ton.

5. The accuracy of results is claimed to be very high.

The Project:

The project was designed to generate as much data as possible utilizing available resources to focus on specific areas of interest. The project was comprised of the followings:

1. To look for correlation between Modulus of Elasticity (E-MOD) determined by sonic resonance and conventional crushing strength (determined by compression) of Gypsum Products (comprising of raw plasters, finished plasters, model stones, and die stones), Phosphate Refractory Die Materials and Phosphate-bonded Investments.

2. To determine whether it can differentiate between an accepted product and a rejected product, for which we selected a number of approved and disapproved batches of Powercast investment to test.

3. To establish the pattern of variation of data as a function of the age of the specimen; which is one of the vital criteria of our product performance.

4. To develop information on materials subjected to firing or burn out processes in order to collect tentative information on data close to the functional conditions (comparison of data on green and fired specimens).

Materials and Method:

All materials used in the project are reported in Table I to Table V. Test specimen of Gypsum Products were made from the same mix prepared at the recommended water/powder ratio and blended mechanically for 30 s at slow speed under vacuum. Specimen were allowed to set for a specific period of time as reported in the tables. The mixes of phosphate refractory die materials and investments were prepared with appropriate liquids at the recommended liquid/powder ratio by mixing mechanically for 60 s at slow speed under vacuum. The specimens, intended for both the GrindoSonic and Compression tests, were prepared using standard split metal molds (40 mm long and 20 mm diameter) as specified in ANSI/ADA Specification No.25 and ISO 6873 and ISO 9694 standards. All specimens were taken out of the moulds after 1 hour, and allowed to age for a specified length of time. After the GrindoSonic readings were taken, each specimen was subjected to compression testing using the Tinius Olson Universal machine, at a loading rate of $300 \pm 50 \text{ Kg/}$ min as specified by the ANSI/ADA and ISO standards. The specimen to assess thermal degradation effects, were aged for a specified time and then fired at 1950°F as shown in tables.

Test measurements and test parameters were made and recorded by three different operators on each specimen. The results generated by each operator were consistent with the others. The summary data reported represent the average and standard deviation of the average of each operator, and not the average and standard deviation of all test data generated for a given property.

The manufacturer's technical assistance had, however, insinuated that the ratio of specimen length to its diameter (or other dimensions, such as ratio of length to width and height) has influenced the accuracy of data. The specimens prepared for comparing Dynamic Young's modulus and crushing strength were good enough for the purpose. They were shorter, however, to provide the required length/diameter ratio for generating the precision of the characteristic vibration data. For this reason, the specimens used in testing the material for dynamic elastic properties alone, had different geometry and dimensions to comply with normally recommended requirements. Those specimen were prepared in a pre-fabricated polyurethane mold which produced three identical rectangular bars approximately 120 mm long, 20 mm wide and 15 mm thick.

The dimensions of each specimen were measured using a metric slide caliper with accuracy of ± 0.01 mm, and they were weighed accurately to 0.01 g on an analytical scale. Each specimen was tested with the GrindoSonic instrument. Again all measurements were performed independently by three different operators. The results

were consistent between operators. The average of the average of three sets of data was the property reported. Some specimen were fired after initial tested to determine burn out properties.

The dimensions, weight and mechanical resonant frequencies of each specimen were entered into the software system loaded in the PC by the manufacturer. The program calculated the density, Dynamic Young's Modulus (E-MOD), Dynamic Shear Modulus (G-MOD) and Poisson's ratio. The averaged value of the three specimens is reported.

Since the values for E-MOD and G-MOD autocorrelate with the controllable variables, such as the age and fired condition of the specimen, we have omitted the data for Dynamic Shear Modulus from this report.

Results and Discussion:

Each of the values of modulus of elasticity and crushing strength reported in Table I, is the average of three averages. Each set of six specimens, made of the various materials under investigation, were allowed to age for 1, 2 and 24 hours respectively. The standard deviation of each set of experiments and the respective relative standard deviation (RSD = Standard Deviation / Average Value, a measure of the relative amplitude of variation) is also shown.

The values of Modulus of Elasticity and crushing strength increase as the specimens aged longer. In most cases, the values obtained at 1h and 2h are not significantly different. The relative values of different materials depend on the inherent traits of each material, such as water/powder ratio, respective density, and characteristic behavior and strength developed upon setting. Hydrocal (B-Base) has a higher W/P ratio (0.30) than Densite (C-Base: 0.23), and the dynamic elastic properties and bulk crushing strength reflect their differences. Products formulated from ordinary plaster (Lab Plaster, Ortho Plaster), from B-Base (Microstone, Quickstone, Orthostone) and from C-Base (Silky-Rock, Jade Stone, Prima-Rock, Hark-Rock and Resin-Rock) exhibit varying amplitude of E-MOD and crushing strength under the same setting/aging condition, illustrating the contributions of their typical properties characterizing the finished products.

The crushing strength relative standard deviation is relatively higher than that of E-MOD. The variability of crushing strength can be due to specimen defects, such as the presence of air bubbles, dimensional deviation, and other operational errors involved in making and breaking the specimens. Whereas, such defects and operational errors have minimal affect on the measurement of resonant frequency. This low relative standard deviation may be an important factor for consideration in the characterization of the gypsum products. It was, however, observed during many of the experiments that the presence of excess water in the specimen impedes the transmission of the resonant frequency resulting in difficulties in registration of readings.

The comparison of E-MOD and crushing strength of the phosphate bonded refractory die materials, set for one and two hours and after firing at 1950°F, is shown in Table II.

The E-MOD relative standard deviations appear to be higher than that of the crushing strength. According to the manufacturer's interpretation, the high E-MOD RSD was due to the low length/diameter ratio of the specimen. If the specimen length is longer and/or diameter smaller, the standard deviation may be lower. We could not make such alteration in the specimen dimension as the same specimen was used to determine the crushing strength. However, when the specimen geometry was changed from a short cylindrical rod to an elongated rectangular bar, presented in Table IV, there is a reduction in the relative standard deviation.

Both the E-MOD and crushing strength increase (or decrease within the first couple of hours) with the age of the specimen depending upon the amount of binders and the nature of the filler system. This is more apparent with the phosphate bonded refractory die materials than in gypsum products. The increase in the E-MOD is many times higher than the crushing strength when the specimens were fired at high temperatures. This drastic increase of E-MOD presents a better picture of the retaining binding force in the specimen after firing than the crushing strength. The crushing strength represents the strength as a bulk property of the material, whereas E-MOD exhibits the internal binding force. A further investigation may help us in resolving the question whether E-MOD data can have added value to our test methodology. The refractory die materials are designed to prepare refractory dies to process dental ceramics. The technique demands a set of different characteristics, such as the thermal stability without crack and deformation during firing cycles, the inertness to the ceramics processed on it. and production of excellent surface with accurate fit. Also during divesting, the die material must not create any difficulty. A further study on E-MOD vs crushing strength properties to discriminate materials may lead us to better conclusion.

Similar investigations on crown and bridge investments show that the particle size distribution of fillers and amount of binders govern the magnitude and nature of their properties. The investments containing coarse sand, as in Ceramigold, undergo substantial increase in E-MOD during the burn out process, whereas the change in the crushing strength seems to be insignificant. On the contrary, the fine investments , such as Cerafina and Powercast, containing fine filler powder with very high magnitude of active surface area than the coarse investment, exhibit significant decrease in E-MOD and relatively small increase in crushing strength during the burn out process. The loss of thermally degraded products during the burn out causes a substantial reduction in specimen density which is a critical parameter in computation of E-MOD values. We are not sure, whether E-MOD or crushing strength represents the usefulness of these contrasting data.

The E-MOD data collected on six batches of Powercast, using rectangular bar specimens of dimensions, 120mm long x 20mm thick x 15 mm wide, that were allowed to set for varying lengths of time, are as shown in Table IV. Three of those batches had acceptable crack resistance, two were rejected for severe cracking and the other was corrected to eliminate cracking. The E-MOD values increase with the specimen age. Since most of the investments are used within the first couple hours. Any value on specimens aged further beyond the initial hours may not have any significance in actual practice. Even if the values for all the six batches are not significantly different, there appears a trend that like the crushing strength values, the lower E-MOD seems to lead no cracking of the casting molds easily, whereas the higher values lead to cracking during burn out. Considering these, the high E-MOD values and higher crushing strength values during the early age of the specimen signal conditions for explosion or major cracking during the burn out. However, to explore this effect, a further study may lead to better understanding.

Many of the materials under investigation, were also studied to evaluate the affect of aging on E-MOD and G-MOD. All of them showed an exponential increase in these properties as a function of increasing setting time until they attained limiting values as illustrated in Figure 2 (for Silky-Rock die stone) and Figure 3 (for Cerafina investment) These results are considered to be inconsequential as they are similar to other physical properties, such as setting expansion, surface hardness, and crushing strength. For this reason, further analysis of these properties has been limited in this report.

Conclusion and Recommendation:

On the basis of the above evidences, it can be concluded that the test method for determining Dynamic Young's Modulus by the use of impulse excitation of sonic vibration could be as good as the determination of crushing strength, if not a superior test for characterization of our different products lines. However, if we incorporate this test method as a routine one, further work and possible correlative studies may lead us to establish better criteria for achieving quality and dependable consistency in conformance and performance. The technique would definitely be a valuable tool for R. & D. It can also be useful for quality control after necessary calibration and standardization for comparison with our existing test methods. Even if the GrindoSonic test itself takes shorter time, the time required to prepare test specimen may not be reduced unless some modification could be incorporated. The most important advantage should be the elimination of the personal and operational errors from our test procedure.

ASTM Standards^(1F) list a number of technical merits and demerits of the test method as follows:

1. The relationships between resonant frequency and dynamic modulus are specially applicable best to homogenous, elastic, and isotropic materials. Other materials need careful consideration due to the effect of inhomogeneities and an isotropy.

2. The procedure involves measuring transient elastic vibrations. Materials with very high damping capacity may be difficult to measure with this technique if the vibration damps out before the frequency counter can measure the signal.

3. The specific surface treatments (coating, machining, grinding, etching etc.) change the elastic properties of the specimen, and there will be accentuated effects on the properties measured by this flexural method, as compared to static/bulk measurements by tensile or compression testing.

4. The test method is not satisfactory for specimens that have major discontinuities, such as large cracks or extreme voids extensive throughout the specimen.

5. This test method for determining modulii is limited to specimens with regular geometries (rectangular, parrallelepiped, cylinders, and discs) for which analytical equations are available to relate geometry, mass, and modulus to the resonant vibration frequencies. The method cannot be used for testing materials that cannot be fabricated into such geometries.

6. The test method assumes that the specimens are vibrating freely, with no significant restrain or impediment.

7. For accurate measurement, the locations of the impulse point and transducer should not be changed in multiple readings.

8. If the frequency reading are not repeatable for a specific set of impulse and transducer locations on a specimen, it may be because several different modes of vibration are being developed and detected in the test. The geometry of the test specimen and desired vibration mode should be evaluated. If the impulse point and transducer locations are shifted to create and measure the single desired mode of vibration, more consistent measurement would be obtained.

However, the acquisition of the GrindoSonic instrument will surely expand our testing capability in both R.& D. and QC areas.

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TABLE I

PRODUCT/	SPECIMEN	MODULUS OF	ELASTICITY	CRUSHING S	TRENGTH	PSI/
SERIAL NO.	AGE(Hrs) -	(GPA)	- RSD	(PSI)	RSD	GPA
HYDROCAL/	1 0622	16.57 ± 0.45	0.0272	3720 ± 225	0.0605	224.50
B-BASE /	2	15.40 ± 1.17	0.0760	3753 ± 945	0.2518	243.70
05156-S	24	16.88 ± 0.65	0.0385	4812 ± 314	0.0653	285.07
DENSITE/	1	21.96 ± 0.36	0.0164	6310 ± 289	0.0458	287.34
C-BASE/	2	22.80 ± 0.26	0.0114	6797 ± 287	0.0422	298.11
05076-S	24	24.24 ± 0.32	0.0132	8183 ± 701	0.0857	337.58
LAB-	1	11.17 ± 0.35	0.0313	2260 ± 132	0.0584	202.33
PLASTER/	2	10.84 ± 0.1	0.0148	2347 ± 112	0.0477	216.51
021296003	24	11.58 ± 0.17	0.0147	3573 ± 249	0.0697	308.55
ORTHO-	1	13.38 ± 0.27	0.0202	3047 ± 104	0.0341	227.73
PLASTER/	2	13.47 ± 0.13	0.0097	3107 ± 16	0.0518	230.66
017196009	24	14.43 ± 0.19	0.0132	4407 ± 201	0.0456	305.40
MICROSTONE	1	19.33 ± 0.20	0.0103	5337 ± 243	0.0455	276.10
052396001	2	19.53 ± 0.20	0.0102	5190 ± 148	0.0285	265.75
	24	21.11 ± 0.06	0.0028	9000 ± 278	0.0309	426.34
QUICKSTONE	1	18.63 ± 0.20	0.0107	4727 ± 239	0.0506	253.73
BUFF/	2	18.88 ± 0.19	0.0101	4693 ± 187	0.0398	248.57
050596003	24	20.68 ± 0.37	0.0179	7460 ± 561	0.0752	360.74
ORTHOSTONE	/ 1	19.13 ± 0.33	0.0173	4773 ± 462	0.0968	249.50
018296003	2	19.27 ± 0.30	0.0156	4873 ± 196	0.0402	252.88
	24	20.89 ± 0.30	0.0144	8733 ± 604	0.0692	418.05

Comparison of Modulus of Elasticity (E-MOD) and Crushing Strength (Compressive) of various Gypsum Products as a function of Setting Time (Age)

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SILKY-ROCK/	1	23.39 ± 0.19	0.0081	6480 ± 235	0.0363	277.04
038596003	2	23.45 ± 0.08	0.0034	6367 ± 544	0.0854	271.51
	24	24.97 ± 0.16	0.0064	8743 ± 544	0.0622	350.14
JADESTONE	1	24.21 ± 0.29	0.0120	6637 ± 474	0.0714	274.14
BLUE/045096002	2	24.71 ± 0.18	0.0073	6457 ± 474	0.0734	261.31
	24	26.25 ± 0.38	0.0145	7963 ± 974	0.1223	303.35
PRIMA-ROCK	1	26.92 ± 0.23	0.0085	7173 + 885	0 1234	266 45
YELLOW/	2	20.92 ± 0.29 27 23 ± 0.19	0.0070	7400 ± 254	0.0343	271 76
045996004	24	27.23 ± 0.13 27.21 ± 0.23	0.0085	8177 ± 399	0.0488	300.51
HARD-ROCK	1	24.68 ± 0.22	0.0089	7240 ± 658	0 0000	203 35
$\frac{1}{2} \frac{1}{2} \frac{1}$	2	24.00 ± 0.22 25.40 ± 0.16	0.0063	7240 ± 050 7887 ± 265	0.0336	300 12
11110 000400001	24	27.16 ± 0.13	0.0048	9453 ± 539	0.0570	348.05
RESIN-ROCK/	1	23.20 ± 0.18	0.0078	6040 ± 367	0.0608	260.34
065596001	-2		0.0173	6300 ± 228	0.0362	272.49
	24	24.44 ± 0.07	0.0029	6740 ± 197	0.0292	275.78

DCI/
MPA
19.71 0.62
25.56 26.98 6.03
47.81 44.29 0.69
37.29 26.73 0.90
17.45 22.14 0.69
17.93 19.34 1.03

Comparison of the Modulus of Elasticity (E-MOD) and Crushing Strength (Compressive) of Phosphate Refractory Die Materials on green and fired specimens

Comparison of the Modulus of Elasticity (E-MOD) and Crushing Strength (Compressive) of a few Phosphate-bonded Investments on green and fired specimens

INVESTMENT/ SERIAL NO.	SPECIMEN	MODULUS OF ELASTICITY		CRUSHING STRENGTH		DOI/
	AGE/ FIRED	(MPA)	RSD	(PSI)	RSD	MPA
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Ceramigold	1 hr	75.43 ± 3.86	0.0512	1153 ± 59	0.0512	15.29
067596002	2 hrs	90.86 ± 7.70	0.0847	1803 ± 80	0.0444	19.84
	Fired	545.72 ± 85.11	0.1560	1012 ± 23	0.0227	1.85
Cerafina	2 hrs	4631.17 ± 76.02	0.0164	913 ±36	0.0394	0.20
077396005	Fired	743.17 ± 82.46	0.1110	1213 ± 56	0.0462	1.63
Powercast	2 hrs	6698.00 ± 219.98	0.0328	893 ± 30	0.0336	0.13
077496004	Fired	1445.33 单 135.46	0.0937	1286 ± 141	0.1097	0.89

TABLE IV

Comparison of the Modulus of Elasticity Data of a number of batches of Powercast Investment with their physical properties and casting data, recorded in QC record.

SERIAL NO. ID	017496002 A	027496002 B	037496006 C	06749600 D	077496002 E	077496004 F
SPECIMEN AGE (HRS)	MODULUS of	ELASTICITY FR	OM SONIC DATA	<u>(in GPA)</u>		
1	6.906 ± 0.127	6.325 ± 0.044	6.655 ± 0.054	5.841 ± 0.158	6.784 ± 0.106	6.589 ± 0.096
2	7.165 ± 0.165	6.722 ± 0.029	6.920 ± 0.094	6.381 ± 0.207	7.321 ± 0.101	7.015 ± 0.100
4	7.700 ± 0.0213	7.407 ± 0.018	7.722 ± 0.204	7.664 ± 0.261	8.365 ± 0.086	7.768 ± 0.091
6	8.988 ± 0.414	8.625 ± 0.189	9.629 ± 0.206	8.488 ± 0.234	9.890 ± 0.252	
24	12.277 ± 0.241	12.813 ± 0.066	12.243 ± 0.040	13.467 ± 0.458	13.353 ± 0.137	13.303 ± 0.09

PHYSICAL PROPERTIES AND CASTING DATA FROM OC RECORDS:

Working Time	8'40"	8'50"	8'30"	8'50"	8'50"	8'55"
Peak Temp(°F)	182	190	182 -	-186	180	182
Slump (mm)	80	82	84	84	84	81
Compresive (psi)	1173	780	1180	727	853	760
CASTING RECORD:	Blew up On Hold	No crack OK	Fin, crack, small casting On Hold	No crack OK	Initially blew up, OK	No crack, good size after correction. OK



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FIGURE 1



FIGURE 2

