CONCLUSIONS.

Although the method employed for apparent relative density determination proved to be quite sensitive, the only variable in the process of specimen manufacture that affected its value for \( V_v \) was the type of densification used during sintering.

Different materials had different densities; those containing alumina having the greatest. When compared with \( V_v \), the presence of extra quartz and pigment in \( V_v \) and \( V_v \) did influence their apparent relative densities slightly. The inherent density of the materials examined appeared to be much more important in governing the apparent relative density than were the presence or absence of voids.

Vacuum-fired \( V_v \) showed a very low pore volume (ca. 1.3 per cent), while air-firing the same material only increased its pore volume by about two per cent. The sealed porosity gained by air-firing \( S_a \) was calculated to be about three per cent. This value was a little below an estimate of about 4.8 per cent determined by lineal analysis of polished sections. It is obvious that the powdered frit for \( S_a \) was not pore free.
Evidence that only small porosity differences exist in air- and vacuum-fired materials was corroborated by the results of volumetric shrinkage tests. All things being equal, the extra pore volume introduced by air-firing modern dental porcelains appeared to be in the order of about two to three per cent.
16. TRANSFORMATION REGIONS OF THE VITREOUS PHASES
OF TWO MODERN DENTAL PORCELAINS.

MATERIALS AND METHODS.

$V_{V_1}$ and $S_{a_1(a)}$ were selected for these tests. The type of physical property versus temperature curve that was studied depended on the measurement of linear thermal expansion. The aim was to determine the general behaviour of these materials, and if possible, to estimate transformation temperatures of their vitreous phases.

Measurements of linear thermal expansion were made on cylindrical, fired specimens of $V_{V_1}$ and $S_{a_1(a)}$ using the dial gauge method. This involved the measurement of the expansion of the test piece transmitted through a fused silica rod. The vertical type of apparatus described fully by Earnshaw (1966) was used; and, under the conditions of these experiments, where a disc of vitreous silica (15 mm. in diameter) distributed the load, the specimens supported a compressive stress of 30 gm./sq.cm.

Compaction by wet mechanical vibration into specially prepared split plaster moulds (36 mm. in length and 15 mm. in diameter) lined with tin foil, provided cylindrical test pieces of $V_{V_1}$ and $S_{a_1(a)}$. Careful
drying for three-quarters of an hour in the furnace doorway was necessary. Again, due to their bulk, vacuum-
sintering for both was done in two stages so as to provide an even vitrification. At first they were fired for four
minutes lying lengthwise on the tray; then their positions were reversed and the sintering process repeated. The
holding temperatures of 1090°C for \( V_{V_{1}} \) and 980°C for \( S_{a_{1}}(a) \) were employed. To prevent cracking, cooling after firing had to be slow.

After sintering and having had their ends ground flat and parallel to one another, the dimensions for \( V_{V_{1}} \) were 31.0 mm. in length and 12.5 mm. in diameter, and for \( S_{a_{1}}(a) \), 30.5 mm. in length and 12.0 mm. in diameter.

During the thermal expansion tests, specimen temperature was recorded by means of a 34 gauge chromel/
alumel thermocouple whose hot junction resided in a tunnel made through the diameter in the middle of the test piece. Corrections for the expansion of the length of fused silica tube surrounding the specimen were made as prescribed by British Standard: 1902: Part 1A: 1966, p.55.

In all the tests, a heating and cooling rate of 10°C/min. was followed as closely as possible. Each specimen was tested three times both during heating and
cooling. Having drawn graphic representations of the results, estimations of the transformation temperatures, \( T_g \), and indeed the dilatometric softening temperatures, \( M_g \), could be made for \( V_v \) and \( S_a \).
RESULTS.

Since the expansion behaviour of glasses depends on their prior heat treatment, it was not surprising to find that results, for different tests on the same specimen, did not exactly coincide. However, what was important, and this applied to both materials, was the fact that certain characteristics in these graphs constantly appeared. Firstly, the heating curves differed from the cooling curves. Figure 19 shows the thermal expansion for Vv₁. Curve A represents the heating stage. No doubt the increased expansion of this material, up to about 573°C, was due to its quartz content. All heating curves studied for Vv₁ and Sa₁(a) showed this characteristic. Beyond this influence the curves levelled out, only to increase the slopes sharply at the transformation range. For Vv₁, this region (Tg) was between 650°C and 700°C (Fig. 19); for Sa₁(a) between 600°C and 625°C.

For both materials the expansions continued until the curves reached the dilatometric softening points, Mg, under the conditions of these experiments. Mg for Vv₁ was found to be about 875°C; for Sa₁(a) about 725°C.

Again, the cooling curves all resembled curve B in Fig. 19. The effects of the quartz phases were not
Fig. 19. -- Linear thermal expansion curve for Vv. A.

Curve A represents the heating stage -
Curve B the cooling stage.

The transformation range (Tg) of the
vitreous matrix was between 650° and
700°C; and the dilatometric softening
point (Mg) was at about 875°C, under
the conditions of this experiment.
reflected here. The only irregularities occurred at the transformation ranges which corresponded to those in the heating curves within the temperature ranges quoted.

Due to the polymorphic transformation of quartz at about $573^\circ C$, it is obvious that cooling below the transformation ranges could result in the development of microstresses and perhaps microcracks (Figs. 10 and 11).

For $S_{a_1}(a)$ this effect could be mitigated by the proximity of its transformation region to this temperature (Fig. 15).
CONCLUSIONS.

Linear thermal expansion curves did display the transformation regions of the vitreous phases of \( \text{Vv}_4 \) and \( \text{Sa}_4(a) \). In all the tests, cooling curves differed from heating curves in character; but they were always both influenced by the transformation regions.

The quartz phase must have been largely responsible for this variance. Seemingly, the closer the vitreous phase transformation region lies to \( 573^\circ \text{C} \), the less chance there would be of microstress development.

Under the conditions of these tests, dilatometric softening points were recorded.
17.

STRENGTH RELATIONS.

Many different quantities having different dimensions are grouped under the heading of strength. Such measurements can be presented in terms of a stress, a strain, or an energy; but only similar quantities with similar dimensions should be directly compared.

Static strength measurements include all those tests in which the material fails by rupture under an observed stress. The load is applied so gradually that all parts are at any instant essentially in equilibrium. Failure is produced in not more than a few minutes.

Dynamic loading involves stress conditions that are necessarily complex. The rate of change of momentum of the parts must be taken into account. In impact, the loaded specimen is usually required to absorb a definite amount of energy. In static loading, the specimen is usually required to resist a definite force.

During impact, and for some time afterwards, the parts are in a state of vibration; and static equilibrium does not supervene until all the kinetic energy possessed by the striking weight at the instant of impact has been absorbed by the specimen and stored up as strain energy or dissipated as heat. One generally regards energy
absorption as being derived from the other two fundamental quantities, viz., static strength (fracture stress) and deformation.

No calculated value of stress, strength, or deformation can be regarded as exact. The formulae used are based on certain assumptions that are only approximately true; and they are derived by mathematical procedures that often entail further approximations (Roark, 1965, p.58). Therefore, great precision in numerical results is not justified.

As with glass, there does seem good reason to believe that rupture occurs in modern dental porcelain only under tension, generally at a surface. But, there appears to be no justification for assuming that the value of this tensile strength will be independent of stresses operating in other directions. Under different conditions of rupture the deformation may differ very widely. Naturally, the result of a strength measurement will depend on any change in the conditions affecting the material as a whole, such as humidity or rate of loading (Black, 1936, Smothers, 1958 & Shevlin and Lindenthal, 1959).

Tests made on vitreous materials should bear some relation to their intended use.
Tensile Strength.

The measurement of tensile strength for brittle materials is a difficult task. Whereas small misalignments in a uniaxial tension test on a ductile material can be corrected by plastic flow without significantly affecting the results, brittle materials have little or no capacity to flow plastically. Hence, any misalignment adds a bending-stress component that can seriously lower the measured strength. A number of alternative methods of estimating the tensile strengths of brittle materials employing specimens of simple shape are in use. Where comparisons have been made, these methods have often yielded values for the tensile strength which differ considerably from those obtained from the direct tension test, (Milligan, 1953 & Berenbaum and Brodie, 1959).

The bend test.

In an attempt to alleviate some of the difficulties associated with the uniaxial tension test, the simple bend test is often used to determine the breaking strength of brittle materials. In a bend test a bar specimen is bent under the action of a three- or four-point loading system and the maximum tensile stress at failure estimated from the applied bending moment using the simple beam theory.
The material is in a state of pure tension at the convex surface of the beam, where the maximum tension exists directly opposite the point of load application (Ritland, 1955). Failure should be caused by the action of this single principal stress only (Berenbaum and Brodie, 1959).

Four-point loading, where possible, provides the most representative and consistent strength values (Duckworth, 1951). It has the advantage of producing a more uniform tensile stress on the surface of the sample.

Because of the important role played by surface imperfections, the measured values of the breaking strength usually show a large variation in vitreous materials. Thus, adequate measurements of strength are inseparable from the characteristics of statistical procedure; and the full implications of this variability must be appreciated before any attempt can be made to apply the conclusions reached from experimental work.

The fraction of the surface area which is under essentially the maximum tension is different for different methods, being least for the simple three-point bending test and equal to the entire area in the case of axial tension. Therefore, data taken by different experimental arrangements should not be directly comparable. Of
course, for comparable data sample size must be constant.

The modulus of rupture, as determined by the bending test, is used primarily for purposes of comparison. Several assumptions are made in deriving the conventional equation:

\[ C_t = \frac{3W}{2bd} \cdot \frac{1}{d} \cdots \cdots \cdots \cdots \cdots (1) \]

where \( W \) is the applied load; \( l \) the length between the transverse supports; \( b \) the breadth of the specimen, and \( d \) the depth of the specimen.

for the tensile stress in the bottom longitudinal fibres of a bar specimen during bending. The result (modulus of rupture) is not a true stress, but it can be used to predict the strength of a similar beam of the same material (Roark, 1965, p.35).

It has been recorded that the modulus of rupture increases as the span/depth (\( s/d \)) ratio decreases (Milligan, 1953), but the variation is slight except for relatively small values of \( s/d \). In beams of small span/depth ratio, the shear stresses are likely to be high and the resulting deflection due to shear may not be negligible.

Analysis by numerical methods have shown that at \( s/d \) between 1.5 and 1, the stress distribution changes radically and the ratio of maximum stress to calculated
maximum fibre stress in the beam \(\frac{M_o}{I}\) becomes greater than one and increases rapidly as s/d becomes still smaller (Roark, 1965, p.130);

\(c\) is a point most remote from the neutral axis of the beam.

\(M\) is the bending moment at the section containing \(c\).

\(I\) is the moment of inertia of the section of the beam with respect to the neutral axis.

The maximum fibre stress in a beam occurs at the section of greatest bending moment \(\frac{M_o}{I}\).

**TABLE XX.**

The influence of s/d on both maximum fibre stress and maximum horizontal shear stress. \(\text{Span} = \frac{23}{24}\) length.

<table>
<thead>
<tr>
<th>length depth</th>
<th>span depth</th>
<th>Max. Stress (tensile) (\frac{M_o}{I})</th>
<th>Max. Stress (compressive) (\frac{M_o}{I})</th>
<th>Max. Stress (shear) (\frac{V}{A^*})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1.915</td>
<td>0.962</td>
<td>2.525</td>
<td>1.70</td>
</tr>
<tr>
<td>1.5</td>
<td>1.4375</td>
<td>1.038</td>
<td>3.585</td>
<td>1.92</td>
</tr>
<tr>
<td>1</td>
<td>0.958</td>
<td>1.513</td>
<td>6.140</td>
<td>2.39</td>
</tr>
</tbody>
</table>

\* \(V/A\) is the average shear stress on the section (Source – Roark, 1965, p.131).
These established facts relating to elastic stresses in short beams, shown in Table XX, appear incompatible with the contrary influence of s/d on the modulus of rupture. The simple beam theory should be applicable only strictly to very thin beams that are not disproportionately wide.

Because the stress is greatest at the outer surface, the bend test is particularly sensitive to the state of the surface of the specimen. In an attempt to estimate the order of magnitude to be expected from surface effects, Berenbaum and Brodie (1959) have produced a simple theory for beams of rectangular cross section with modified surface layers. From their calculations they predict that the effect of modified surface layers should be much greater in thin specimens of all types.

The diametral compression test.

Since the bend test accentuates the effects of surface condition on measured strength, another method of estimating tensile strength has been devised. Referred to as the diametral compression test, the Brazilian test, or the indirect tension test, it is based on the state of biaxial stress developed within a cylindrical elastically isotropic specimen when it is compressed between two
diametrically opposite generators. The maximum tensile stresses act across the loaded diameter and have a constant magnitude:

\[ C_t = \frac{2W}{\pi tD} \]  

(2)

where \( W \) is the applied load and \( t \) and \( D \) are the thickness and diameter of the disc (Mitchell, 1961; Addinall and Hackett, 1964 and 1965, & Rudnick et al, 1963).

The other principal stress, which acts along the loaded diameter, is always compressive. Varying in magnitude from point to point, it ranges from a minimum value of three times the constant tensile principal stress at the centre to very large values as the crushing platens are approached (Mitchell, 1961). With a concentrated load, the specimen will fail at the loading points due to the compressive stresses. Since fracture must be initiated by the tensile stresses if the test is to yield useful results, it is obvious that proper load distribution is essential to reduce any stress concentrations due to edge effects. Soft cardboard platens seem to provide the necessary load and stress distribution (Mitchell, 1961) to initiate tensile failure in the central part of the specimen. However, the surface condition of the exposed end surfaces
of the diametral specimen must influence the results to a degree (Rudwick et al, 1963).

Photoelastic studies indicate that the platen effects are quite localized. Peltier's (1954) calculations suggest that the tensile stresses can be held uniform over a reasonable proportion of the loaded diameter if the width of the bearing area is less than one fifth the specimen diameter. For small specimens it is practical to use a wide, thin pad. The contact width is then limited by pad thickness. This results in a high peak pressure and makes the exact width of contact indeterminate.

The specimen length influences the test results very little when a platen is used (Rudnick et al, 1963). Of the tension tests, Mitchell (1961) believes that the diametral test gives the best reproducibility; and the results seem to be in agreement with other more complex methods of tension testing.

The use of cushion materials affects the value obtained for tensile strength. The softer the cushion material, the higher the tensile strength and the greater the range of values obtained (Addinall and Hackett, 1964).

Proper padding is a function of the mechanical properties of the specimen. The platens are usually
selected by experiment and their type and dimensions must be specified. The basic requirement is that they produce tensile rather than shear or compressive failures. Rudnick et al. (1963) indicate that the triple-cleft type of fracture is only a variation of the normal diametral plane tensile fracture. Thus, data obtained from triple-cleft fractures can be used to compute tensile strength.

Rather than a "true" strength, we should refer to a characteristic statistical distribution of strengths which, for a given material, is determined by the stress state and specimen size under which it is obtained (Addinall and Hackett, 1965(a) & 1965(b)).

All the tensile tests require that the material under test must be able to withstand large shear stresses. Fortunately, for many really brittle materials, failure occurs first in tension.

For brittle materials, which are known to be sensitive to the presence of irregularities at the surface or to the effects of the environment, differences beyond those predicted by statistical theory would be expected between tests that limit maximum stresses to the surface and the diametral compression test.
Impact Strength.

Measurements of the modulus of rupture may not adequately assess the sudden application of stress. Preston, (1931b) & Hazen (1943) have expressed total breaking energy in terms of ultimate flexural strength; but it is improbable that in any actual case of impact the stresses can be accurately calculated.

Each type of impact test has its own peculiar area of use and thus its value lies in its connection with field-service performance (Davis et al, 1955, p.191). Telfair and Nason (1945) believe that the state of stress produced in the specimen during a test is one of the most important factors in impact testing. Its critical nature is demonstrated by changing the dimensions of the test piece.

A S T M Test Method D 256-56 is the only widely published test for impact resistance of ceramic materials. Multer (1966) found that measurements are meaningless and misleading when this method was applied to many common ceramics. The section of Methods D 256 dealing with ceramics specifies a Charpy test. Here the results are grossly distorted by the energy consumed in tossing the specimens after fracture. The Izod and Charpy tests share
the same principle. They are pendulum-type impact machines. Unfortunately, both tests possess errors when applied to brittle materials (Richardson and Worner, 1945 & Hazen, 1943).

Only that portion of the energy used in fracturing the specimen is of practical significance. The drop-ball impact machine seems to measure only this energy (Andrews, 1961, pp. 518-522). Such a method is a necessary prerequisite to any attempt to correlate impact strength with other properties. The rebound of the falling weight on a rigid specimen is, however, a disadvantage that can be eliminated when using a pendulum to deliver the impact.

Haward (1944) broke squares of simply supported glass by dropping steel ball bearings from gradually increasing heights. The increment of height did not vary; the lowest height was chosen so that only one piece of glass was broken under this impact. His experiments indicated that the formation of a cone flaw in the upper surface did not so weaken a specimen that the following impact from a greater height necessarily caused the fracture of the plate.

The coefficients of variation ranged from 38 to 53 per cent, and he quoted this as the margin of error to
be expected. The readings were in centimetres.

Haward (1944) found that as the weight of the ball was reduced, and the velocity of impact therefore increased, the energy required to break the plate declined. However, slow breaking experiments using balls of widely varying size showed no significant difference.

Under impact conditions, inertia of the specimen can result in a decrease in its deformation and energy absorption. In all cases, where the velocity of impact is sufficiently large to yield initial localized stresses around the point of impact comparable to the breaking stresses, a break should result following the lines of compression at right angles to the lines of maximum tension. The process of high velocity impact is very different from that which occurs at low velocity impact, when the bending of the material is the dominant feature responsible for the absorption of energy.

Haward (1944) was of the opinion that wherever the specimen broke at the bottom face under tension, the radius of the balls, as in a static experiment, had little effect. However, he did not really investigate this possible cause of error. His results show clearly that the increase in bending strength under impact can be fully accounted for by the time factor.
If we increase the energy of impact by small steps until the specimen breaks, we should approach the minimum energy required to fracture it. The source of error in energy required to project the fragments and the superfluous kinetic energy remaining in the ball after failure are thus minimized.

Actually, in the impact, some kinetic energy is dissipated. This loss, which can be estimated by equating the momentum of the entire system before and after impact, is most conveniently taken into account by multiplying the available energy (measured by $h$ or by $v^2$) by a factor $K$, the value of which, for a member of uniform section, is as follows:

A moving body of mass $M$ strikes transversely the centre of a simple beam of mass $M_1$, then

$$K = \frac{1 + \frac{17}{35} \frac{M_1}{M}}{\left(1 + \frac{5}{8} \frac{M_1}{M}\right)^2} \ldots \ldots (3).$$
290.

If there be a body of mass $M_2$ attached to the beam at its centre, then

$$K = 1 + \frac{17}{35} \frac{M_1}{M} + \frac{M_2}{M} \frac{1}{\left(1 + \frac{5}{8} \frac{M_1}{M} + \frac{M_2}{M}\right)^2} \ldots \ldots \ldots (4)$$


We know that the elastic curve of a beam under impact is different from that under static loading; but this difference is less marked for low than for high velocities of impact.

The palliative effect of the inertia of the body struck, and of attached bodies, as expressed by $K$, is greatest when the masses of these parts are large compared with that of the moving body. When this is the case, impact can only be serious if the velocity is relatively high (Roark, 1965, p.373).
THE BEND TEST.

MATERIALS AND METHODS.

In 1932, Murgatroyd asserted that tests made on vitreous materials should bear some relation to their intended use. Indeed, it is of the utmost importance to relate specimens or models to functional size, either by scale or actual size. To this end, specimens formed from both moulds, (A) and (B), were tested (see Section 10.1).

Although short beams and very wide beams are not considered to be ideal for estimating tensile strength in bend tests, it should be remembered that those cited in this work are regarded purely as comparative tests. Nevertheless, Table XX (p.281) shows that, for span/depth ratios between 1.5 and 1, there is not an inordinate difference between maximum tensile stress and the calculated maximum fibre tensile stress.

In view of the comparatively small span/depth ratios in the selected test pieces, a system of three-point loading was employed.

All tests were performed on a Hounsfield Tensometer *. The compression attachment was assembled

* Hounsfield Tensometer, Type W., Tensometer Ltd.,

81 Morland Road, Croydon, Surrey, U.K.
into the machine; and within this, one compression die and a Brinell ball (5 mm. diam.) bolster opposed one another.

In all cases the contact surfaces of the specimens, loading head and supports were smooth; and a soft-metal pad of brass improved the uniformity of load distribution at the contact surfaces. The Brinell ball served as the loading head which was centred at mid-span. Rounded, hardened-steel supporting rods (0.0913 in. diam.) rested parallel to one another, 0.25 inches apart at their centres, in the brass pad (1" x 7/16" x 7/16"). This assembly was attached to the compression die directly opposite the loading head. Figure 20(a) illustrates this loading system. The glass test piece shown resembles specimens of porcelain from mould (A) in shape and size. Figure 20(b) exhibits a two-dimensional representation of the stress pattern to be expected under the conditions of these experiments.

In all tests on the two specimen types, the rate of tensile loading at the convex surfaces approached 6,000 lb/in²/minute. This value was calculated using the conventional modulus of rupture formula (1).

Attempts to standardize and treat the surface conditions of test pieces were made. As these methods
Fig. 20. — Three-point loading system — photoelastic analysis.

(a) Before the application of stress to a strain-free glass test piece representing the specimens of porcelain from mould (A), in shape and size.

(b) A two-dimensional representation of the distribution and intensity of stress in this test piece, when a force was applied to the loading head.
varied for different experiments, they will be specified in
their appropriate sections.

Differences in relative humidity during testing
procedures were circumvented by conducting all strength
tests on specimens thoroughly moistened with water. Such
a procedure should have not only eliminated differences
caused by changes in relative humidity; but it should have
tested specimens under the severe conditions encountered in
the oral environment.

18.1 The Effect of Condensation
on the Modulus of Rupture.

(a) Condensation during specimen formation
    before firing.

Samples of Vv, were prepared in different ways
from mould (A), as described in Section 14.1. Sintering
took place at 1090°C for a period of four minutes.

(b) Type of sintering.

Representative samples from each group were
vacuum-fired; others were air-fired. For every test piece
the rate of cooling was moderate.

All specimens were ground on grade 220-A silicon
carbide abrasive paper under running water. The direction
of grinding on all four sides (not the ends) was longitudinal.
Before testing, the breadth and depth of each sample were measured with a micrometer and recorded.

18.2 The Effect of Sintering Time on the Modulus of Rupture.

Preparation by mechanical vibration into mould (A) provided samples of $Vv_1$ which were vacuum-sintered at 1090°C for times ranging from one to ten minutes. Similar groups of $Vv_1$ were also air-sintered for varying times.

For all test pieces, the rate of cooling was moderate. Surface grinding, as described in Section 18.1, prepared each specimen before testing.

18.3 The Effect Different Moulds used in Specimen Manufacture have on the Modulus of Rupture.

After mechanical vibration into moulds (A) and (B), samples of $Vv_1$ were vacuum-fired. Surface preparation was identical with that described in Section 18.1.

18.4 The Modulus of Rupture of Different Materials.

Samples of $Vv_1$, $Vv_2$, $Vv_3$, $Ev_1$, $Ta_1$, $Sa_1(a)$, $DAv_0$, $DAv_1$ and $VAv_0$ were prepared from mould (A); and $Vv_1$, $Ta_1$, $DAv_0$ and $VAv_0$ from mould (B). The surfaces of all test pieces were abraded as described in Section 18.1.
18.5 The Effect Rate of Cooling has on 
the Modulus of Rupture.

Specimens of $Vv_1$, from mould (A), were vacuum-
sintered and cooled at different rates. The group that 
experienced a moderate rate of cooling remained in the 
furnace entrance for ten minutes before being withdrawn. 
The rapidly cooled group were chilled to room temperature 
immediately; and the group that underwent a slow rate of 
cooling remained in the furnace muffle when the current was 
turned off. They cooled with the furnace over a period of 
six hours.

All specimens were ground as in Section 18.1.

18.6 The Effect Surface Treatment has 
on the Modulus of Rupture.

On different groups of $Vv_1$, from moulds (A) and 
(B), that had been vacuum-sintered, surfaces were prepared; 
by grinding as described in Section 18.1; by vacuum-firing 
for eight minutes and chilling to room temperature; by 
grinding and etching in 40 per cent hydrofluoric acid for 
ten seconds at room temperature, followed by thorough 
washing; by grinding, vacuum-fire-finishing for eight 
minutes and chilling to room temperature; and by grinding, 
air-fire-finishing for eight minutes and chilling to room 
temperature.
18.7 The Effect Surface Compression, created by Low-Temperature Ionic Exchange, has on the Modulus of Rupture.

From the results obtained in Section 13, it appeared that the vitreous phases in $Vv_1$ and $Sa_1(a)$ represented sodium-potassium aluminosilicate glasses. Realizing this, it seemed not unreasonable to expect that some stress could be induced at the surfaces of these materials by low-temperature ionic exchange. Potassium ions, so abundant in molten potassium nitrate, could replace the smaller sodium network-modifying ions in the vitreous matrix. Figure 21 is a simplified model of the surface ionic crowding which should take place in the glassy phases of these materials.

Accordingly, samples of $Vv_1$, $Vv_0$ and $Sa_1(a)$ were employed in these experiments. Mould (A) provided test pieces of $Vv_1$ and $Sa_1(a)$; mould (B), samples of $Vv_1$ and $Vv_0$. The opaque dental porcelain $Vv_0$ was included in these tests for practical reasons. If preferential pre-stressing by ionic exchange be possible in some dental porcelains, then it would be highly desirable that $Vv_0$, and similar materials, were amongst them.
Fig. 21. — Simplified model of the process of ionic exchange.

Ionic crowding results from low-temperature exchange of potassium ions for smaller sodium ions. While this process is strongly temperature dependent, surface compression would be reduced at temperatures where there is considerable stress release, for the glass under consideration.
Fig. 21. Crowding from low-temperature exchange of $K^+$ for $Na^+$ ions.
After abrading the surfaces, as in Section 18.1, the groups of $Vv_1$ and $Vv_0$ were immersed in molten potassium nitrate at $475^\circ C$ for 17 hours. But for the temperature, viz., $400^\circ C$, the $S_{a1(a)}$ series underwent similar preparation. Upon removal from the bath, each specimen was cooled to room temperature and washed.

In an attempt to gauge the effect of further surface treatment in these series, after surface abrasion, another group of $Vv_1$ was vacuum-fire-finished before its chemical treatment.
300.

RESULTS.

18.1 The Effect of Condensation on the Modulus of Rupture.

Table XXI displays no great differences in modulus of rupture for \( Vv_1 \), however the samples were prepared from mould (A). Although, in comparable groups, air-sintering tended to produce lower values, neither the types of condensation employed during specimen formation in these groups, nor the modes of densification during sintering, could be made to produce specimens that showed any predictable difference in strength under these conditions.

18.2 The Effect of Sintering Time on the Modulus of Rupture.

For \( Vv_1 \) under the conditions specified, from the time of "vitrification" at two minutes right up to ten minutes sintering at 1090°C, either air- or vacuum-firing, Table XXII shows no obvious change in modulus of rupture.

18.3 The Effect Different Moulds used in Specimen Manufacture have on the Modulus of Rupture.

All things being equal, for \( Vv_1 \), specimens made from mould (A) provided a higher modulus of rupture than those prepared from mould (B), (Table XXIII). This
difference was highly significant (>99.9 per cent level of confidence).

18.4 The Modulus of Rupture of Different Materials.

Table XXIV displays just how similar are the strengths of specimens of $Vv_1$, $Vv_2$, $Bv_1$ and $Sa_1(a)$, made from mould (A). $Vv_3$ showed a higher strength than $Vv_1$ (at about >99 per cent but <99.9 per cent level of confidence). Of interest are the results obtained for $Ta_1$; these were higher than for $Vv_1$, $Bv_1$, $Sa_1(a)$, and comparable with the strengths of $DAv_0$, $DAv_1$ and $VAv_0$, the aluminous materials.

Despite the lower alumina content of $DAv_1$, its strength was comparable with that of both $DAv_0$ and $VAv_0$ under these conditions of testing. All the aluminous porcelains were stronger than $Vv_1$.

Results from specimens of different materials from mould (B) displayed the same relative strength levels (Table XXV) as those from mould (A) (Table XXIV); but, with the exception of $VAv_0$ (Series D, Table XXV), the higher strengths of $Ta_1$ and $DAv_0$ could only be described as tendencies. $VAv_0$ did show a higher modulus of rupture than $Vv_1$ (at about >99 per cent but <99.9 per cent level of confidence).
TABLE XXI.

MODULUS OF RUPTURE.

The effect condensation, in specimen formation and densification during sintering, has on the modulus of rupture. Samples of Vv. were formed in mould (A) and fired at 1090°C for four minutes. Surfaces were abraded with grade 220-A silicon carbide paper.

<table>
<thead>
<tr>
<th>Series Reference</th>
<th>Type of condensation in specimen formation.</th>
<th>Number of Specimens</th>
<th>Type of Sintering</th>
<th>MODULUS OF RUPTURE (p.s.i.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>A</td>
<td>Wet mechanical vibration for 5 mins. with continual absorption of moisture.</td>
<td>24</td>
<td>VACUUM</td>
<td>8,750</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>10</td>
<td>AIR</td>
<td>8,650</td>
</tr>
<tr>
<td>C</td>
<td>No mechanical vibration.</td>
<td>3</td>
<td>VACUUM</td>
<td>10,370</td>
</tr>
<tr>
<td>D</td>
<td>Moisture absorbed.</td>
<td>3</td>
<td>AIR</td>
<td>10,030</td>
</tr>
<tr>
<td>E</td>
<td>Wet mechanical vibration as above, using powder containing no organic dye**.</td>
<td>3</td>
<td>VACUUM</td>
<td>9,800</td>
</tr>
<tr>
<td>F</td>
<td>Wet mechanical vibration with low amplitude for $\frac{1}{2}$ hour. Moisture only absorbed at end of process.</td>
<td>3</td>
<td>VACUUM</td>
<td>11,400</td>
</tr>
<tr>
<td>G</td>
<td></td>
<td>3</td>
<td>AIR</td>
<td>8,670</td>
</tr>
</tbody>
</table>

* For calculation of 95% confidence limits for the true mean.

** Organic dye had been washed out.
TABLE XXII.
MODULUS OF RUPTURE.

The effect sintering time has on the modulus of rupture. Samples of Vv. were formed in mould (A) and fired at 1090°C. Surfaces were abraded with grade 220-A silicon carbide paper.

<table>
<thead>
<tr>
<th>Series Reference</th>
<th>Sintering time (mins.)</th>
<th>Number of Specimens</th>
<th>Type of sintering</th>
<th>MODULUS OF RUPTURE (p.s.i.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>A (i)</td>
<td>1</td>
<td>3</td>
<td>VACUUM</td>
<td>4,530</td>
</tr>
<tr>
<td>A (ii)</td>
<td>2</td>
<td>3</td>
<td>VACUUM</td>
<td>8,870</td>
</tr>
<tr>
<td>A (iii)</td>
<td>3</td>
<td>3</td>
<td>VACUUM</td>
<td>9,900</td>
</tr>
<tr>
<td>A (iv)</td>
<td>4</td>
<td>3</td>
<td>VACUUM</td>
<td>8,330</td>
</tr>
<tr>
<td>A (v)</td>
<td>5</td>
<td>3</td>
<td>VACUUM</td>
<td>8,200</td>
</tr>
<tr>
<td>A (vi)</td>
<td>6</td>
<td>3</td>
<td>VACUUM</td>
<td>8,600</td>
</tr>
<tr>
<td>A (vii)</td>
<td>7</td>
<td>3</td>
<td>VACUUM</td>
<td>8,830</td>
</tr>
<tr>
<td>A (viii)</td>
<td>8</td>
<td>3</td>
<td>VACUUM</td>
<td>8,500</td>
</tr>
<tr>
<td>A (ix)</td>
<td>10</td>
<td>3</td>
<td>VACUUM</td>
<td>8,730</td>
</tr>
<tr>
<td>B (i)</td>
<td>4</td>
<td>3</td>
<td>AIR</td>
<td>9,300</td>
</tr>
<tr>
<td>B (ii)</td>
<td>8</td>
<td>3</td>
<td>AIR</td>
<td>9,070</td>
</tr>
<tr>
<td>B (iii)</td>
<td>10</td>
<td>4</td>
<td>AIR</td>
<td>7,850</td>
</tr>
</tbody>
</table>

* For calculation of 95% confidence limits for the true mean.
The effect of different moulds used in specimen manufacture have on the modulus of rupture.

After mechanical vibration, samples of W1-A silicon carbide paper were vacuum-fired at 1090°C. Surfaces were scored with grade 220-A silicon carbide paper.

<table>
<thead>
<tr>
<th>Series Reference</th>
<th>Number of Specimens</th>
<th>Type of Mould</th>
<th>Mean (p.s.i.)</th>
<th>S.D.</th>
<th>f.s.d.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>24</td>
<td>(A)</td>
<td>8,750</td>
<td>1,010</td>
<td>12</td>
</tr>
<tr>
<td>B</td>
<td>12</td>
<td>(B)</td>
<td>6,425</td>
<td>1,390</td>
<td>883</td>
</tr>
</tbody>
</table>

* For calculation of 95% confidence limits for the true mean.
TABLE XXIV.

MODULUS OF RUPTURE.

The modulus of rupture of different materials. After mechanical vibration into mould (A), samples were fired for four minutes. Surfaces were abraded with grade 220-A silicon carbide paper.

<table>
<thead>
<tr>
<th>Series Reference</th>
<th>Porcelain</th>
<th>Number of Specimens</th>
<th>Holding temp.(°C)</th>
<th>Type of sintering</th>
<th>MODULUS OF RUPTURE (p.s.i.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>A</td>
<td>Vv₁</td>
<td>24</td>
<td>1090°</td>
<td>VACUUM</td>
<td>8,750</td>
</tr>
<tr>
<td>B</td>
<td>Vv₂</td>
<td>10</td>
<td>1090°</td>
<td>VACUUM</td>
<td>10,180</td>
</tr>
<tr>
<td>C</td>
<td>Vv₃</td>
<td>10</td>
<td>1090°</td>
<td>VACUUM</td>
<td>10,260</td>
</tr>
<tr>
<td>D</td>
<td>Bv₁</td>
<td>10</td>
<td>1090°</td>
<td>VACUUM</td>
<td>9,500</td>
</tr>
<tr>
<td>E</td>
<td>Ta₁</td>
<td>10</td>
<td>900°</td>
<td>AIR</td>
<td>12,370</td>
</tr>
<tr>
<td>F</td>
<td>Sa₁(a)</td>
<td>6</td>
<td>980°</td>
<td>AIR</td>
<td>9,490</td>
</tr>
<tr>
<td>G</td>
<td>DAv₀</td>
<td>10</td>
<td>900°</td>
<td>VACUUM</td>
<td>12,370</td>
</tr>
<tr>
<td>H</td>
<td>DAv₁</td>
<td>10</td>
<td>900°</td>
<td>VACUUM</td>
<td>12,520</td>
</tr>
<tr>
<td>I</td>
<td>VAv₀</td>
<td>10</td>
<td>980°</td>
<td>VACUUM</td>
<td>13,500</td>
</tr>
</tbody>
</table>

* For calculation of 95% confidence limits for the true mean.
TABLE XXV.

MODULUS OF RUPTURE.

The modulus of rupture of different materials. After mechanical vibration into mould (B), samples were fired for four minutes. Surfaces were abraded with grade 220-A silicon carbide paper.

<table>
<thead>
<tr>
<th>Series Reference</th>
<th>Porcelain</th>
<th>Number of Specimens</th>
<th>Holding temp. (°C)</th>
<th>Type of sintering</th>
<th>MODULUS OF RUPTURE (p.s.i.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>A</td>
<td>Vv₁</td>
<td>12</td>
<td>1090°</td>
<td>VACUUM</td>
<td>6,425</td>
</tr>
<tr>
<td>B</td>
<td>Ta₁</td>
<td>10</td>
<td>900°</td>
<td>AIR</td>
<td>7,720</td>
</tr>
<tr>
<td>C</td>
<td>DAv₀</td>
<td>8</td>
<td>900°</td>
<td>VACUUM</td>
<td>8,280</td>
</tr>
<tr>
<td>D</td>
<td>VAv₀</td>
<td>8</td>
<td>980°</td>
<td>VACUUM</td>
<td>8,135</td>
</tr>
</tbody>
</table>

* For calculation of 95% confidence limits for the true mean.
TABLE XXVI.
MODULUS OF RUPTURE.

The effect rate of cooling has on the modulus of rupture. After mechanical vibration into mould (A), samples of Vv₁ were vacuum-fired at 1090°C. When cooled at various rates, surfaces were abraded with grade 220-A silicon carbide paper.

<table>
<thead>
<tr>
<th>Series Reference</th>
<th>Cooling rate</th>
<th>Number of Specimens</th>
<th>MODULUS OF RUPTURE (p.s.i.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>A</td>
<td>MODERATE</td>
<td>24</td>
<td>8,750</td>
</tr>
<tr>
<td>B</td>
<td>RAPID</td>
<td>4</td>
<td>9,700</td>
</tr>
<tr>
<td>C</td>
<td>SLOW</td>
<td>3</td>
<td>9,230</td>
</tr>
</tbody>
</table>

* For calculation of 95% confidence limits for the true mean.
TABLE XXVII.
MODULUS OF RUPTURE.

The effect surface treatment has on the modulus of rupture. Samples of Vv4 were formed in mould (A) and vacuum-fired at 1090° C.

<table>
<thead>
<tr>
<th>Series Reference</th>
<th>Sintering time, (mins.)</th>
<th>SURFACE TREATMENT</th>
<th>Modulus of Rupture (p.s.i.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Abraded with SiC paper.</td>
<td>Fire-finishing</td>
<td>Number of Specimens</td>
</tr>
<tr>
<td></td>
<td>grade 220-A</td>
<td>type (mins.)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>fire-finishing</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Other</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>4</td>
<td>YES nil nil nil</td>
<td>24</td>
</tr>
<tr>
<td>B</td>
<td>8</td>
<td>NO nil nil</td>
<td>Chilled to R.T.</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
<td>YES nil nil</td>
<td>Etched (HF 4.0% 10 secs. at R.T.)</td>
</tr>
<tr>
<td>D</td>
<td>4</td>
<td>YES 8 VACUUM</td>
<td>Chilled to R.T.</td>
</tr>
<tr>
<td>E</td>
<td>4</td>
<td>YES 8 AIR</td>
<td>Chilled to R.T.</td>
</tr>
<tr>
<td>F</td>
<td>4</td>
<td>YES 8 VACUUM OR AIR</td>
<td>Chilled to R.T.</td>
</tr>
</tbody>
</table>

* For calculation of 95% confidence limits for the true mean.
The Effect Rate of Cooling has on the Modulus of Rupture.

When the surface skin had been removed by grinding, no significant difference in strength was detected between groups of Vv₁ that had been cooled at widely varying rates (Table XXVI).

The Effect Surface Treatment has on the Modulus of Rupture.

Table XXVII shows how fire-finishing and chilling to room temperature increased the modulus of rupture of Vv₁ samples from mould (A), regardless of the method used.

While vacuum-fire-finishing tended to produce stronger specimens than did air-fire-finishing, the difference was not highly significant ( >99 per cent but < 99.9 per cent level of confidence). Etched samples were not stronger than ground specimens; and they were weaker than the vacuum-fire-finished series.

For test pieces of Vv₁ made from mould (B), ground and etched specimens again showed no great change in strength from the abraded group (Table XXVIII). But added to this, vacuum-fire-finishing abraded specimens followed by chilling to room temperature did not increase
the modulus of rupture significantly. However, the fire-finished group were stronger than the ground and etched group (at about > 99 per cent but < 99.9 per cent level of confidence).

18.7 The Effect Surface Compression, created by Low-Temperature Ionic Exchange, has on the Modulus of Rupture.

Chemical treatment of samples manufactured from Vv₁, Vv₀ and Sa₁(a) produced a dramatic effect on their measured strengths (Table XXIX).

Specimens of Vv₁ formed from mould (A) (Series B, Table XXIX) showed an average increased strength of about 68 per cent. Fire-finishing the surfaces before chemical pre-stressing tended to raise the modulus of rupture more, but not significantly (Series C). For Sa₁(a), the treated group (Series E) was about 47 per cent stronger than the untreated group (Series D).

With samples from mould (B), the effect became even more pronounced. The average measured strength of Vv₁ rose by 122 per cent (Series F and Series G, Table XXIX). Vv₀ displayed the same high strengths when treated (Series H).
The effect surface treatment has on the modulus of rupture. Samples of \( Vv' \) were formed from mould (B) and vacuum-fired at 1090°C for four minutes.

<table>
<thead>
<tr>
<th>Series Reference</th>
<th>SURFACE TREATMENT</th>
<th>Number of Specimens</th>
<th>MODULUS OF RUPTURE (p.s.i.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Abraded with Fire-grade 220-A finishing</td>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td></td>
<td>SiC paper. time.(mins.) finishing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>YES</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>B</td>
<td>YES</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>C</td>
<td>YES</td>
<td>8</td>
<td>VACUUM</td>
</tr>
</tbody>
</table>

* For calculation of 95% confidence limits for the true mean.
The effect surface compression, created by low-temperature ionic exchange, has on the modulus of rupture. The surfaces of all specimens were abraded immediately after sintering for four minutes.

<table>
<thead>
<tr>
<th>Series</th>
<th>Porc.</th>
<th>Type holding</th>
<th>Type of temp.</th>
<th>Sintering</th>
<th>Finishing</th>
<th>Specimens</th>
<th>Temp. of KNO₃</th>
<th>Time of immersion</th>
<th>MODULUS OF RUPTURE (p.s.i.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>A</td>
<td>Vv₁</td>
<td>(A) 1090°</td>
<td>VACUUM</td>
<td>nil</td>
<td>24</td>
<td>nil</td>
<td>nil</td>
<td></td>
<td>8,750</td>
</tr>
<tr>
<td>B</td>
<td>Vv₁</td>
<td>(A) 1090°</td>
<td>VACUUM</td>
<td>nil</td>
<td>10</td>
<td>475°</td>
<td>17</td>
<td></td>
<td>14,705</td>
</tr>
<tr>
<td>C</td>
<td>Vv₁</td>
<td>(A) 1090°</td>
<td>VACUUM (vacuum)</td>
<td>10</td>
<td>475°</td>
<td>17</td>
<td></td>
<td></td>
<td>15,560</td>
</tr>
<tr>
<td>D</td>
<td>Sa₁(a)</td>
<td>(A) 980°</td>
<td>AIR</td>
<td>nil</td>
<td>6</td>
<td>nil</td>
<td>nil</td>
<td></td>
<td>9,490</td>
</tr>
<tr>
<td>E</td>
<td>Sa₁(a)</td>
<td>(A) 980°</td>
<td>AIR</td>
<td>nil</td>
<td>6</td>
<td>400°</td>
<td>17</td>
<td></td>
<td>13,975</td>
</tr>
<tr>
<td>F</td>
<td>Vv₁</td>
<td>(B) 1090°</td>
<td>VACUUM</td>
<td>nil</td>
<td>12</td>
<td>nil</td>
<td>nil</td>
<td></td>
<td>6,425</td>
</tr>
<tr>
<td>G</td>
<td>Vv₁</td>
<td>(B) 1090°</td>
<td>VACUUM</td>
<td>nil</td>
<td>7</td>
<td>475°</td>
<td>17</td>
<td></td>
<td>14,255</td>
</tr>
<tr>
<td>H</td>
<td>Vv₀</td>
<td>(B) 1090°</td>
<td>VACUUM</td>
<td>nil</td>
<td>8</td>
<td>475°</td>
<td>17</td>
<td></td>
<td>14,475</td>
</tr>
<tr>
<td>I</td>
<td>VAv₀</td>
<td>(A) 980°</td>
<td>VACUUM</td>
<td>nil</td>
<td>12</td>
<td>nil</td>
<td>nil</td>
<td></td>
<td>12,987</td>
</tr>
<tr>
<td>J</td>
<td>VAv₀</td>
<td>(B) 980°</td>
<td>VACUUM</td>
<td>nil</td>
<td>8</td>
<td>nil</td>
<td>nil</td>
<td></td>
<td>8,210</td>
</tr>
<tr>
<td></td>
<td>DAv₀</td>
<td>(A) 900°</td>
<td>VACUUM</td>
<td>nil</td>
<td>10</td>
<td>nil</td>
<td>nil</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DAv₀</td>
<td>(B) 900°</td>
<td>VACUUM</td>
<td>nil</td>
<td>8</td>
<td>nil</td>
<td>nil</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* For calculation of 95% confidence limits for the true mean.
Of great interest was the fact that the calculated modulus of rupture from chemically preferentially pre-stressed \( V_{v_1} \) specimens made from mould (B) matched that found for mould (A) samples, which had undergone the same treatment.

By way of rough comparison with the chemical strengthening attained, groups of dispersion-strengthened materials were included in Table XXIX. For mould (A), the average increase recorded was about 48 per cent (Series A and I); for mould (B) only approximately 28 per cent (Series F and J).

From the results above, it is obvious that chemical preferential pre-stressing the surfaces of \( V_{v_1} \) samples from mould (A) produced measured strengths at least comparable with the aluminous materials, tested under identical conditions. But, for mould (B) test pieces, there was no comparison. These pre-stressed specimens of \( V_{v_1} \) possessed a much higher modulus of rupture than the aluminous group.
CONCLUSIONS.

Under the conditions of testing, no mode of specimen formation and/or type of densification during sintering used could be made to influence the modulus of rupture of Vv₁ enough to be of any great consequence. Although all vacuum-fired groups tended to be a little stronger than the comparable air-fired series, in no individual case could this difference be predictable with any degree of certainty. It appears that the extra porosity incurred during air-firing (about two to three percent) was not sufficient to have a significant effect on the measured modulus of rupture.

When surfaces had been abraded in a similar fashion, sintering time did not seem to be an important factor determining the modulus of rupture of Vv₁.

Under ordinary conditions, when all other things were equal, the results from bend tests on specimens of Vv₁ manufactured from moulds (A) and (B) were not comparable. They were different. Probably, this fact could be explained as being largely due to differences in the surface areas under tensile stress during testing.

The strengths of Vv₁, Vv₂, Bv₁ and Sₐ₁(a), under the conditions specified, were not dissimilar. However,
presumably, a lower quartz content and perhaps the absence of pigment in Vv₃ made it a little stronger than Vv₁ (at about > 99 per cent but < 99.9 per cent level of confidence). The high strengths recorded for Ta₄ samples from mould (A) might be related to its relatively homogeneous structure. Apart from porosity, very few major flaws can be detected in its matrix (see Fig. 16).

The fact that DA_w₁ was no weaker than DA_w₀ and VAV₀, under the conditions specified, seemed to limit the effectiveness of alumina as a dispersion-strengthening agent to the lower volume proportions found in DA_w₁, all things being equal.

Presumably, the differences gained when testing different materials made from mould (A) were minimized when mould (B) was employed because of the magnification of other factors. The involvement of serious surface flaws due to the increased area under tensile stress is one; an increase in the possibility of a mean free path of glassy phase, due to the thinness of the specimens, could be another.

Apparently, for Vv₁, when the surfaces had been abraded, various rates of cooling did not affect the material enough to influence its modulus of rupture to any great extent.
Fire-finishing abraded samples of \( Vv_1 \) from mould (A), followed by chilling to room temperature made them stronger — not so with etching. For mould (B) specimens, fire-finishing and chilling had no significant effect on abraded strength, although it produced a higher modulus of rupture than did etching. A common finding for the two moulds was that vacuum-fire-finishing increased the modulus of rupture above that of etched specimens.

One might relate these observations to stressed surface-skin effects associated with actual surface integrity. It could have been that the preferential pre-stressing effected by chill-tempering was minimal for the thin specimens from mould (B).

No doubt can exist that chemical preferential pre-stressing was possible for \( Vv_1, Vv_0 \) and \( Sa_1(a) \); and its effect on the strength of thin specimens was most marked — a situation to be expected with any surface modification (see p.282). Despite the different values for modulus of rupture obtained for abraded \( Vv_1 \) test pieces from moulds (A) and (B), both values became high and comparable when these surfaces were pre-stressed chemically. What better display of the dependence of strength on the surface condition could we have? When pre-stressing the surface
has ironed out the probability of influence from serious surface defects, the same formula (1) produced similar modulus of rupture values for the two specimen types.

Dispersion-strengthening proved to be comparable with chemical preferential pre-stressing in raising the modulus of rupture for the thick test pieces. For the thin samples, it was quite the inferior method.
19. THE DIAMETRICAL COMPRESSION TEST.

MATERIALS AND METHODS.

By way of comparison with the bend tests, an estimation of the tensile strength by the diametral compression test was thought to be desirable. This method does not purport to accentuate the effects of surface condition on measured strength.

\( Vv_1, Sa_1(a), Bv_1 \) and \( DAv_0 \) were used in the formation of specimens from the diametral mould. The surfaces of the test pieces from most groups remained in the as-fired condition after four minutes sintering. Groups of \( Vv_1 \) were both air- and vacuum-sintered; and one series was abraded at the ends, vacuum-fire-finished for three minutes and chilled to room temperature. Another set of \( Vv_1 \) test pieces was preferentially pre-stressed chemically on as-sintered surfaces.

Experiment showed that the use of cardboard platens, 0.0236 inch thick, provided the necessary stress distribution to initiate tensile failure in all the specimens tested. The triple-cleft type of fracture was common amongst the stronger samples.

All tests were made on moist specimens. The rate of diametral tensile loading, as calculated using formula (2) (p.283), approached 2,000 lb/in\(^2\)/min.
RESULTS.

Again, air-fired samples of $Vv_1$ only tended to be weaker than the vacuum-fired series (Table XXX, Series A and B). Surface treatment by vacuum-fire-finishing and chilling to room temperature did not affect the measured tensile strength of $Vv_1$ to any degree (Series C).

The strength of $S_{a1(a)}$ was comparable to that of $Vv_1$, but not that of $Bv_1$. $Bv_1$ appeared to be slightly weaker than $Vv_1$ (Series A and E), at better than the 99.9 per cent level of confidence.

$DA_{0}$ did not possess a greater strength than $Vv_1$ under these conditions that was highly significant (Series A and F); but $Vv_1$ with chemically pre-stressed surfaces did, at better than the 99.9 per cent level of confidence (Series G). From Table XXX it can readily be seen that this group of chemically treated $Vv_1$, was not really stronger than the aluminous group of $DA_{0}$.
TABLE XXX.
TENSILE STRENGTH.
(DIAMETRAL COMPRESSION TEST)

The tensile strength of samples made from the diametral mould. All specimens were fired for four minutes. Cardboard platens, 0.0236 inch thick, were used in all tests.

<table>
<thead>
<tr>
<th>Series Reference</th>
<th>Porcelain</th>
<th>Number of Specimens</th>
<th>Holding temp. (°C)</th>
<th>Type of Sintering</th>
<th>Surface treatment at the ends</th>
<th>TENSILE STRENGTH (p.s.i.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>A</td>
<td>Vv₁</td>
<td>10</td>
<td>1090°</td>
<td>VACUUM</td>
<td>As sintered</td>
<td>8,635</td>
</tr>
<tr>
<td>B</td>
<td>Vv₁</td>
<td>10</td>
<td>1090°</td>
<td>AIR</td>
<td>As sintered</td>
<td>8,050</td>
</tr>
<tr>
<td>C</td>
<td>Vv₁</td>
<td>10</td>
<td>1090°</td>
<td>VACUUM</td>
<td>Abraded; vacuum-fired-finished for 3 mins; chilled to room temp.</td>
<td>8,080</td>
</tr>
<tr>
<td>D</td>
<td>Sa₁(a)</td>
<td>10</td>
<td>980°</td>
<td>AIR</td>
<td>As sintered</td>
<td>8,740</td>
</tr>
<tr>
<td>E</td>
<td>Bv₁</td>
<td>5</td>
<td>1090°</td>
<td>VACUUM</td>
<td>As sintered</td>
<td>7,060</td>
</tr>
<tr>
<td>F</td>
<td>DAV₀</td>
<td>10</td>
<td>900°</td>
<td>VACUUM</td>
<td>As sintered</td>
<td>9,550</td>
</tr>
<tr>
<td>G</td>
<td>Vv₁</td>
<td>10</td>
<td>1090°</td>
<td>VACUUM</td>
<td>As sintered; immersed in KN₂O₃ at 475°C for 17 hours.</td>
<td>9,690</td>
</tr>
</tbody>
</table>

* For calculation of 95% confidence limits for the true mean.
CONCLUSIONS.

It was remarkable just how closely the measured tensile strength of \( Vv_1 \), using the diametral compression test, followed the modulus of rupture calculated for abraded samples of \( Vv_1 \) from mould (A). This fact leads one to accept such a bend test on thick specimens as one with some merit for these materials.

The diametral compression test, apparently, was no better in separating air- and vacuum-fired strengths than were the bend tests. But, it did separate \( Bv_1 \) from \( Vv_1 \); and this could probably be related to the "coarse" microstructure of \( Bv_1 \). It has a pigment-oriented "loculated" appearance with the largest size-ranges for quartz and pigment working units of all the porcelains examined (Table IV).

While dispersion-strengthened samples could not be shown to be significantly stronger than \( Vv_1 \), the chemically treated group of \( Vv_1 \) were. From this observation one must conclude that perhaps for practical purposes this diametral test is not of great value in measuring the undoubted increase in practical strength to be gained from aluminous porcelains under certain conditions; and that the
results from this test can be significantly affected by surface modification. These findings lend weight to the practical validity of the transverse strengths calculated for aluminous materials that had been made into thin specimens.
THE IMPACT TEST.

MATERIALS AND METHODS.

In order to study the behaviour of modern dental porcelains under dynamic loading, a specialized impact test had to be devised.

The state of stress developed during the test is a most important factor. Hence, in an attempt at uniformity, identical three-point loading systems to those described in Section 18 were employed on samples from both moulds (A) and (B).

Figure 22 shows a drop-ball impact machine that was designed by the author and manufactured by Chapman and Goldsmith Pty. Ltd.*.

The specimen supporting block used in the bend tests was bolted onto a steel plate and located and held in the desired position on a magnetic chuck. An anvil of tool steel (hardened to 600 B.H.N.), into which a Brinell ball (5 mm.) bolster had been fitted, served to transmit the impact. Before any test, the impacting head was centred at mid-span. The anvil assembly weighed 182 grammes

* Chapman and Goldsmith Pty. Ltd., Engineers,
Bathurst Street, Sydney, 2000, Australia.
Fig. 22. — Impact Testing Apparatus.

(a) Before impact.
(b) After impact.

COMPONENTS.

1. Steel base (14\(\frac{1}{2}\)" x 14\(\frac{1}{2}\)" x \(\frac{3}{4}\)") supported by four levelling screws.

2. Flexible metal measuring tape.

3. Universal levelling and locking device for magnetic chuck (4).

4. Magnetic chuck (4\" diam.).

5. Lever to activate magnetic chuck.

6. 12 volt – 1 amp. output transformer.

7. Test specimen.

8. Adjusting device for (13).

9. Block housing for linear circulating ball bearings (Thomson Ball Bushing B-122026).

10. Tool steel anvil (3" x \(\frac{3}{4}\)" diam., hardened to 600 B.H.N.) with a Brinell Ball (5 mm.) impact head.

Weight of this assembly equals 182 grammes.

11. Vertical support for sliding height indicators (27" high, \(\frac{1}{2}\)" diam.).

12. Height indicators.

13. Vertical support for electro-magnetic release mechanism (27" high, \(\frac{1}{2}\)" square).

14. 22.2 mm. diameter steel ball bearing (44.6 gms. wt.)

15. Hollow-ground electro-magnetic release mechanism insulated by \(\frac{1}{2}\)" square Lucite bar.

16. Adjusting device for (15).
Fig. 22.
and it was allowed free movement only in the vertical direction.

This arrangement not only resembled that used in the static tests, but standardized the size and shape of the impacting head. Also, it could be used to direct every blow accurately to the small samples.

A steel ball weighing 44.6 gm. was selected for all the tests. A foot switch activated the electromagnetic release mechanism. For mould (A) samples, impacts began at 15 cm. — for mould (B), at 4 cm. The height increments between each release did not vary. They remained constant at 0.5 cm.

From preliminary trials, no correlation could be made between the number of impacts and the measured impact strength. Nevertheless, in the following experiments, all test pieces from comparable moulds experienced identical treatment up until fracture occurred. Naturally, the strongest samples received the highest number of blows.

In every case fracture was dramatic at the recorded fracture heights. Figure 22(a) and (b) demonstrates how measurement of the height was made. When the sample survived a blow, rebound of the ball onto the anvil could be eliminated by catching it in the hand. This
proved to be simple and effective. The right hand was held upwards with the ring and middle fingers separated wider than the upper part of the anvil just above the level of impact. After impact, closing the fingers prevented the ball's return to the anvil from the height of rebound.

If equation (4) (p. 290) can be applied to the conditions described, K would be approximately 0.2:-
where the mass of the test piece was about 0.5 gm.; the mass of the moving body, 44.6 gm.; and the mass of the anvil assembly, 182 gm. That is, for this arrangement an estimation of the dissipated kinetic energy could be gained by multiplying the available energy by 0.2.

From mould (A), Vv₁, both air- and vacuum-fired, and DAv₀ samples were made and tested in the as-fired surface condition. A series of Vv₁ was chemically strengthened and included in the experiments.

Similar groups from mould (B) were manufactured and tested. All specimens were sintered for four minutes.
RESULTS.

For Vv₁, the types of failure encountered from specimens manufactured from moulds (A) and (B) differed. On mould (A) samples, the damage stemmed mostly from the upper surface—sometimes shattering, other times one or two slivers—with crescentic fracture paths leaving a dome-like base. This domed fracture was, by far, most common with the chemically preferentially pre-stressed samples. Apparently, when the surface had been pierced, the resulting break followed a path at right angles to the lines of maximum tension. In the pre-stressed samples, the interior must already have been under some tension before impact.

With mould (B) test pieces, the fracture path always involved the lower surfaces between the supports. The chemically treated samples generally broke into many fragments.

For the aluminous material, DAᵥ₀, manufactured from mould (A), the fracture path mostly involved the lower surface. Remarkably little shattering was sustained. Mould (B) samples showed the same features.

Table XXXI displays how samples of Vv₁ from mould (A) could absorb much more energy than those from mould (B). Although the same tendencies, found in the other tests, held,
**TABLE XXXI.**

**IMPACT STRENGTH.**

All specimens were fired for four minutes.

<table>
<thead>
<tr>
<th>Series Reference</th>
<th>Porcelain</th>
<th>Type of Mould</th>
<th>Number of Specimens</th>
<th>Holding temp. (°C)</th>
<th>Type of Sintering</th>
<th>Surface Treatment</th>
<th>HEIGHT OF BALL REQUIRED TO CAUSE FRACTURE (cms.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean s.d. Coefficient of variation (%)</td>
</tr>
<tr>
<td>A</td>
<td>Vv₁</td>
<td>(A)</td>
<td>20</td>
<td>1090°</td>
<td>VACUUM</td>
<td>As sintered</td>
<td>25.2  6.3  25  2.9</td>
</tr>
<tr>
<td>B</td>
<td>Vv₁</td>
<td>(A)</td>
<td>12</td>
<td>1090°</td>
<td>AIR</td>
<td>As sintered</td>
<td>23.5  4.9  21  3.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>As sintered; immersed in KNO₃ at 475°C for 17 hours.</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Vv₁</td>
<td>(A)</td>
<td>10</td>
<td>1090°</td>
<td>VACUUM</td>
<td></td>
<td>17.4  1.4  8  1.0</td>
</tr>
<tr>
<td>D</td>
<td>DAV₀</td>
<td>(A)</td>
<td>10</td>
<td>900°</td>
<td>VACUUM</td>
<td>As sintered</td>
<td>43.9  14.7  33  10.5</td>
</tr>
<tr>
<td>E</td>
<td>Vv₁</td>
<td>(B)</td>
<td>10</td>
<td>1090°</td>
<td>VACUUM</td>
<td>As sintered</td>
<td>10.7  1.4  13  1.0</td>
</tr>
<tr>
<td>F</td>
<td>Vv₁</td>
<td>(B)</td>
<td>10</td>
<td>1090°</td>
<td>AIR</td>
<td>As sintered</td>
<td>10.3  1.8  17  1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>As sintered; immersed in KNO₃ at 475°C for 17 hours.</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>Vv₁</td>
<td>(B)</td>
<td>11</td>
<td>1090°</td>
<td>VACUUM</td>
<td>As sintered</td>
<td>18.1  2.2  12  1.5</td>
</tr>
<tr>
<td>H</td>
<td>DAV₀</td>
<td>(B)</td>
<td>10</td>
<td>900°</td>
<td>VACUUM</td>
<td>As sintered</td>
<td>13.6  3.9  29  2.8</td>
</tr>
</tbody>
</table>

* For calculation of 95% confidence limits for the true mean.
no significant differences could be developed between specimens that were air- or vacuum-fired.

Notable were the low values obtained for the chemically treated Series C in Table XXXI, and the high values for the aluminous samples in Series D. These $DAV_0$ specimens were able to absorb by far the greatest amount of energy without serious failure. Probably, this can be related to their structural heterogeneity. In these thick samples, the mean free path of the vitreous phase would be small compared to the depth of the specimen; and their ability to absorb the energy of fine cracks produced under localized dynamic stress conditions would be enhanced by such a situation.

In the case of thick pre-stressed $VV_1$ samples, it is not hard to imagine how, under these stress conditions, initial localized forces around the point of impact could overtax the already strained interior. The result of course is a lower capacity to absorb energy under these conditions of testing — significantly lower even than the unstressed samples.

However, for the thin specimens from mould (B), the reverse was the case. Table XXXI shows how chemically pre-stressed test pieces of $VV_1$ (Series G) were much
tougher than the untreated Series E, and stronger than DAy₀ (Series H) at between the 99 per cent and the 99.9 per cent levels of confidence.

These facts demonstrate graphically just how the results from impact tests, particularly, rely on the state of stress produced.

The group of DAy₀ from mould (E) (Series H) tended to be tougher than the untreated Vv₁ groups from the same mould (Series E and F). But, this increased toughness was not highly significant. One might relate this finding to the thinness of these test pieces. All things being equal, there would be more chance of uninterrupted crack propagation from the lower surface through the vitreous matrix than for thicker samples.

For all the impact tests, the coefficients of variation ranged from eight to 33 per cent (Table XXXI).
CONCLUSIONS.

The method of testing impact strength that was devised proved to be of some value for modern dental porcelain. Its effectiveness can be gauged by the range of coefficients of variation recorded; viz., eight to 33 per cent. This was more than comparable with Haward's range of 38 to 53 per cent.

The ability of dispersion-strengthened porcelain, in thick cross section, to absorb energy was recorded in no uncertain manner — so too was the susceptibility of pre-stressed surfaces to chipping, under certain localized states of stress.

However, wherever the specimens all seemed to break at the lower surface under tension, chemically strengthened porcelain proved to be the toughest.
21.

DISCUSSION.

The crown is the form into which most dental porcelain is made in dental ceramic laboratories. The method developed in this work for duplicating the coronal shape appeared to be highly successful in that the reproducibility of these specimens, as assessed by firing shrinkage, weight, volume and apparent relative density, was as good, if not better, than that of other more simply shaped test pieces.

The firing shrinkage of these crowns was remarkably uniform. However, when one wishes to relate linear firing shrinkage of a porcelain to the linear firing shrinkage of these articles made from this porcelain, only some external coronal dimensions are applicable - certainly not the thickness of the crown. While I regard 11.7 ± 1.2 per cent to represent the true linear shrinkage of a material formed and fired into crowns, the thicknesses of these articles shrank roughly 25 per cent. Obviously, the volumetric firing shrinkage of about 34.0 ± 1.0 per cent could refer to the same material manufactured into any form, when all things were equal.

Hence, when talking of coronal linear firing shrinkage, one must specify to which dimensions he refers.
I believe such neglect has led to some little confusion in the past.

The study of the behaviour of modern dental porcelain in the coronal form provides us with information as to dimensional changes on firing and density, but it only complicates progress in the study of mechanical properties. For this reason simple, symmetrical specimen shapes were developed with the practical aspects of manipulation and application of these dental ceramic materials held in mind.

Although Sayre (1938), Skinner and Fitzgerald (1938) and Hodson (1959(a)) fired simple test pieces on platinum foil, this technique proved quite unsatisfactory. Firing on a pad of fine alumina prevented the excessive warpage that the restriction of platinum foil produced. All samples were of similar volume to one another and to the crowns. Under identical conditions the sintering behaviour of these specimens was indistinguishable from that of the coronal samples.

These test pieces provided various simple shapes that could be associated in a very general way with the coronal and other applications of dental porcelain. More than this, these different forms enabled me to examine the
effects that varying the relative dimensions of specimens has on the results.

In agreement with Hodson's (1959(b)) findings for low-fusing porcelains, most of the modern dental porcelains examined contained a very high proportion of glassy matrix. In the powders supplied by the manufacturers, this vitreous component was in the form of amorphous frit particles. Their sizes mostly ranged from two to 80 microns. The greatest range examined, and this was characteristic of one brand, extended from two to 150 microns.

Those materials which had a markedly lower proportion of vitreous phase contained large amounts of crystalline alumina deliberately added belatedly to the frits. Contrary to Hodson's descriptions, no crystalline feldspar or feldspathoid could be identified in any of these modern dental ceramic materials - nor was any mullite precipitation visible at the magnifications used.

Although Hodson (1959(b)) only found quartz present in small amounts in a wide range of materials, this was true merely for two of the non-aluminous porcelains examined. The other brands contained considerable quantities of quartz - comparable with that proportion shown in the classical whiteware.
Quartz and alumina grains were the only birefringent constituents. All the modern dental porcelains had been fritted and all must have had a very low kaolin content. The sizes of quartz grains mostly ranged from five to 50 microns, although the material with the largest frit particles also contained the largest quartz grains (95 microns). The sizes of alumina particles ranged from five to 35 microns in one brand and five to 40 microns in another.

Since greater homogeneity in any substance is conducive to translucency, it is not difficult to understand why the translucent materials tended to display a lower quartz content than the body types from the same brand.

Colouring of dental porcelain is done by a process of pigmentation; such a method is quite uncommon for vitreous materials. The optical properties of the matrix and the presence of voids and/or other light scattering phases undoubtedly affect the geometry of the whole pigmented system. In order to match a particular shade with two materials - one vacuum-fired and the other air-fired - it is quite likely that the types and amounts of pigment required could be somewhat different.
Pigment appeared in the powders supplied by the manufacturers either within some of the frit particles or free. The free pigment tended to flocculate and increase the size ranges of the ultimate working units of the pigment suspension in the sintered specimens. Not infrequently these flocculants partially enveloped frit particles or quartz grains.

Although each brand could be readily identified microscopically, sintered modern dental porcelains present a unique microstructure. Their closest relatives would probably be some of the industrial porcelain enamels. The importance of their major vitreous phases must be comprehended. For at least two brands, this groundmass represents a sodium-potassium aluminosilicate glass. Due to a high viscosity at their melting regions, pseudomorphic outlines of the frit particles are visible in some of the sintered materials. However, these become less distinct on further heating.

Low-pressure sintering proved to be extremely effective in limiting the porosity of sintered vitreous bodies. Voids were sparse and ranged from one to four microns in diameter. These were much smaller than those described by Vines et al (1958). They quoted an average
maximum diameter of 22 microns. Sintering the same material at atmospheric pressure resulted in a void size range of two to 20 microns. A larger range of two to 35 microns in diameter resulted for air-fired porcelains that were designed to be sintered in this fashion. Again, these values are much lower than that of 55 microns for the average maximum diameter quoted by Vines et al (1958). One can only assume that the pore configuration in the materials examined by these workers differed quite markedly from all the materials studied in this research.

Besides being more or less porous, the vitreous phase often appeared to have been disrupted in the regions close to quartz grains. Similar manifestations were not found around alumina grains in the aluminous materials. They occurred much more frequently in materials whose vitreous phases were extremely viscous at 573°C - or those whose transformation regions (temperature ranges at which the viscosity of the glass allows the rapid release of ordinary mechanical stresses to occur) were much above this temperature. The polymorphic transformation of quartz occurs at about 573°C.

We know alumina has a thermal coefficient of expansion and contraction much closer to that of a selected
338.

vitreous matrix than quartz. On cooling, alumina can fit the glass better and apparently does not crack the surrounding stiffening matrix. A more regular expansion in a glass-quartz composite could be effected by increasing the vitreous alkali content; but one still has to cope with the rapid crystalline inversions of quartz.

Although Clark (1935), Sayre (1944) and Hodson (1959(a)) have described gaseous evolution from feldspathic decomposition, such an occurrence appears to be related more to the older materials. Modern dental porcelains suffer very little visible change microscopically from overfiring. Pigment breakdown or solution and loss of shape of the ware seem to be the only detrimental changes and these can be readily detected by a cursory macroscopic examination.

Firing shrinkage, for a particular material, could not be affected greatly by the method of specimen formation. In an extreme situation, only about 2.5 per cent difference in linear shrinkage for length, and about 4.5 per cent for volumetric shrinkage was recorded.

All the materials showed a constant tendency towards a differential linear shrinkage under certain conditions; when all things were equal, air-firing
magnified this disparity. It appears that there is a direction of least resistance for shrinkage to take place. This, of course, can be associated with the natural cleavage characteristics of the materials and the preferential alignment of their particles. Particle shape - not size - was responsible for these observations. All porcelains examined showed this tendency; however, another factor was involved in the registration of a differential shrinkage - and that seemed to be the shape of the mould. Apparently, the shape of a particular mould can regulate or disturb the particle orientation during wet vibratory condensation of the slip. It seems that a cylindrical mould can give rise to a more haphazard particle packing than one that is rectangular. Naturally, this should be conducive to a higher volumetric firing shrinkage. Such was found to be the case.

For samples of one brand that had been well condensed into mould (A), different methods of densification during sintering did not separate the results for linear shrinkage of the length. This appeared to be the direction of least resistance for the firing shrinkage of these specimens. However, vacuum-sintering did produce greater shrinkages in breadth and height than sintering at atmospheric pressure.
For these reasons, when recording linear shrinkage one should always specify the measurements of the mould from which the test pieces were formed and to which dimension the shrinkage refers.

After the stage of sintering had been reached when the specimens had become impervious to water, at least for one brand, sintering time affected both linear and volumetric shrinkage imperceptibly. Only flow of the samples under their own weight, in the more prolonged firing schedules, tended to influence the differential linear shrinkage measurements.

Values for volumetric firing shrinkages of some materials were similar to those published by Skinner and Fitzgerald (1938), Moldal (1939), Sartori (1939) and Sacchi and Paffenbarger (1957). Of the vacuum-fired porcelains, the brand with the greatest particle size range shrank least. McLean and Hughes (1965) recorded that the porosity of "green" compacts of an aluminous porcelain averaged 43.8 per cent. This figure agrees very closely with the volumetric shrinkage registered in this research for two types of aluminous porcelain produced by the same manufacturer. However, these findings do not support McLean and Hughes' statement that the addition of alumina decreases
firing shrinkage. These particular materials had the highest shrinkages of the whole series. Absolute particle size and particle size distribution were unquestionably the cause.

Materials that were designed by the manufacturers for air-firing, when air-fired, showed comparable shrinkages to most of those designed for vacuum-firing, when they were vacuum-fired. Here again, the different particle size distributions can cause this apparent anomaly.

The method used to determine relative density in this research was quite sensitive; but, for a given material, only different sintering methods affected the result. This was the case regardless of the means used, otherwise, to condense the ware. Of course, samples that were poorly compacted had to shrink more to achieve a comparable fired density to others that were well condensed and fired in a similar fashion.

The inherent densities of the constituents of a porcelain proved to be much more important in governing its apparent relative density than the presence or absence of voids. Contrary to the reports of Sayre (1938) and Skinner and Fitzgerald (1938), the results in this work support Moldal's (1939) observations: different brands of
modern dental porcelain showed different apparent relative densities. The presence of alumina (3.96 gm./cm.³) affected the measurements greatly. Quartz (2.65 gm./cm.³), the densest form of silica, also influenced results when its proportion was changed. The amount the presence of different pigments affected the apparent relative density readings appeared to be overshadowed by more influential factors. This reduces Semmelman's (1957) statement, that the presence of different pigments can obscure the effects due to porosity, to relative insignificance.

Vacuum-sintering reduced the porosity of one brand of modern dental porcelain to about 1.3 per cent; air sintering the same material only increased its porosity by about two per cent. In a material that was designed to be air-fired, the extra sealed porosity incurred in the ware, when air-fired, measured about three per cent. But its powdered frit, as supplied, was not pore free and the total sealed porosity approached 4.8 per cent. These estimations were not greatly dissimilar from those published by Vines et al in 1958, viz., 0.08 per cent and 4.5 per cent porosity for vacuum-fired and air-fired porcelain.

When all things were equal, the extra porosity
eliminated by vacuum-sintering appeared to be about two to three per cent. However, this apparently small difference influences the optical properties dramatically.

Using the same porcelain, the manufacture of reproducibly dense samples did not pose a great problem.

If any criticism can be levelled at modern dental porcelains, it is their mechanical inadequacy in service. The tests for strength developed for this research were revealing and I believe in some way applicable to certain states of stress that might be encountered in practice. The mechanical behaviour of these materials was characteristic of that described for ordinary glasses. The effect of the most dangerous flaw in the stressed area seemed to be of prime importance; differing chemical compositions of the vitreous matrices became of minor interest when related to strength under these conditions.

These facts indicate very definitely that the major phase in modern dental porcelain would show the property of static fatigue; and it would be governed by the same agents which limit the practical strength of vitreous substances. Two additional factors complicate the picture - the presence of small spherical voids in varying numbers and microstresses or microcracks in the matrix associated with the quartz phase.
In contrast to Sayre’s (1938) propositions, specimen condensation during formation had no effect on strength, nor did sintering time when the surfaces were abraded.

The values for modulus of rupture calculated for some of the different materials were not unlike when derived from similar tests; but, when different rectangular moulds had been used to produce samples of the same porcelain, diverse values for the modulus of rupture were recorded. This finding can only be related to the surface area under tension during testing. It typifies the materials’ brittle behaviour. The importance of comparing only those calculated strengths derived from similarly shaped specimens cannot be overemphasized.

In agreement with Hodson (1959a) and McLean and Hughes (1965), strength appeared to be little affected by porosity. Although in all cases the air-fired results tended to be lower than the vacuum-fired, they were not significantly different. This refers to results from the dynamic tests as well as the static tests. These impact measurements do not support those published by Fox et al (1960) and Kulp et al (1961) indicating that vacuum-firing increases toughness considerably. Because every test for
strength that was used in this work failed to show a predictable difference in strength between samples that were air-fired and those that were vacuum-fired, it is hard to explain the claims made by the authors above.

A possible interpretation of the findings in this research is that microcracks are more dangerous flaws than voids. The microcracks around quartz could eclipse any weakening effect that internal voids produce. Air-fired samples were never really weaker than vacuum-fired materials that contained quartz. In fact, a very porous air-fired material that contained little macrocrystalline quartz and had a low softening temperature was stronger than other vacuum-fired materials under certain conditions. It was very interesting to find that its strength was comparable to that of the aluminous porcelains. The absence of microcracks appears to be more important than the absence of pores. This leads one to suspect that the extra strength shown by the aluminous materials, under certain conditions, was effected by the matrix-crystal fit - and not necessarily by the inherent strength of the dispersed phase itself. There was, in fact, a limitation of the flaws introduced by the aluminous dispersed phase when compared to quartz. Perhaps in association with this
is an increased modulus of elasticity of the composite suggested by Frey and McKenzie (1967). In agreement with Batchelor and Dinsdale (1960) an increased alumina content above about 25 per cent did not seem to influence the strength markedly.

When specimens from mould (A) were tested, all the aluminous materials were stronger than most of the quartz-bearing porcelains. However, when the same tests were carried out on mould (B) samples, these differences were reduced to tendencies. Apparently, under these conditions, the greater surface area under tension and the reduced thickness of the samples became even more important than other factors which increased measured strength under different circumstances of testing. These findings are very significant if such materials are to be employed in shell or wafer forms.

When surfaces were abraded, for a brand containing a considerable proportion of quartz, the rate of cooling these small samples had no great effect on the results; but fire-finishing and chill-tempering did increase the strengths for the samples from mould (A). Such strengthening could not be induced in the thinner mould (B) pieces. Apparently, preferential pre-stressing
by chill-tempering requires more thickness in the ware than that possessed by these thin, broad specimens.

For the same quartz-containing brand, surface etching did not increase the strengths of both sample types over abraded strengths. This might be related to a preferential etching determined by the microstresses or cracks in the glassy matrix around the quartz grains. Such a situation would tend to increase surface irregularity rather than reduce it.

When the surfaces of samples from both moulds were preferentially pre-stressed by ionic exchange, markedly increased values for the modulus of rupture resulted. In fact, both types of specimen produced comparable strengths — obviously due to some lessening of the dangerous effects of surface flaws. The compression at the surfaces would have to be overcome to allow a surface flaw to become dangerous. These experiments have proven Berenbaum and Brodie's (1959) theory to be correct (see p.282). When the surface layers were really modified, a greater effect on the calculated modulus of rupture was shown by the thin specimens. While chill-tempering was ineffective for these thin test pieces, chemical pre-stressing undoubtedly produced the desired effect. Indeed,
for the samples from mould (B), chemical strengthening an
abraded, quartz-bearing body was much more effective in
raising the modulus of rupture than replacing this material
with another that was dispersion-strengthened with 40 to 50
per cent alumina.

Information gained from the diametral compression
test only tended to reinforce what has been said so far.
The calculated modulus of rupture for the thick, abraded
specimens does not seem unrealistic when compared with
results from the indirect-tension tests. The maximum
tensile stresses acting across most of the loaded diameter
in these diametral specimens tends to increase the effect
of serious internal flaws on the results. It appears that
a material containing some very coarse quartz grains was
shown to be slightly weaker than the others embodying finer
quartz by this test for this very reason. No such
difference was recorded from bend tests on the same
materials. Here again, as for the bend tests on thin
samples, the increased strength displayed by an aluminous
material can only be described as a tendency. With a
constant tension over most of the diametral plane of these
specimens, not only would occasional serious flaws be more
often involved in this relatively large area, but the
probability of effective crack arrestment taking place over this plane of high tensile stress would tend to be reduced.

Major surface modification in the form of chemically pre-stressing these diametral specimens is apparently necessary to produce a small, but significant rise in strength.

While bend tests attempt to record the maximum tension at the convex surface of the beam at rupture, and the diametral compression test tries to assess the tensile strength of the material that is relatively unaffected by surface condition, dynamic testing introduces other factors which could be of practical importance. The values gained from the impact test devised show relatively little variation. This fact makes the test method all the more valuable. In agreement with Telfair and Nason (1945) it was found that different states of stress influenced the results markedly. Consequently, it is valid only to compare results derived from identical testing procedures.

Under conditions where a high local stress state was generated around the point of impact, aluminoous samples formed from mould (A) proved to be the toughest of all, by far. This supports McLean's (1965) claim that aluminoous porcelain has high impact resistance. But, it is only for
a particular situation. On thin samples, any increase in toughness over a non-aluminous material was reduced merely to a tendency again. The chances of uninterrupted crack propagation through the relatively flexible, thin specimens from their undersurfaces must be much greater than those from the upper surfaces of the relatively thick, inflexible samples under the extremely localized stress conditions encountered.

Chemically pre-stressing the surfaces of samples of a quartz-bearing porcelain formed from mould (B) increased their toughness a little, but it decreased the ability of mould (A) specimens of the same material to resist chipping. Under these circumstances of impact testing the localized high stresses probably pierced the thin stressed layer at the surface and very quickly overtaxed the interior which was already in tension. A finding that supports this idea is that untreated specimens of the same material from mould (A), proved to be tougher under exactly the same conditions of testing.

The fact that the energies absorbed by the pre-stressed samples of a material manufactured from moulds (A) and (B) before failure were remarkably similar is probably not just coincidental; particularly when untreated samples
of the same material from these two moulds were so different in this ability. A marked stiffening of the thinner specimens would have been produced by their surface modification. It could be that their form of fracture under these dynamic conditions was not dissimilar from the upper surface breakdown, characteristic of the thicker samples. Naturally, being thin, any failure would involve the lower surfaces. Undoubtedly, much would be gained from increasing the thickness of a pre-stressed surface along with the toughness of the interior.

The maximum strengths recorded for modern dental porcelains in this work are probably still not great enough to cope unfailingly with all the stresses involved in mastication; but they are a step in the right direction. More research is necessary to develop materials and techniques which might improve practical strength even further.

Under static conditions of stress, fatigue of the vitreous matrix of these materials must be a factor affecting their service. Hence, great value might be derived from investigating surface compression on experimental compositions. The degree of surface stress and the thickness of this modified layer could be determined. Perhaps more efficient immersion treatments could be evolved.
When potassium ions are replacing sodium ions at the surface, it would seem much more desirable to be working with a matrix consisting of a pure sodium aluminosilicate rather than a sodium-potassium aluminosilicate glass. The softening temperatures of this sodium aluminosilicate matrix would not need to be lowered; more effective diffusion takes place at higher temperatures and a pre-stressed surface only results when the viscous glass still allows little strain release to occur. A study of abrasion resistance of these compressed surface layers would be very profitable.

Since the effectiveness of stressing the exterior is limited by the internal strength, this aspect also requires further attention. Perhaps quartz should be removed entirely. It could be replaced with alumina in similar quantity, or some other thermally compatible material with a refractive index closer to that of the matrix. With a combination of a dispersion-strengthened body enveloped by a highly stressed surface much more desirable mechanical properties may be developed. All this might be done with relatively little effect on translucency.
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BIBLIOGRAPHY.


Boow, J. and Turner, W.E.S. -- The effect of annealing in a 
sulphur dioxide -- containing atmosphere on the 
modulus of rupture of sheet glass. J. Soc. Glass 

Bowden, F.P. and Field, J.E. -- The brittle fracture of 
solids by liquid impact, by solid impact, and by 

Bragg, W.L. -- Atomic arrangement in the silicates. Trans. 

Brannan, R.T. -- Further evidence against the orientation of 
structure in glass fibres. J. Amer. ceram. Soc., 

British standard 1902 : Part 1A : 1966. -- Methods of testing 
refractory materials. British Standards Institution, 
London.

Budnikov, P.P. and Gevorkyan, Kh.O. -- Role of feldspar in 
the formation of the structure of porcelain. 

Ass., 14: 8, 1459-1463 (Aug.) 1927.

Chiloote, J.H. -- The influence of composition of the feldspar 
constituent on the properties of a porcelain body. 


Felcher, F.R. -- Dental porcelain subject as seen from experimental laboratory. Dent. Cosmos, 76: 12, 1266-1270 (Dec.) 1934.


Gordon, J.E -- Some considerations in the design of engineering materials based on brittle solids.

Green, H. -- The physics of pigments in dispersed systems.


Hodson, J.T. -- A preliminary study of dental porcelains. 

Hodson, J.T. (a). -- Some physical properties of three dental 
Apr.) 1959.

Hodson, J.T. (b). -- Phase composition of crown and inlay 
porcelains. J. dent. Res., 38: 3, 483-490 (May-
June) 1959.

Hoffman, L.C. and Statton, W.O. -- Structure in vitreous 
silicates as shown by low-angle scattering of X-rays. 

Holland, A.J. and Turner, W.E.S. (a). -- The effect of width 
on the breaking strength of sheet glass. J. Soc. 

Holland, A.J. and Turner, W.E.S. (b). -- The breaking 
strength of glass. The effect of flaws and 
scratches. J. Soc. Glass Tech. Trans., 20: 
279-302, 1936.

Holland, A.J. and Turner, W.E.S. -- The effect of sustained 
loading on the breaking strength of sheet glass. 

Hughan, R.R. -- Ceramic behaviour of various types of silica. 
Clay Prod. J. Aust., 18: 8, 3-7 (June) 1951.


Kauzmann, W. — The nature of the glassy state and the
behaviour of liquids at low temperatures. Chem.

Kaye, G.W.C. and Laby, T.H. — Physical and chemical
constants and some mathematical functions. London,

Keller A. — see discussion Haward, R.N. and Mann, J. —

Kerper, M.J. and Scuderi, T.G. (a). — Modulus of rupture of
glass below room temperature. Bull. Amer. ceram.

Kerper, M.J. and Scuderi, T.G. (b). — Mechanical properties
of chemically strengthened glasses at high tempera-
tures. J. Amer. ceram. Soc., 49: 11, 613-618
(Nov.) 1966.

King, B.W. Jr. and Tesar, A.O. — Ceramic pigment patents.
Ceramic abstr., Patents, May, 1953 (p.87c).

Kingery, W.D. — Introduction to ceramics. New York, John

Kistler, S.S. — Stresses introduced into glass by replacing
alkali ions near the surface by other alkali ions
from a melt. Bull. Amer. ceram. Soc., 40: 4,


Murgatroyd, J.B. -- The testing of commercial glassware.


Murgatroyd, J.B. (a). -- The strength of glass fibres.


Murgatroyd, J.B. (b). -- The strength of glass fibres.


Murgatroyd, J.B. (d). -- Mechanism of brittle rupture.


Murgatroyd, J.B. and Sykes, R.F. (a). -- The delayed elastic effect in silicate glasses at room temperature.


Schiller, K.K. -- Strength of highly porous brittle materials.  

Schiller, K.K. -- Porosity and strength of brittle solids 
with particular reference to gypsum (Mechanical 
properties of non-metallic brittle materials. 

Schueller, K.H. -- Development of structure in porcelain: 
VI, chemical aspects and reactivity on the liquid 

Semmelman, J.O. -- A method of measuring porosity of 
(Dec.) 1957.

Seth, S.B. -- Evaluation of porcelain and acrylic as a 
replacement of natural teeth. Dent. Mag., Lond., 

Shand, E.B. (a). -- Experimental study of fracture of glass: 
I, the fracture process. J. Amer. ceram. Soc., 
37: 2, 52-60 (Feb.) 1954.

Shand, E.B. (b). -- Experimental study of fracture of glass: 
II, experimental data. J. Amer. ceram. Soc., 37: 
12, 559-572 (Dec.) 1954.

Shand, E.B. (a). -- Fracture velocity and fracture energy of 
glass in the fatigue range. J. Amer. ceram. Soc., 
44: 1, 21-26 (Jan.) 1961.


Smithsonian tables, compiled from various authors. —
Handbook of chemistry and physics. Cleveland,
Ohio, Chemical Rubber Publishing Co., 38th ed.,

Smothers, W.J. — Effect of water on mechanical strength of
selected ceramic compositions. J. Amer. ceram.

Smothers, W.J. — Strains created in quartz grains by
surface grinding of porcelain. J. Amer. ceram.

Stanworth, J.E. — Physical properties of glass. London,

Stevels, J.M. — Glass as a polymer. Ceramic Abstr.,

Stockdale, G.F., Tooley, F.V. and Ying, C.W. — Changes in
the tensile strength of glass caused by water
immersion treatment. J. Amer. ceram. Soc., 34:
4, 116-121 (Apr.) 1951.

Stuart, D.A. and Anderson, O.L. — Dependence of ultimate
strength of glass under constant load on temperature,
ambient atmosphere, and time. J. Amer. ceram. Soc.,
36: 12, 416-424 (Dec.) 1953.


