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MECHANISMS OF ATTACK ON GLASSES
IN AQUEOUS MEDIA

by

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INTRODUCTION

In studying the attack of any substance on a glass
surface, both physical and chemical processes are import-
ant. Electronic and thermodynamic principles are involved
and in part determine the extent to which the glass is at-
tacked. It is convenient, however, to treat the chemical
reactions separately from the physics of the attack. In
most instances one is able to do this with no loss in under-
standing.

Glass Structure

Before attempting to describe the chemical reactions
at the glass surface, it is necessary to know something of
the glass structure. At the present time the structure is
not well known and there is no theory which can explain all
physical properties of glass. There are two major theories,
broadly defined as the "crystallite" theory and the "random
network" theory.

The random network theory, whose major proponents are
American, was first introduced by Zachariasen in the early
thirties. Zachariasen's theory, as interpreted by Stevels,[1]
assumes a three dimensional network constructed from irre-
gularly arranged polyhedra, the corners of which are occu-
pied by oxygen ions. The centers of the polyhedra (tet ..

hedra or triangles) are occupied by multiplicharged ions
such as Si^{+4} or P^{+5}. These, together with the oxygen ions,
are the main constituents of the structure and are called
"network formers". The oxygen ions are bonded to the net-
work forming ions and are either "bridging" (bonding two
polyhedra to each other) or "non-bridging" which, as the
name implies, belong to only one polyhedra. Fig. 1 shows a
pure vitreous silicate structure having only bridging oxy-
gen ions, while Fig. 2 shows an alkali-silicate glass
having both bridging and non-bridging oxygen ions.

When there are non-bridging oxygens present there
will be an excess negative charge in the glass since these
oxygen ions are negatively charged. Electronic neutrality
is achieved by introduction of metal ions such as Na^+, K^+,
or Ca^{++} which are electrostatically attracted to positions
of electron excess and balance the negative charge on the
oxygen. Although these metal ions are not part of the main
network they do influence glass properties and are called
"network modifiers".

Comparing Figs. 1 and 2 it is seen that as the number
of non-bridging ions increases, the network becomes less
connected. The three dimensional network is periodically
broken, the interstitial positions become larger, and the
cations are more free to migrate in the glass. Properties
such as the thermal coefficient of expansion, electrical

conductivity and viscosity, which would be affected by the above structural changes, are found experimentally to vary with the content of non-bridging oxygen ions.[1] The thermal coefficient of expansion and electrical conductivity both increase with increasing non-bridging oxygen content while viscosity and melting point are found to decrease.

The random network theory, however, is not able to explain all properties of glass and many workers, mainly Russian, have proposed a theory which considers silicate glass to be an accumulation of submicro-crystalline formations of silicates and silica.[2] These formations are separated by amorphous regions where the degree of ordering decreases with increasing distance from the crystalline regions. The microcrystalline regions are not of a perfect crystalline structure, but are considered to be somewhat deformed while retaining the basic structure of a normal lattice.

Experimental support for the crystallite theory of glass structure is supplied by the abrupt changes found in the refractive index of many glasses.[2] This change, which occurs in specific temperature ranges, corresponds to certain heterogeneous transformations in crystalline silica. The crystallite theory also postulates a microheterogeneous structure for many glasses, the existence of which is verified by the following experiment described by Evstropyev.[2]

"If a plate of sodium borosilicate is bent and treated
with acid in that condition to leach out the sodium
borate component, and the bending stress is removed,
the plate resumes the form it had before the deforma-
tion and leaching. Therefore, the fundamental struc-
ture of the plate remained unchanged during the lea-
ching, and retained the deforming stresses. This ex-
periment provides direct proof of the independent exis-
tence of two structures in the glass: silica and sod-
ium borate."

The random network theory does not predict this phenomena

since formations of definite chemical compositions are ig-

nored. As noted by Holland,[3] however, when one considers the

crystallite theory he is speaking of crystal dimension of

only 10-20 $\overset{\circ}{A}$ and it is difficult when dealing with such

small entities to see where the concepts of an irregular

network and short range order begin to differ. On the basis

of X-ray diffraction data Warren,[4] calculates the Si-O bond

length to be 2.63 $\overset{\circ}{A}$ and the width of one tetrahedra is on

the order of 7 $\overset{\circ}{A}$. Using this fact, it would indeed be dif-

ficult to define a crystalline region of the glass only 10-

20 $\overset{\circ}{A}$ in width. Warren was not able to determine any

interatomic distances beyond the nearest neighbor distance,

a fact often cited as evidence for the random network theory.

The Boric Oxide Anomaly

It would be expected from the random network theory of

glass structure that SiO_2 would form a tetrahedral structure

in the vitreous state having an oxygen atom at each corner

connected to two tetrahedra giving rise to the random net-work. Using the same physical reasoning, one would expect that a boric oxide glass (B_2O_3) would have triangular co-ordination with boron in the center of a triangle formed by 3 oxygen atoms. Each would be bonded to two boron atoms again yielding a random network. (See $Fig. 3$)

It has been shown by X-ray diffraction of soda-boric oxide glasses that the length of the B-O bond increases with increasing soda content while that of Si-O bond remains con-stant. Using this fact, Warren[4] postulates that as Na_2O is introduced into the glass some of the boron will trans-form from triangular to tetrahedral co-ordination. The dual existence of boron in each structure is known as the boric oxide anomaly and is explained by Warren in the fol-lowing way. As the soda is added to the glass, the amount of oxygen is increased accordingly. The boron uses this oxygen to increase its co-ordination and transforms to the tetrahedral structure. This process continues until the composition of Na_2O reaches 13%.

There are two questions to be answered. First, why do the borons assume the tetrahedral co-ordination at small Na_2O content and secondly, why does the process stop at 13% Na_2O? Warren answers these questions on the basis of the number of non-bridging oxygen ions introduced into the glass by Na_2O. If all the boron were to remain in triangular co-

ordination there would be, upon the addition of Na_2O, two kinds of oxygen, bridging and non-bridging.

The sodium ions being positively charged will try to assume a position in which its charge will be balanced by non-bridging oxygens. At low soda content this is very hard to accomplish since the number of Na^+ ions and partially charged oxygens are small and are therefore widely separated. If as many as possible of the borons were to change to the tetrahedral structure there will be a four fold increase in the number of partially charged oxygens. In triangular co-ordination there would be a full negative charge on one non-bridging oxygen ion. After the transformation there will be 4 oxygens with partial charges. This is because each tri-valent cation B^{+3} has half interest in 4 doubly charged oxygens. With the increase in the number of unsaturated oxygens there is a greater opportunity for the sodium ion to become electrostatically neutral. The neutralized cation represents a lower energy state for the glass and the process is therefore favorable. When the soda content reaches a certain level there will be sufficient unsaturated ions to provide the necessary surroundings for the Na^+ and there is no further need for the transformation to take place. Warren calculates this concentration to be about 12.5% Na_2O.

There are aspects of the boron anomaly, as presented

by Warren, which are not satisfactorily explained and an alternate approach to this problem is suggested.

In a boric oxide glass containing no soda, all boron will be in triangular coordination. The electronic configuration will be as shown below.

In the above there are 3 sp^2 bonds, but if the boron can obtain one more excess charge, 4 sp^3 bonds may be formed leading to a rather stable tetrahedral structure. A rough estimate of the energy gain for such a transformation may be made by using the stretching force constant of the B-O bonds in both tetrahedral and triangular coordination. (7) In the triangular configuration the total bond energy would be the product of the number of bonds and the stretching force constant.

$$E = (3)(5.3)(const) = 15.9(const)$$

For the tetrahedral coordination the stretching force constant is 4.2(const) and the total energy is;

$$E = (4)(4.2)(const) = 16.8(const)$$

a total bond energy gain of .9(const) is seen to result from the transformation. It is therefore suggested that this is the main driving force for the transformation.

Warren's hypothesis neglects the influence of the boron and assumes the driving force to arise from the sodium ion trying to obtain its equilibrium coordination. It is

the contention of the authors, however, that because of its relatively low field strength (1.1 as compared to 75.0 for B^{+3}) the Na^+ ion will have a negligable effect on the co-ordination of the boron.

A second objection to Warren's explanation of the boron anomaly is the soda content given at which the trans-formation stops. This value of approximately 15 mole % soda has been questioned by several workers.(5,6). J. Krogh-Moe (5) states that there is no saturation of tetrahedrally coordinated boron in the range of 15-20 mole % alkali and that the limiting value is more nearly 33%. Using infrared spectoscopy Borrelli, et al. (6) have also shown that there is no saturation in the range of 15-20 mole %. However, certain property changes of alkali boric oxide glasses sug-gest a limiting value of alkali content. It is found, for instance, that if the volume of glass containing 1 mole of oxygen is plotted as a function of alkali content, the curve contains a minimum which may be associated with a maximum in BO_4^- tetrahedra.(7)

A plausible alternative as to the reason for this minimum is as follows. It is suggested that the limiting force prohibiting further coordination transformation originates from a volume consideration. In a pure boric oxide glass, which contains only B_2O_3 triangles, the

structure is rather loose since each triangle is connected along only 3 directions. The intersticial sites, which would be filled by a cation entering the glass, are large. When soda is introduced into the glass as many as possible of the boron change to the tetrahedral structure. In doing so the network becomes bonded in 4 directions and is more tightly knit. As more boron assumes the tetrahedral structure the intersticial sites become smaller. It is suggested that the limiting soda content would be that concentration at which the strain energy, caused by the sodium ion entering the intersticial sites is equal to the driving force for the transformation. (i.e. the gain in total bond energy on transforming to the tetrahedral structure.)

The reaction which now may take place is shown below.
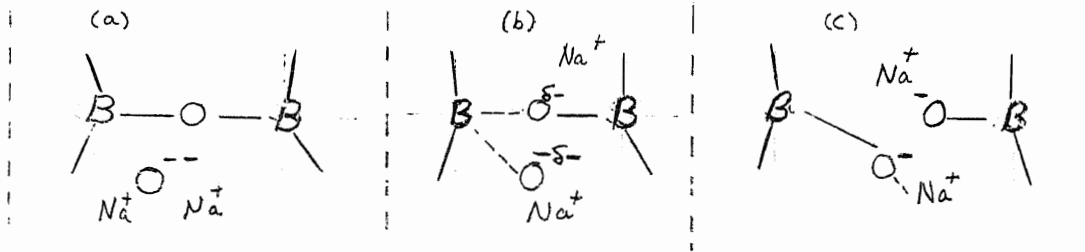
In the above reaction, which involves the replacement of an oxygen in one triangle by the oxygen introduced by the soda, and the formation of two non-bridging oxygen ions, the result is a "looser" boron network. Since the inter-sticial position would be too small to accommodate more Na^+ ions the favorable reaction is to break the B-O-B bond thereby increasing the size of the intersticial sites and providing suitable atmosphere for the Na^+ ions.

Experimental evidence supporting the above explanation is found in a paper by Krogh-Moe (7). In a plot of volume of glass containing 1 mole of oxygen (V_m) versus alkali content (x) the minimum in the curves were found at K = 4 mole %, Na = 17 mole % and Li = 30 mole %. This is to be expected since the ionic radii of K^+, Na^+, and Li are 1.33Å, .95Å and .60Å respectively. It is seen that the ion with the largest radius produces a minimum in the V_m vs x curve at the lowest mole concentration.

The above explanation also explains the fact that Aluminum, which is also trivalent, exists almost 100% in the tetrahedral structure. The B-O bond is much tighter than the Al bond and therefore the intersticial positions are smaller. It is therefore easier for the alkali ions to enter an intersticial position in a glass with high aluminum content.

It should be noted that there are many conflicting theories used to describe the boron anomaly, and there is also much conflicting data. A complete understanding of the problem will necessitate more reliable experimental techniques in measuring the limiting fraction of boron tetrahedra. As yet the methods used are not well understood (6) and the results must therefore be carefully screened. It should also be apparent that quantum as well as classical mechanics should be applied to the problem

since purely classical mechanical approaches have failed to explain the phenomena completely.

Surface Structure and Inhomogenities

Although Zacharesen's theory works well in most cases, there is evidence that it does not truly represent the surface structure of many glasses. Hensley[8], found that in "Pyrex" and some soft glasses, there are no polyvalent metal ions at the surface. Yates and Tribilcock (9) propose that a completely random distribution of the metal ions is not one which leads to a minimum in surface energy and therefore certain components will tend to reside away from the surface layer. Magnesium ions have a small radius and are doubly charged. These ions therefore have a high force field and would be a high surface energy constituent. Other cations having high force fields are Li^+ and Ca^{++}. Sodium ions on the other hand are singly charged and have a radius comparable to that of calcium, and therefore have a relatively low force field.

The authors of this paper have reported in a separate report (10) on the absence of Ca^{++} ions in the surface structure of "E" glass. It is believed that in this glass any non-bridging oxygen ions at the surface are balanced by low surface energy cations such as sodium and that the calcium tends to reside away from the surface. It is also

found that in many glasses volatilization of certain con-
stituents from the surface can create a surface structure
quite different from that of the bulk, and in some cases
can cause devitrification of a surface layer. (11)

Other inhomogenities found in glass are stones,
bubbles and cords. (12) Stones, unmelted silicons, occur
very rarely and are of little importance in this work.
Bubbles may be in the batch by air or water vapor. Cords
are regions where one or more components are segregated.
These regions may appear because of a nonhomogeneous batch,
non uniform melting of various constituents in the batch,
and because of certain reactions at the surface of the
glass such as volatilization of certain constituents.

Phase separation may occur to an appreciable extent
in many glasses. W. Vogel (2) states that when a liquid
glass melt is cooled, the same forces which cause crystal-
lization in metals cause aggregation of like atoms or atomic
groups in the glass. He states that if the cations in the
glass have only a slight field strength, there is little
aggregation and the glass is best described by the random
network theory. On the other hand, cations with high field
strengths have a high rate of ordering and there may be
formation of crystallites in a cell like region of high
cation content. Electron micrographs are used as evidence.

It would be expected that phase separation would lead to preferential chemical attack on the glass structure. Evidence that this is indeed the case is provided in a later section of this report. A more detailed analysis of the reasons for phase separation will also be given.

Electronegativity Effects

In considering the glass structure as proposed by Zachariasen it must be remembered that the bonding between the network formers and oxygen ions is not completely co-valent. This is of extreme importance when considering mechanisms of attack on glass. Since oxygen has a greater electronegativity (EN) than does silicon or boron, the probability of finding the shared electron around the oxygen ion is greater than that around the network former. Consequently, the oxygen will behave as a center of negative charge and there will be an effective positive charge associated with the network formers. Table 2 contains the electronegativities of the elements of interest. It is seen from the table that Al, a network former, has a relatively low EN and it would be expected that the aluminum sites in the glass would be centers of attack by bases while they would be most stable under acid attack. Boron has an EN comparable to that of oxygen and one would expect a boric oxide glass to be more stable under attack by bases than

glasses containing either Al or Si. This is not the case however. The electronegativities of the glass constituents provide a starting point upon which the theories of aqueous attack may be based, but for many glasses, especially those containing trivalent ions such a boron and aluminum, one must take care not to give too much importance to the electronegativities. Glasses containing trivalent network formers will be discussed more fully in a later section of this report.

Mechanisms of Attack

One of the best theoretical treatments of chemical attack on silicate glass is given by Budd.[13] The author classifies attacking reagents in two groups. Electrophillic reagents are those which seek to attack positions of excess electrons and nucleophillic reagents seek regions of an electron deficit. Examples of each type are given below:

O^{-2} - strongly nucleophilic

OH^- - strongly nucleophilic

F^- - moderately nucleophilic

H^+ - strongly electrophilic

It would be expected that OH^- and O^{--} would attack the Si-O-Si bond since, due to the electronegativity difference, the electrons are still more tightly bonded to the oxygen leaving the Si with an effective positive charge,

which is then a center of nucleophilic attack. The network
modifiers, although they do not take part in a chemical re-
action, are affected by the attack. Due to the presence of
OH^- and O^{--} a negative charge is built up at the surface.
Cations such as Na^+, K^+, or Ca^{++} may migrate to the surface
in order to balance the negative charge and thus lower the
surface energy. At the surface these ions may take part in
an ion exchange process with H^+ ions. Metal ions enter the
solution and the H^+ enter the glass to preserve electronic
neutrality. Which cations migrate depends on the magnitude
of the electrostatic interaction between them and the non-
bridging ions, and on the size of the cations.[14]

At this point it would be instructive to give specific
examples of these mechanisms. The following examples are
taken from Budd's work, and are applicable to most silicate
glasses.[13]

1. Electrophilic attack on non-bridging oxygen ions:
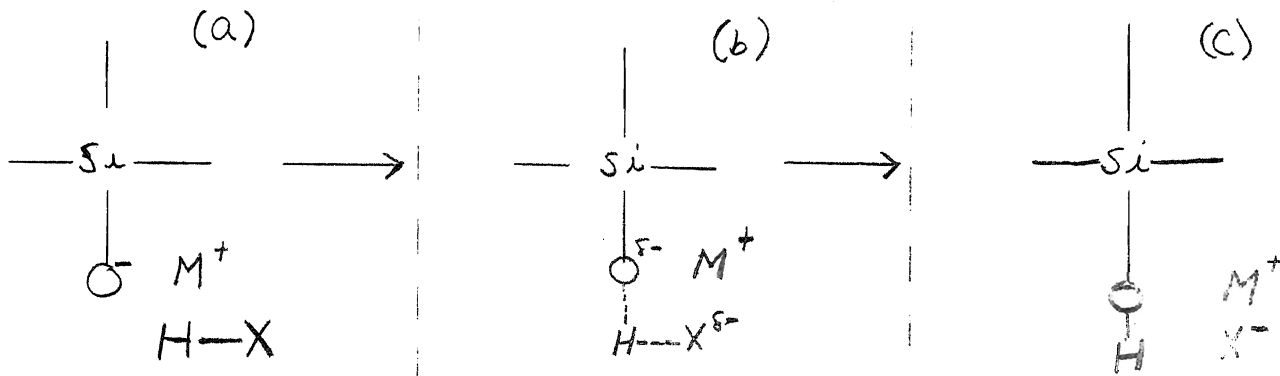
In the above reaction the following mechanism governs.
Initially there is an electrostatic attraction between the O
and M^+ ions. When H-X is introduced it becomes partially

bonded to the O⁻ ion, the negative charge of the O⁻ being shared with the X⁻ ion as shown in the second step. Finally the H⁺ will be completely bonded to the O⁻ and the X⁻ ion will be left with a minus charge. The metal ion M⁺ will seek a new position since there is no longer a need for it to balance the O⁻ charge. This new position may be in the solution or as a latice ion in the crystal MX.

2. N cleophilic attack on silicon atoms:

(a). Attack by O⁻⁻ of -metal oxides-
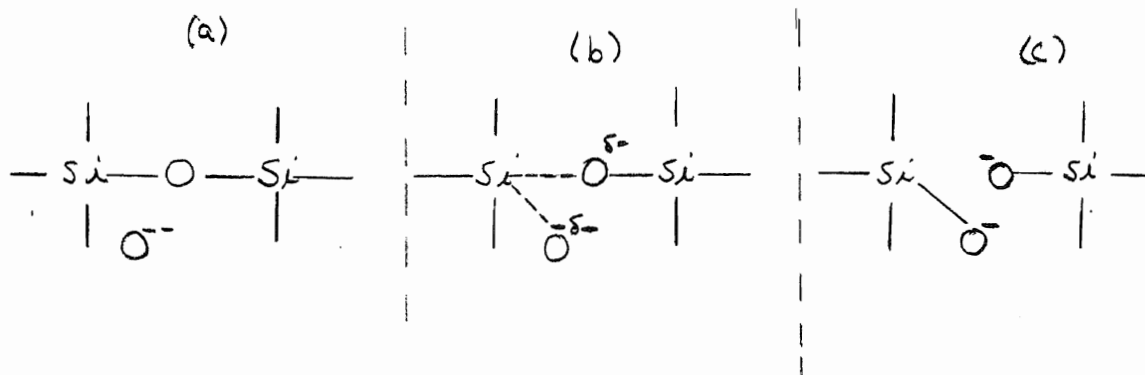
In the above example, the doubly charged ion will be electrostatically attracted to the positively charged region around the silicon. Silicon will react with this doubly charged oxygen with the result that the Si-O-Si bond is split with the O⁻⁻ ion replacing the O in one tetrahedra. The final result is a fractured network with two non-bridging oxygen ions, each of a single negative charge. Cations may now enter the glass to preserve electronic neutrality by residing in the region of these non-bridging ions. The above reaction may be considered as what happens when a metal oxide dissolves in the glass during its formation.

(b). Attack by OH⁻ ions:
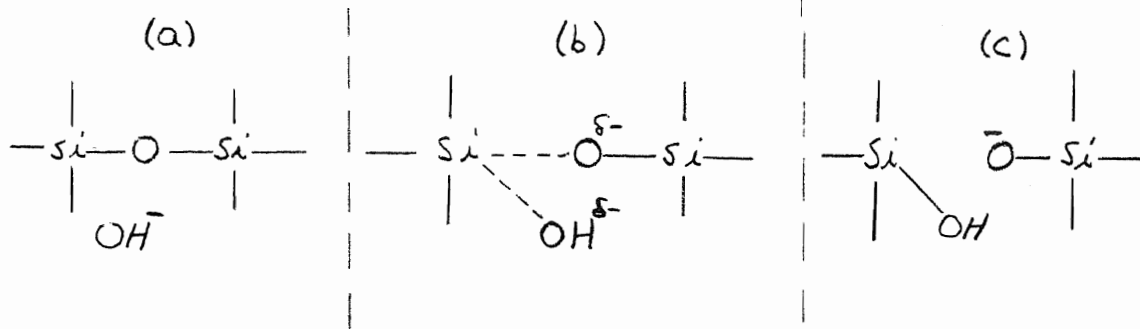
Here again the OH⁻ ion being strongly nucleophilic is attracted to the positively charged region about the silicon. The OH⁻ reacts with the silicon and replaces the bridging oxygen. The result is again a fractured network with one silicon forming a Si-OH, group and the other tetrahedra having a non-bridging oxygen ion. Electronic neutrality may be achieved by two possible mechanisms.

I. M^+ may diffuse into the glass.

II. Electrophilic attack on the non-bridging oxygen may take place by $(H_3O)^+$ which leads to the regeneration of an OH⁻ ion. In this way, the process is continuous with the OH⁻ ion serving as a catalyst for the attack of H_2O on the network.

(c). Attack by H_2O
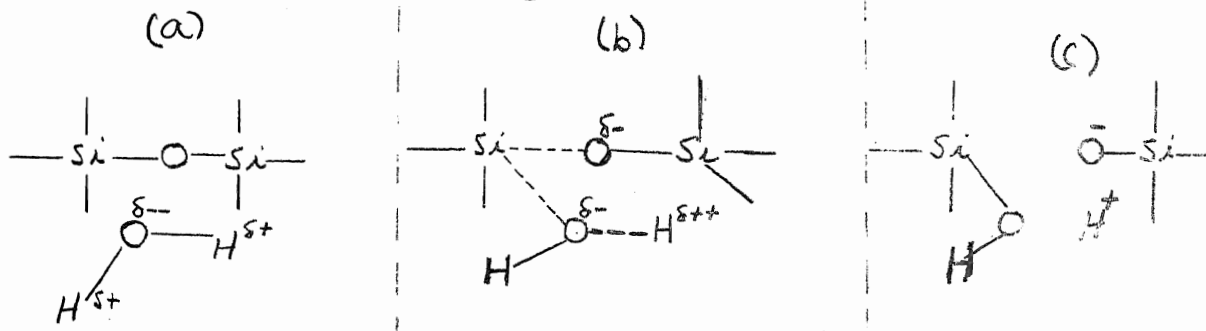
H_2O is a weak nucleophile since there is only a partial charge on the oxygen and hydrogen atoms. Due to the EN difference, however, the oxygen has an effective negative charge and therefore will be weakly attracted to the silicon sites. As it becomes more closely united with the silicon one of the hydrogens will be ionized leaving a hydroxyl ion which splits the network and replaces one oxygen leaving one silicon tetrahedron with a non-bridging ion.

The discussion given above has been concerned with an idealized silicate glass and reagents. Such things as an inhomogenous structure, surface irregularities, and some special reagents will necessitate modifying or adding to the theory. Molchanov and Pukkisko for example,[15] list hydroxide solutions in the order of decreasing destructive action as $NaOH > KOH > NH_4OH > Ba(OH)_2 > H_2O > Ca(OH)_2$. This does not agree with the expected order based on disassociation constants. One would expect to find $Ca(OH)_2$ above H_2O, a weak nucleophile which has limited disassociation. The action of calcium hydroxide is weak because a secondary reaction, involving the formation of insoluble calcium silicate, retards the attack by forming a protective coating.

Some special reagents are able to attack a glass to a much greater extent than one would expect. Hydrofloric

acid, for example, attacks silicate glass much more strongly
than HCL even though both are completely disassociated in an
H_2O solution. The mechanism for the attack is basically the
same as in the other cases. H^+ attacks the non-bridging
oxygens to form the silanol group, but in this case the re-
action rate is increased due to the simultaneous attack of
the F^- ion on the silicate structure as shown below. (13)
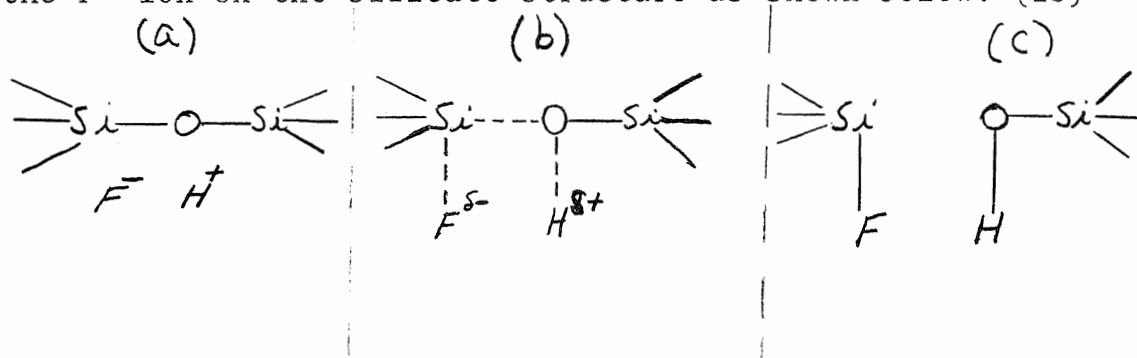
The fluorine atom, since its EN is greater than that
of oxygen, is able to replace the oxygen in one silicate
tetrahedra. The Si-O-Si bond, thus broken, leaves a non-
bridging oxygen ion which in turn is attacked by the H^+ ions.

Physical Aspects of Attack

The effects of heating a glass in the attacking so-
lution is well known. Boiling the attacking reagent is
widely used as a method of accelerating the attack. Not
only does the solution usually disassociate to a greater
extent, but the glass network opens considerably, which
allows the cations to migrate quite freely in the glass. (14)
One further physical effect which deserves attention is that
of preferential attack at surface irregularities such as

non-homogeneous regions and stress raisers (microcracks, fracture steps, bubbles). Tichane and Carrier (16) have shown by election microscopy that a weathered soda-lime glass surface becomes almost completely smooth, at a magnification of 80,000X, under the action of HF and H_2O. Nitric and phosphoric acids also produce a clean, smooth surface. The glass may not have appeared smooth on the macroscopic scale, but any microscopic irregularity has been removed or smoothed by the action of the reagent.

The mechanism of this attack was not given by the above authors, but it is clear that around any surface irregularities there will be a stress concentration. Any reaction which decreases the stress in these regions would be favorable. Chemical attack is such a reaction. By dissolving the glass at such positions the stress becomes more uniform. The attack also takes place at all other regions, but since the glass is highly stressed in these irregularities, it has a weakened network which is more susceptible to attack. The final result of the preferential attack is a rounding of points and depressions, yielding a smooth surface.

Regions of non-homogeneous composition such as those given by Vogal,[2] may be preferentially attacked or left unaffected. If a silicate glass, with Na_2O, has alternating regions of high silicon content and high soda content one would expect the regions of high SiO_2 to be relatively un-

affected under acid attack while the Na_2O rich regions, due
to the high proportion of non-bridging oxygen ions, would
be preferentially dissolved. The mechanism of ion exchange
would also operate in these regions. The glass would show
pits where Na_2O was concentrated and very little attack in
regions of high SiO_2 content.

Rate Laws

In most cases when dealing with glass corrosion one
is interested in weight loss per unit time or the variation
of some other quantity with time. Such values give a good
indication of the ability of the glass to resist attack. The
attack described in the preceding sections are generally
found to be governed by one of two time laws. (13) In acid
and neutral solutions the rate of attack is found experimen-
tally to be a diffusion controlled process. In soda-lime glass
specifically, the diffusion of Na^+ ions is found to be the
controlling factor. In alkaline solutions, which attack
and degrade the complete network, a linear time dependence
is found. Specific examples of these time laws and others
are given by Holland. (3) Of course, there are many var-
iables which may affect the rate of attack such as temper-
ature, surface films, and the inital state of the glass
surface. However, a treatment of all possible deviations
from the basic time laws is beyond the scope of this paper

and only the more general findings will be listed.

The attack of alkali glass by water is attributed to an ion exchange mechanism in which hydrogen ions diffuse into the glass from the solution in order to maintain electronic neutrality as sodium ions diffuse out. (3) A parabolic rate law is obtained for this process when one assumes the reaction to be governed by the diffusion of sodium ions to the surface. Allowance must be made, however, for the initial state of the surface. In freshly formed glass, for instance, the alkali content at the surface is higher at the surface than in the bulk while on a weathered surface the surface would have a lower alkali content. As noted by Oldfield and Wright [11] volatilization of the alkali may also take place which would tend to deplete the surface layer of these ions.

It was stated earlier that the rate of alkaline attack is linear in time. It is found, however, that the surface conditions may also affect this rate of attack. [3] If powdered glass is subjected to alkaline attack the rate of attack is parabolic if the alkalinity of the reagent is not controlled, whereas when the reagent is continually changed, the rate of attack is linear. It was established that due to the large surface to weight ratio of the powder a large amount of silica and other components were dissolved leading to a greatly reduced attacking power of the reagent.

It has been shown (3) that the attack of a glass

surface follows the Arrhenius relation since activation of
sodium diffusion or a surface reaction is activated. The
velocity of this attack may be written as:

$$\log_{10} V = - \frac{E}{2,303RT} + C$$

Where V is the velocity of attack, C is a constant, E is the
activation energy (cal/g-mol), R is the gas constant (cal/deg-
g-mol), and T is the absolute temperature. Alkaline attack
which is not controlled by diffusion is found to follow this
relationship, showing a linear plot of log V vs 1/T. The
slopes of the plots are found to vary among different glasses,
however, which implies that in some glasses the rate of attack
may vary to such an extent with temperature that observations
made at high temperatures may not be valid when generalizing
the results to lower temperatures. When comparing the dur-
abilities of glasses on the basis of high temperature data
this may be of considerable importance since the glasses
which are highly attacked at high temperatures may well be
more duable under normal operating temperatures.

EXPERIMENTAL ANALYSIS

Techniques

Experimental determination of the attack of aqueous
solutions on glass was accomplished through the use of the

the electron microscope. Freshly fractured surfaces of E
and 994 plate glasses were boiled in a refluxer for a period
of 24 hours. The solutions used in the treatment were buf-
fered with pH values ranging in steps of one from 2 to 11.
Treatments with .1N solutions of NaOH and HCl were also made
to determine the limiting cases of the attack. The use of
freshly fractured glass permitted observation of a surface
free of scratches and weathering effects and the buffered
solutions minimized the effects of the dissolved glass con-
stituents on the attack. In unbuffered solutions it is found
that the attack may be accelerated by ions from the glass
entering the attacking solution, and raising the pH of the
solution. It was found that using the buffered solutions
kept the pH within .4pH units of the inital value.

In order to identify specific regions of the glass
surface a grid was scratched on the surface with a diamond
point. The matrix elements formed by this grid were identified
by numbers which allowed comparison of each region before
and after treatment.

Since the glass samples were too thick to observe
directly in the microscope a double replication technique (17)
was employed which produced an exact replica of the glass
surface. A primary replica was made by coating the grided
surface with a thin layer of 10% parlodian in amyl acetate.
After drying this layer, it was stripped from the glass

and a replica of the parlodian was made. This was done under vacuum by, first, evaporation of Ge at an angle of 20°, then a 90° evaporation of carbon. The purpose of the Ge was to produce contrast on the replica which could not be achieved by a single carbon evaporation. Fig. 4 illustrates the end result of the Ge "shadowing." The primary replica which now had the C - Ge film on it was cut into sections corresponding to the inscribed grid and each section was placed on a 300 mesh Cu grid. Acetone was employed to dissolve the primary replica leaving a very thin C - Ge film on the specimen grid. These specimens represented the actual surface of the glass as one would see it looking through a conventional microscope. Depressions on the glass surface would appear as depressions and rises would appear as rises.

When the parlodian was completely dissolved the Cu grids were placed in the electron microscope and micrographs were taken of each glass sample before and after treatment. Figs. 5 and 6 show micrographs of typical regions of E and 994 glasses. The surface appears very smooth at this magnification. The texture of both glasses are similar though that of 994 glass appears to be a little rougher. Fig. 7, also showing an untreated fracture surface of E glass, reveals a different type of fracture which leaves a very rough surface containing fracture steps, ridges, and depressions. With the exception of a few cases these regions were not used in

the analysis of the attack. It was found that due to the gross features of such regions, no meaningful conclusions could be reached regarding the attack. Only regions whose untreated surface was similar to those of Fig. 5 and 6 were used. It must be noted that Fig. 5 and 6 are shown at 8600X while those of the treated surface are shown at 5500X. The higher magnification used on the untreated sample was necessary to show the texture of the fracture surface. Since the attacked surface had much more detail, the features could easily be picked up at 5500X.

Results

pH 2 - Treatment of E glass with a pH 2 oxalic acid buffer solution yielded the formation of a calcium silicate film on the fracture surface. Replication of the surface was rendered impossible by this film since the film was very thick and covered the glass surface. The formation of this film is treated separately by the authors and the findings are reported in a separate paper. (10)

No film was observed on 994 glass at pH 2 and replication was possible. Micrographs of this glass are shown in Fig. 8 and 9. These micrographs clearly show the effect of the treatment. Even at 5500X the surface appears much rougher than that of the untreated glass. Phase separation and preferential attack are also observed on the glass.

pH 3 - E glass treated in a pH 3 buffer solution is shown in Fig 10. Comparison with the untreated glass surface of Fig. 5 reveals a highly attacked surface. The attack appears quite uniform and there is no evidence of phase separation. 994 glass shown in Fig. 11 is also seen to have a roughened surface similar to that treated at pH 2. Again a region of phase separation is shown and the difference in attack on the two phases is evident. The texture of the 994 glass appears to be finer than that of E glass and it would appear that this glass is attacked somewhat less than E glass.

pH 4 - E glass treated at pH 4 is shown in Figs. 12 and 13. Fig. 12 shows the basic texture of the glass while Fig. 13 shows a region where some pitting has occured, preferentially dissolving some components or imperfection of the glass. The background texture of the pitted region is seen to be the same as that of Fig. 9. Figs. 14 and 15 show micrographs of the 994 glass surface. Fig. 14 is most typical of the glass treated at this pH while Fig. 15 again reveals phase separation. In the region of phase separation, the background texture of the glass appears to be much more highly attacked than that of fig. 14 while the small circular regions are attacked to about the same extent. This would imply that these regions are more nearly of the same composition and structure of the bulk glass than is the background structure.

pH 5 - E glass treated in a pH buffered solution is shown in

Fig. 16. The attack is seen to be much more uniform. Although there are some regions of preferential attack, pitting has not occured to a great extent. Comparing Figs. 13 and 14 with Fig. 16, a slight change is seen in the texture. The pH 4 treated glass has a somewhat finer texture than that treated at pH 5, although the glass treated at pH 5 has a more continuous, smoother appearance. A plausible explanation for this will be given in a later section. A similar trend to a smoother texture, but more highly attacked glass is found in 994 glass treated at pH 5. Fig. 17 shows a micrograph of this glass which is typical of the surface resulting from the pH 5 treatment. Fig. 18 shows a region of phase separation and again the texture of the separated phase is seen to be much finer, being almost like that of the untreated glass. In this case, however, the phase separation was very localized and does not seem to affect the attack in the surrounding regions. It is suspected that if the phase separation had occured over a wider area, the attack would have been affected similar to that at pH 4.

pH 6 - E glass treated at pH 6 is shown in Figs. 19 and 20. An isolated region of non uniform fracture is shown which is probably due to phase separation. The attack differs from that seen in Fig. 20 but within this region there is no difference in attack. Fig 20 shows a more typical region of very uniform and very little attack. There is no evidence of

preferential dissolution of alkali or any other constituent in this region.

Figs. 21 and 22 show typical regions of 994 glass treated at pH 6. The effect of phase separation is clearly visible in Fig. 21. In the phase separated region the surface is quite rough while in the region adjacent to it the glass appears very uniform and smooth. Fig. 22 shows a more typical region of the attack. The surface is like that seen at pH 5 possibly showing a more preferential dissolution of one constituent which would lead to the type of surface observed.

pH 7 - A slight change in the type of attack observed occurs at pH 7. Areas are observed in which the surface, while not like that of the untreated glass, is still very smooth and uniform. In other regions the attack still resembles that observed at lower pH values. Figs. 23, 24, and 25 clearly show this. The texture of the E glass of Fig. 23 is seen to be quite smooth. The attack has not progressed very far and has been very unifrom. A different section of the same glass is shown in Figs. 24 and 25. Fig. 24 is a transition zone where the background texture is similar to that of Fig. 23 but there are many more gross features caused by dissolution of the glass. Fig. 22 shows an area of uniform attack which appears much like that of the glasses treated at pH 5.

994 glass exhibits the same phenomena. Fig. 26 shows

a region of very uniform texture which appears to be some-
what like those observed at lower pH values. Other areas are
similar in appearance to Fig. 27 which shows a mixture of
roughened, pitted areas and smooth areas. In both glasses
the general appearance is one of varied attack with very
smooth areas intermingled with areas of very tiny pits from
which some component was preferentially dissolved. The pits
appear to be much larger in 994 glass.

pH 8 - The texture of both glasses at pH 8 has become quite
smooth. E glass as shown in Fig. 28 is very smooth. The
texture is quite unlike that of the glass treated at acidic
pH values. The microstructure is seen to consist of rounded
points rather than the intensely leached surface observed
at the lower pH values. The only pitting observed occurred
in the regions whose untreated surface is similar to that of
Fig. 7. (See Fig. 29) Even here, however, the basic struc-
ture is smooth and attack quite uniform. This is also true
of 994 glass treated with the pH 8 solution. Fig. 30 shows
the most typical area observed. The surface appears very
smooth and no preferential attack has occured. Fig. 31,
however, does show a rough surface. Here again, however,
the untreated glass surface was similar to that of Fig. 7.

pH 9 - At pH 9 the attack on E glass is about the same as
at pH 8. Fig. 32 shows the texture of the glass surface to
be very smooth. The very small features are rounded and

appear to be the result of very uniform dissolution. There
is evidence of some preferential attack, however, as shown
by the large circular features in the micrograph. These
were not present in the untreated glass and must be considered
a result of the attack. It should also be noted, as further
evidence, that circular regions of this type were not ob-
served at any lower pH values. Many of the regions blend
into one another, but some of them have distinct boundaries
which appear to have been preferentially dissolved. There
is, however, no noticable difference in the texture of these
regions, which would indicate that they are either of the same
composition or are attacked in about the same manner. It
may be that the boundaries are of a different composition.

The circular regions appearing on E glass are not
observed on the 994 glass. In this glass there is a rather
wide range of attack. Some regions appear almost featureless
while others exhibit the type of attack resembling that seen
at pH 7. At this pH, however, there is practically no
pitting and there is none of the type observed at lower
pH values. Fig. 33 shows a micrograph of a typical region
of 994 glass. The attack has proceeded in such a way as to
remove layers at a time. The textures of the two layers
are about the same. Fig. 34 shows a region of slight phase
separation. There is some effect of the phase separation on
the attack although it is difficult to determine whether

the small features surrounding the phase separated areas are pits or simply smaller phase separated regions.

pH 10 - There is a decided difference in E and 994 glass at pH 10. In all cases at this pH value the texture of E glass is very smooth. There are a few cases noted of preferential dissolution, but this is very localized. Fig. 35 shows such an area. The background texture of this area is typical of the glass. The first example of definite phase separation in E glass is seen in Fig. 36. An earlier example of possible phase separation was given, but it was not possible to make a definite conclusion. In this case the existence of two distinct phases is obvious. Dendritic growth of one or more components is observed in this region. It should be added that this was rather localized and was not seen on other regions of the glass. The attack is not affected at all by the phase separation in this case.

The surface of 994 glass subjected to the pH 10 solution is quite different from that of E glass. Although there are a few small areas which are very smooth, the most typical regions are those shown in Figs. 36 and 37. Fig. 36 shows some small areas which are very smooth. There is clearly some preferential attack as evidenced by the pitting which has occurred. Fig. 37 shows a very uniform region where the attack has dissolved away all components of the glass to about the same extent. It should be noted that the pref-

erentially attacked regions of Fig. 36 are more like the
region seen in Fig. 37 than are the smooth areas. Although
no micrographs are shown, phase separation was also observed
in the 994 glass and the attack was affected in exactly the
way observed at pH 9.

pH 11 - E glass treated at pH 11 differs strongly from 994
glass in the attack. E glass surfaces treated at this pH
were nearly featureless resembling the untreated E glass.
(See Fig. 38) There are a few regions which are pitted pref-
erentially, but could not be called typical of the glass.

Micrographs of 994 glass treated at pH 11 are shown
in Figs. 39 and 40. The surface features are very gross in
both cases, but are uniformly attached. The surface texture
is almost destroyed in some regions, as evidenced by Fig. 39,
while other regions retain a rather fine texture. Fig. 40
resembles those micrographs taken at pH 7 in that the
attack seems to have progressed by dissolution of complete
layers of the glass.

DISCUSSION

Before discussing the results obtained it is necessary
to recall a few facts about the structure of the specific
glasses we are using. Both 994 glass and E glass have tri-
valent network formers, Al in 994 glass, Al and B in E glass.
Al normally has the tetrahedral coordination in the vitreous
state and Boron may assume both triangular and tetrahedral

coordination. Since their ions are trivalent, there will be
an excess negative charge associated with each tetrahedron
which is balanced in 994 glass with Mg^{++} ions and in E glass
with Ca^{++}, Na^{+}, and Mg^{++} ions. Si^{+4} is capable of forming
covalent bonds with 4 oxygens with no resulting negative
charge on the tetrahedra, and therefore no metal ion is
found around the silicate tetrahedra unless a non-bridging
oxygen is present. It would therefore be expected that the
silicate network, because of a small non-bridging oxygen ion
content would be relatively uneffected under acidic attack,
while the boron and aluminum tetrahedra will be effected by
dissolution of the metal ions.

Another factor associated with the fact that Al and B
may be tetrahedrally coordinated is the degree of ionicity of
the Al-O and B-O bonds. Because of electronegativity dif-
ferences the Al-O bond is normally quite ionic in nature. Al
has an effective positive charge associated with it and the
oxygen ion an effective negative charge even in triangular
coordination. When Al and B become tetrahedrally coordinated
the energy per bond decreases although the total bond energy,
determined in a previous section of this paper, increases.
The degree of ionicity of each bond also increases since
the trivalent Al and B now must share 4 oxygen ions. Each
Al-O and B-O bond will therefore be more ionic in nature
with the electrons spending more time in the oxygen orbitals,

with the result being that each oxygen has a greater effective
negative charge than in triangular coordination.(18) This
can be of importance at acidic pH values. In silicate
tetrahedra the Si-O-Si bonds are stable and H^+ ions do not
significantly attack these bonds. In the Al tetrahedra,
however, where the Al-O-Al bonds are weakened and quite
ionic, H^+ ions will have an increased effect. Since the
hydrogen ion is a strong electrophile it will be attracted
to the partially charged oxygens of the Al tetrahedra, and
by electrophilic attack on the bridging oxygens the alum-
inum network may be broken. The reaction for this is shown
below.

(a) $-Al-O-Al-$ with H^+ below the Al

(b) $-Al\cdots O^{\delta-}-Al-$ with $H^{\delta+}$ below the O

(c) $-Al \quad O-Al-$ with H below the O
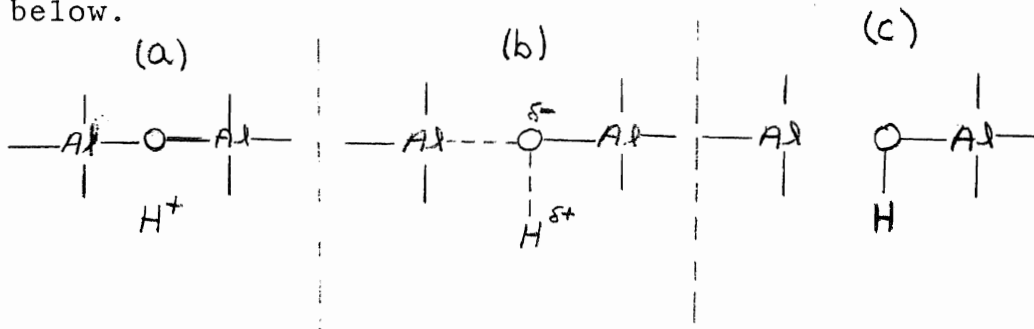
It should be noted from the above reaction that since
Al is trivalent there is no need for an OH^- ion to bond to
the, now triangularly coordinated, Al ion. If the bond
being attacked were the Al-O-Si bond the following reaction
would govern.

(a) $-Al-O-Si-$ with H^+ below the O

(b) $-Al\cdots O^{\delta-}-Si-$ with $H^{\delta+}$ below the O

(c) $-Al \quad O-Si-$ with H below the O
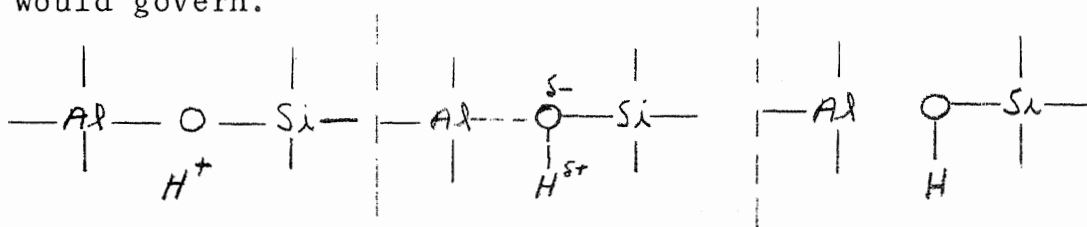
In the above reaction it is noted that the H+ ion must combine with the oxygen of the silicon tetrahedra in order to preserve electronic neutrality. It is also seen that if further attack is to take place on these tetrahedra a OH⁻ ion will be required to insure electronic neutrality. It is therefore believed that this reaction is of secondary importance at low pH values. It should also be noted here that in some glasses (994 glass being one example) whose O/Al ratio is greater than two, some Al may be found as a network modifier in the intersticial positions and such Al ions will be preferentially dissolved at low pH values as will the other modifiers. (18)

As was stated, the mechanism of electrophilic attack of H+ ions on the Si-O-Si and Si-O-Al networks is believed to be of little importance at low pH values, but electrophilic attack on the Al-O-Al bond is thought to be of some importance even at these low pH values. The micrographs of 994 glass treated at pH 2 and 3 provide evidence for this. The intense pitting observed at pH 2 is most probably the result of the H+ ion preferentially attacking regions of high Al content thus creating the pits. k The background texture is seen to be quite smooth. This would be expected since the regions having a high silicon content would be unaffected by acidic attack.

Comparing 994 and E glasses at the low pH values the difference is seen to be quite pronounced. 994 glass is strongly attacked in very small regions of phase separation

while the E glass is quite uniformly attacked. The result
of the attack on E glass is seen to be a very porous surface.
Brooks and Eakins (14) found by chemical analysis of the
attacking reagent that the non silica structure of E glass
is preferentially dissolved below pH 4. The micrographs
taken at pH 3 substantiate this. Although the attack is
uniform, showing no evidence of large scale phase separation,
the degree to which the surface of fig. 10 is attacked would
indicate that more than Ca^{++}, Na^+, and Mg^{++} ions have been
dissolved. It is probable that the mechanism of electro-
philic attack on the non-silica network has also taken place.

As the pH of the attacking solution is increased
from 2 to 5, the 994 glass surface becomes somewhat rougher
than that of E glass. Even though the cation concentration
of the 994 glass is lower than that of E glass, it must be
remembered that in 994 glass the Al is practically all
tetrahedrally coordinated and there may also be some Al with
a coordination of 6. It is believed that pH 5 is about the
value at which the OH^- concentration would be high enough
to attack the Al-O-Si bond causing the somewhat rougher
surface of 994 glass. At pH 6 the preferential attack is
clearly evident in regions of phase separation. The basic
texture has followed the trend toward a smoother glass
surface of more rounded features. This is in contrast to
the very rough surfaces found at pH 2-3, especially on E
glass.

As the pH of the attacking solution was increased to 7, a distinct change in the appearance was observed. At these pH values both electrophilic and nucleophilic attack is taking place, but since neither H^+ or OH^- are present in the solution to a great extent, the attack is limited. Again the surface seems to be preferentially attacked, although both glasses do show regions of uniform attack. It is thought that the mechanism described earlier is controlling the attack at this point. The silica network is somewhat attacked, but as evidenced by the surface, some constituents are attacked much faster, leading to the type of surface most typically shown in the micrographs of E glass treated in pH 7. The nature of the attack is evident as about 50-60% of the area has a structure which would be expected of a high silicate content glass. The rest of the glass, however, consists of rather small, deep pits which would be caused by the non-silica network being dissolved. This explanation of course, requires the existence of more than one phase, and as will be shown later, this is indeed the case for all borosilicate glasses. (19) 994 glass also exhibits the same type surface. Since our work has established the existence of phase separation in 994 glass on a rather large scale the explanation would also be valid for this glass.

As is noted in the micrographs of both glasses, the behavior of the two glasses begins to deviate some-

what at pH 8 and above, E glass appears to be attacked more
or less uniformly at the higher pH values while 994 glass
exhibits preferential attack. Considering E glass, it is
seen that except for isolated regions of phase separation,
which was observed, the surface has very few gross features.
The glass is attacked uniformly in most cases and the basic
texture approaches that of the untreated glass. The uniformity
of the attack may be associated with the structure of E glass.
As we have seen, most phase separation which occured in the
E glass used has been on too small a scale to observe at
low magnification. The glass may therefore be considered
more or less a continuous, random network consisting of
boron, aluminum, and silicon polyhedra. At high pH values
even if the submicroscopic Al and Boron phases were pref-
erentially dissolved, the silicate network would be exposed
to the attack with the net result being a very smooth surface.
If the separated phases were much larger, it would be ex-
pected that the surface would appear similar to that of 994
glass.

Fig. 30 of the E glass surface suggests lim-
ited phase separation in E glass. The roundish regions seen
in this micrograph were not observed on untreated glass or
at a pH below 8. The boundaries, some of which are quite
well defined, have been preferentially dissolved. This would
suggest that they are either of a different composition from

the inner regions and/or that there is a stress concentration at the bondaries. The stress could be caused by a difference in composition or be a result of non-uniform cooling of the batch.

A plausible explanation of the preferential attack occurring at the boundaries of these regions is that a localized distortion of the network is caused by a rather high boric oxide concentration in these regions, although a boric oxide phase has not precipitated. It is known (20) that the boric oxide triangles and silica tetrahedra are not compatable. That is, the triangles being of different geometric shape and size cause a considerable distortion of the silicon network bonding. Separation into two phases could occur, but in the case of E glass, phase separation, on a large scale, is absent. Therefore, a stress concentration in these regions would have been frozen in, which would make the glass in these very localized regions more susceptible to attack.

It was noted that these regions were not observed at acidic pH values. This is explained by the fact that H^+ ions are not capable of attacking the SiO_4 or B_2O_3 network. Since it is the network which is being attacked in these regions the H^+ has little effect. As the OH^- concentration increases, attack on the network increases and preferential attack of the weakened network takes place.

At the highest pH values studied, the attack on

on the two glasses is seen to be quite different. 994 glass
at the pH 10-11 level inhibits a very rough surface, while
the E glass has been uniformly attacked. Again the dif-
ference in attack may be attributed to the structural dif-
ference in the glasses. 994 glass having a high Al content,
but low non-bridging ion content, would be much more highly
attacked due to the preferential dissolution of the AlO_4
structure which opens the glass network to the attacking
solution resulting in an accelerated attack.

Although the E glass contains Al, it is not
present to the same extent as in 994 glass, and, as we have
shown earlier, it is expected that the network is a random
distribution of Al, B and Si. It should also be noted that
boron has a high electronegativity and is not attacked to
as great an extent as Al. The combined effect of the random
composition of the network and the retarding action of the
boron tends to limit the attack on E glass. The result as
seen from the micrographs is a uniformly attacked surface
with very few gross features.

Phase Separation

Since phase separation does play an important
role in the attack on 994 glass and also does have some ef-
fect on E glass it would be profitable to discuss some of
the reasons for the occurrance of the phase separation and
the effects which it has on the attack. As was discussed

earlier, the +3 valence of Al can affect the chemical attack
on 994 and E glass. This charge difference between Al and
Si is also thought to play an important role in the phase
separation of 994 glass. Substitution of aluminum into the
network for a silicon atom will cause a localized disturbance
in the Si-O-Si bonding. There are two reasons for this:
first, Al and Si have a different atomic radii, .50Å and .41Å
respectively. The second reason is that normally aluminum is
found in the form Al_2O_3, having triangular coordination. As
was noted earlier, however, when Al is substituted in the
glass network it tends to assume the tetrahedral coordination.
There is an effective negative charge on the Al tetrahedron
which causes some distortion of the Si-O-Si and/or Si-O-Al
bond in the immediate neighborhood of the aluminum. Further-
more, in order to satisfy electroneutrality, there is, assoc-
iated with each Al tetrahedra, a cation which occupies an
intersticial position. The cation can also interrupt the
chemical bonding as well as further distort the network
physically. It has been found (20), for instance, that
even though the arrangement of the oxygen ion in the silicate
network is largely determined by the silicon ions, the ca-
tions, will influence this arrangement by attempting to
achieve their equilibrium coordination. The result of this
is a distortion of the silicon-oxygen bond angles. For
ions such as Na^+ and K^+ whose field strengths (1.1 and .57

respectively) are small, the effect is negligable. They
may be accommodated with little distortion of the network
bonding. Magnesium which has the highest field strength
of all network modifiers may impose intolerable distortion
on the silicon-oxygen network. The combined effects of the
aluminum and magnesium in 994 glass lead to the large
phase separated regions observed.

One other important point must be emphasized
in connection with the phase separation. The glasses we
are dealing with are rather thick, being approximately 1/4
inches in thickness. Because of this, there will be a
large temperature gradient in the glass as it forms. It
is probable that in these glass plates the center cooled
sufficiently slowly to allow the phase separated regions to
grow quite large. It would be expected that in glass fibers,
which are very thin, the temperature would pass the critical
point quickly and that the phase separation would only occur
on a submicroscopic scale. It should be remembered, how-
ever, that 994 glass does exhibit a strong tendency for
phase separation and that the attack is definitely affected.

The mechanism by which phase separation af-
fects the attack may be explained in the following way. In
994 glass there are two major possibilities for a separated
phase. Either a pure silicate or a magnesium-aluminum
silicate phase may develop. It is doubtful that a pure

magnesium-aluminum phase would be formed since the silicate
concentration is very high in 994 glass. If one were to
form with such a composition it would therefore be limited
in its size. A phase containing aluminum as the primary
network former, and silicon to a lesser extent would, there-
fore, be more probable.

In most cases the separated phases observed in
994 glass are thought to be of the silicate structure con-
taining very little aluminum. The small separated phases
are seen to be less attacked at the acidic pH values,
while the area immediately surrounding the regions are
more highly attacked than the basic glass structure. Since
silica is very stable under acid attack it is thought
that the small regions are high in silicon. Further evidence
for this is the fact that the region immediately surrounding
the silicate regions are more highly attacked. This is be-
cause the high silicate regions form using silicon from the
surrounding regions, leaving the surrounding glass network
much higher in aluminum and magnesium. Such a network is
attacked much more readily at acidic values. The resulting
glass surface is therefore much rougher and the attack is
seen to penetrate the glass much more deeply.

Very few regions were observed where the sep-
arated phase was high in aluminum. One such region is
shown in Fig. 41. The opposite effect on the attack is

seen to occur in these regions. In the high aluminum content phase the attack is seen to have penetrated quite deep by preferential dissolution of this phase while in the region immediately surrounding it the attack is negligable. As the distance from this phase is increased the attack resembles that seen in the non-phase separated regions. Since the phase separated region is high in aluminum it will have depleted the glass in the adjacent region in this component leaving an almost pure silicate structure which is negligably attacked at pH 6.

CONCLUSIONS

It should be emphasized that the results of this work do not provide information as to the extent to which the glasses were attacked. Some conclusions as to which constituent of the glass was dissolved may be drawn, but quantities such as weight loss of a specific constituent and total weight loss were not investigated.

The effects of large and small scale phase separation were observed and it was found that in 994 glass the regions surrounding and within a highly phase separated area were attacked to a greater or lesser extent depending on which phase had separated. At acidic pH values the attack was found to be much more gross in regions where a silicate phase had separated, while in regions

where a high aluminum content phase had formed there was little attack on the surrounding glass. The aluminum in such regions was found to be preferentially dissolved at low pH values causing deep pits in the separated phase, while the surrounding glass, having a higher than normal silicon content, was negligably attacked. This may be related to the attack on glass reinforced plastics. It is probable that if such non-uniform regions occur in the glass fibers they will act as sites for preferential dissolution of the glass, thereby destroying the glass-plastic bonding and opening the interface to further attack by the solution.

In E glass very little phase separation was observed on a large scale. It has been found, however, (19) that phase separation, on the submicroscopic scale, does occur in all borosilicate glasses and this mechanism would also be important in glass reinforced plastics using boro-silicate fibers.

With few exceptions it was also found that preferential attack was of less importance when dealing with high pH values. One possible exception was seen on E glass treated at pH 11. It is suspected, however, that a stress concentration frozen into the glass during formation was the cause of the preferential attack rather than phase separation.

As a result of the observations of the attacked surfaces possible mechanisms for acidic attack on glasses containing trivalent network formers have been suggested. These mechanisms involve the electrophilic attack of H^+ ions on the non-silicate network at very low pH values, and the combined electrophilic and nucleophilic attack of H^+ and OH^- on Al-O-Si bonds at pH values of 4 through 7. It is probable that these mechanisms may be extended to most glasses which contain an appreciable amount of trivalent network formers. It was also found that as the pH value was increased above pH 7 the mechanisms described above decreased in importance since the silicate structure is also susceptable to attack at the higher pH values.

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LIST OF TABLES

GLASS	SiO_2	B_2O_3	Al_2O_3	PbO	Na_2O	CaO	MgO	F	Fe_2O_3	K_2O
			%	by	weight					
E	54.5	10.0	14.5	—	0.5	15.9	4.4	0.3	0.4	—
994	64.0	—	26.0	—	—	—	10.0	—	—	—
"PYREX"	80-82	12-15	—	—	3-4	—	—	—	—	0-1
Soda-Lime-silica	70-74	0-0.2	0.5-2.0	—	12-17	5-10	0-4	—	—	—
Lead GLASS	56-58	—	0-1	30	0-13	—	—	—	—	0-13
Boro Silicate Heat resisting	80.5	12	2	—	4.5	0-1	0-1	—	—	—
Boroaluminate	—	33-70	10-25	—	—	10-45	0-45	—	—	—

TABLE 1

ELEMENT	Si	B	Al	P	O	F	Cl	Ca
EN	1.8	2.0	1.5	2.1	3.5	4.0	3.0	1.0

TABLE 2

ELEMENT (ION)	Si^{+4}	B^{+3}	Al^{+3}	P^{+5}	Ca^{+2}	Mg^{+2}	Na^{+1}	K^{+1}
IONIC Radii Å	.41	.20	.50	.34	.99	.65	.95	1.33
Field Strength	23.8	75.0	12.0	43.2	2.04	4.70	1.11	.57

TABLE 3
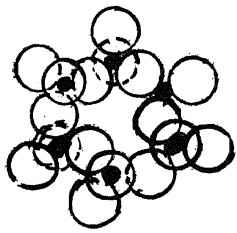
LIST OF FIGURES

● silicone

○ Oxygen

⊙ Fourth silicone directly over oxygen

a.
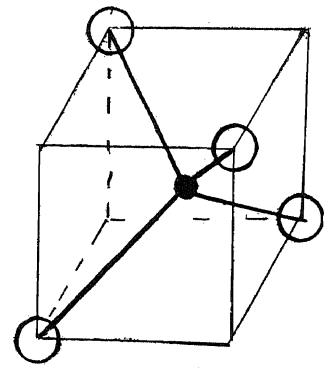
2 dimensions

b.

3 dimensions

FIG 1

● Silicone   ○ Oxygen   ⬤ AlKALI

Foutth Oxygen not shown

FIG 2

●—Boron

○—oxygen

FIG. 3

Specimen
before Ge
"Shadowing"

(a)

Ge

Specimen
After Ge
"Shadowing"

(b)

——— "unshadowed", No Ge

━━━ Covered by Ge
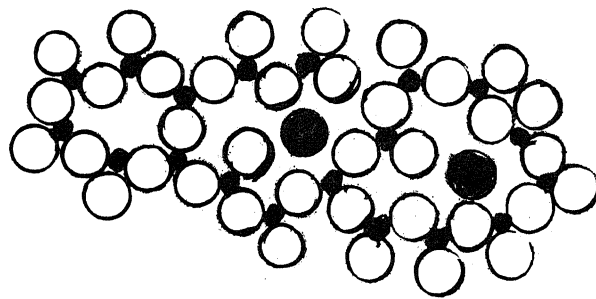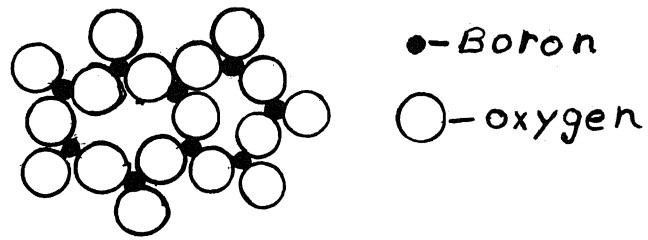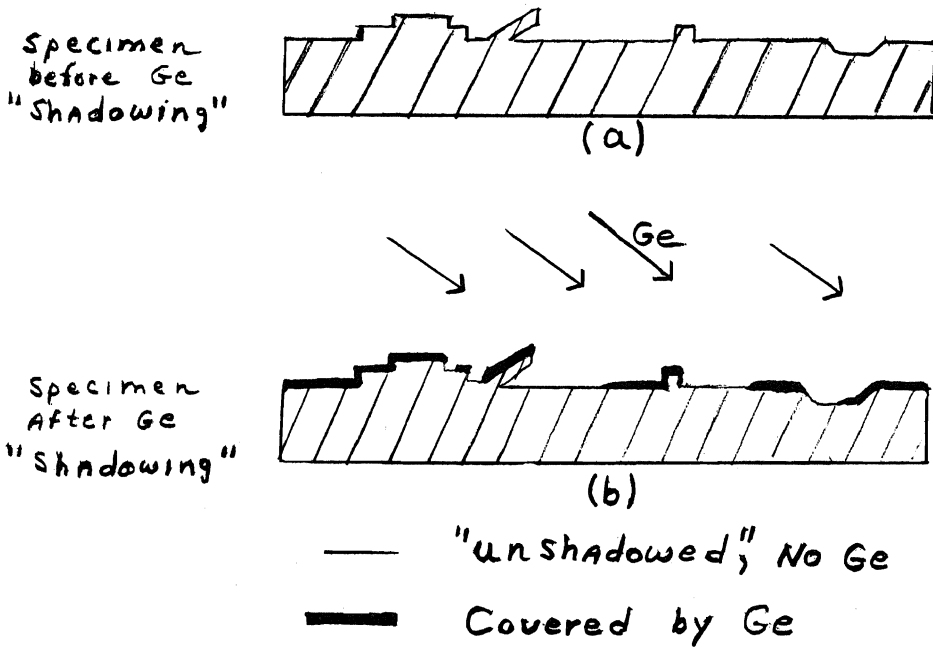
FIG. 4
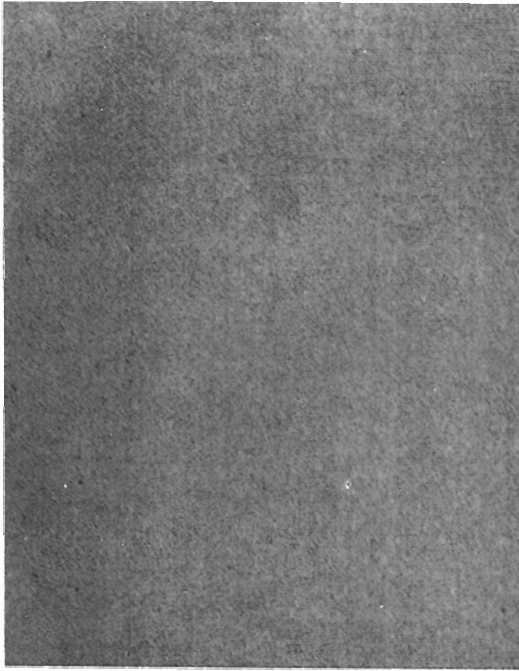
Fig. 5   8600X before repro-
duction.   Total mag. = 17,000X

Fig. 6   17,000X
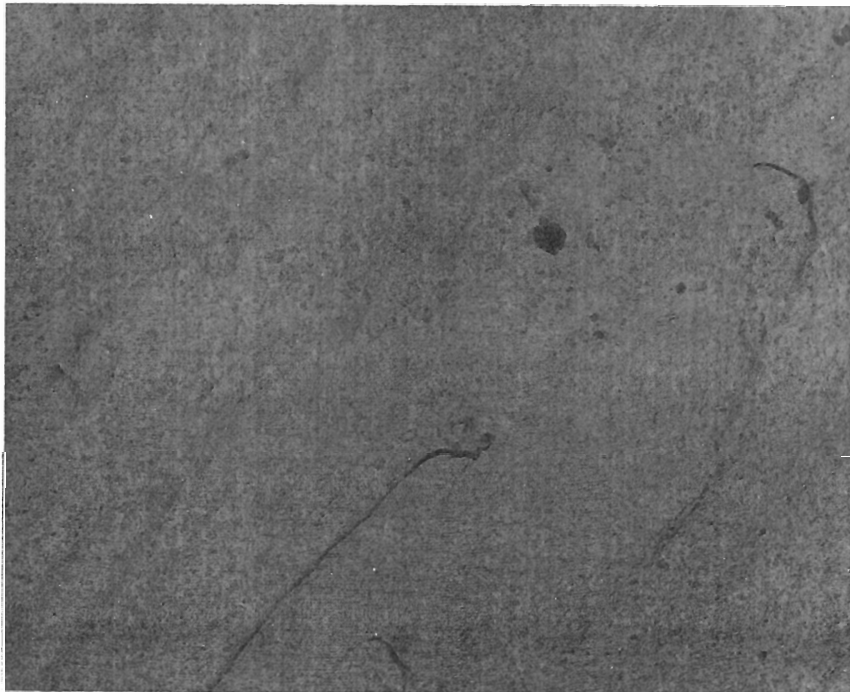
Fig. 7   17,000X
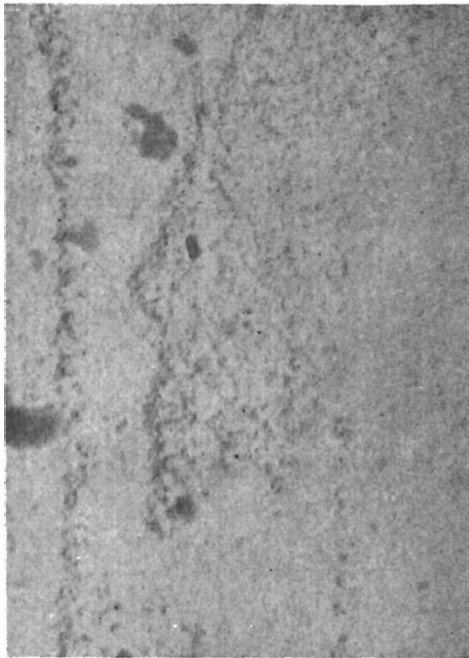
Fig. 8   5500X Before repro-
duction. Total mag. = 11,000X
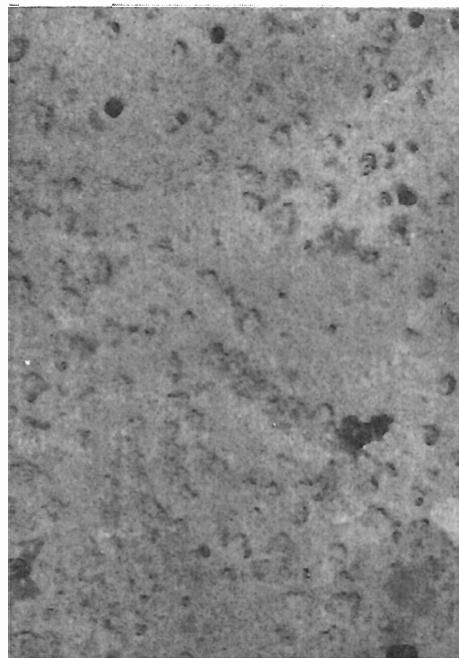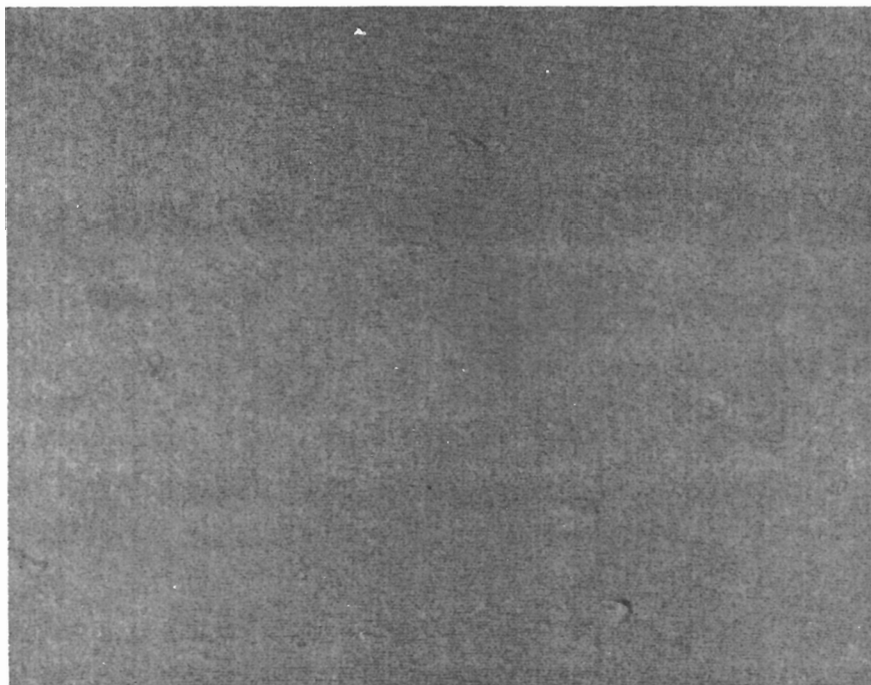

Fig. 9-41 at 11,000X

Fig. 10
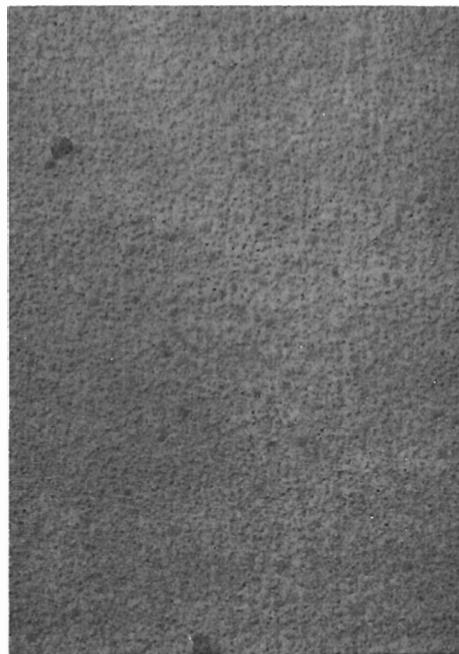
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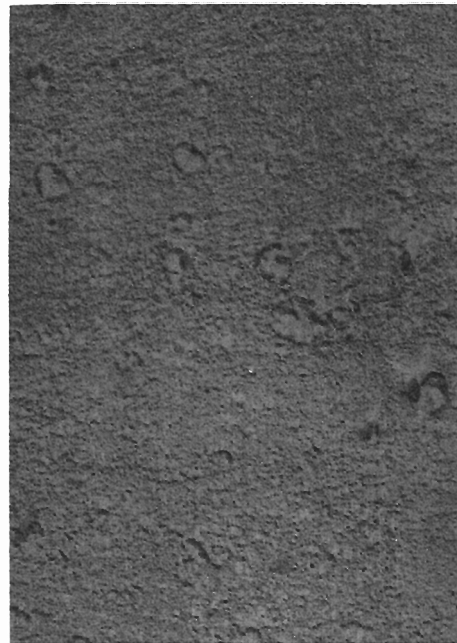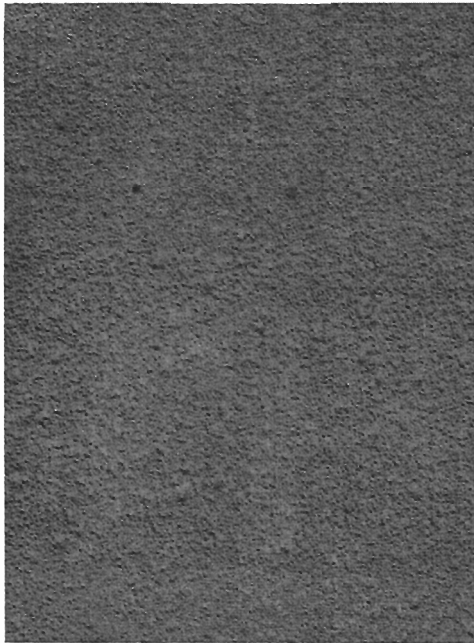
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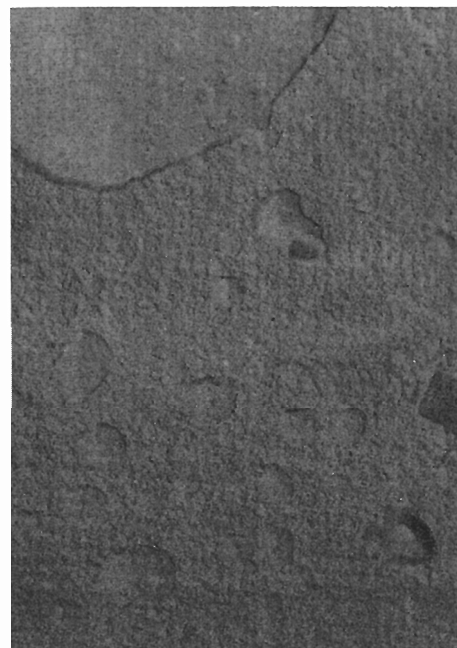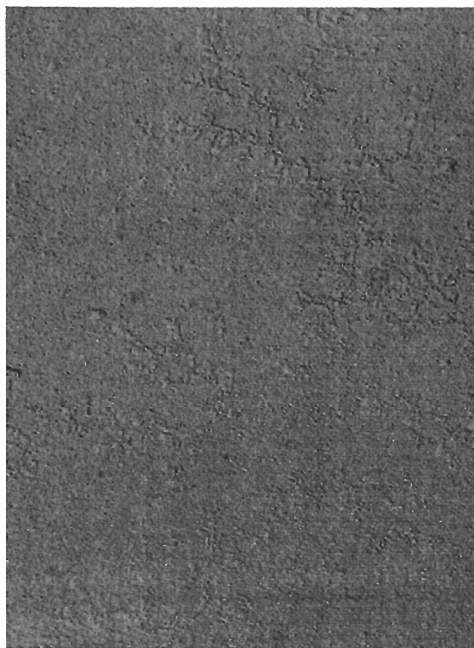
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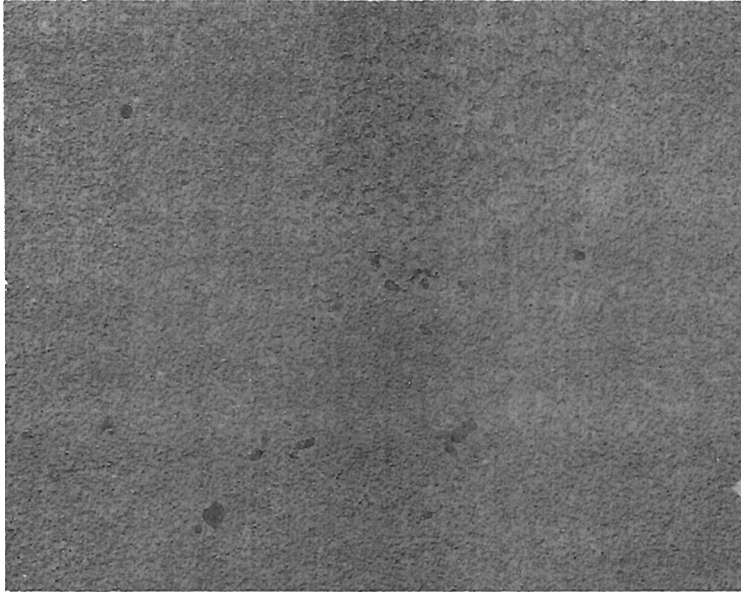
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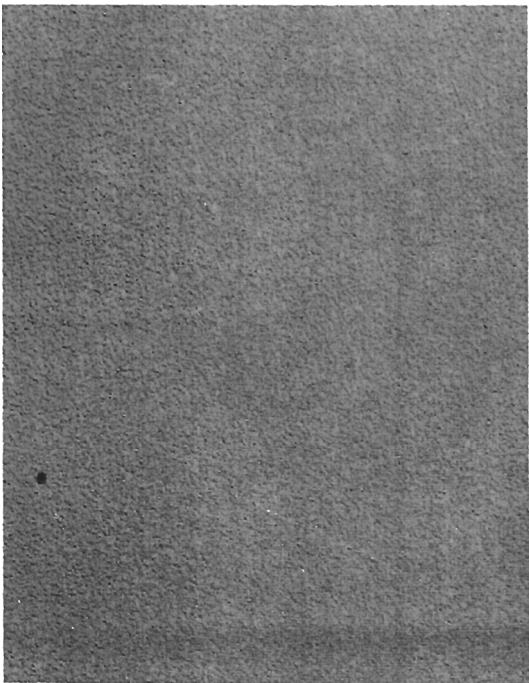
Fig. 17
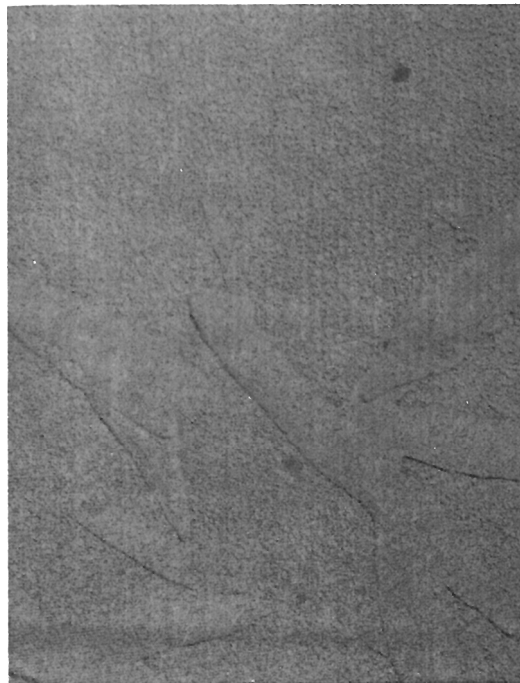
Fig. 18

Fig. 19
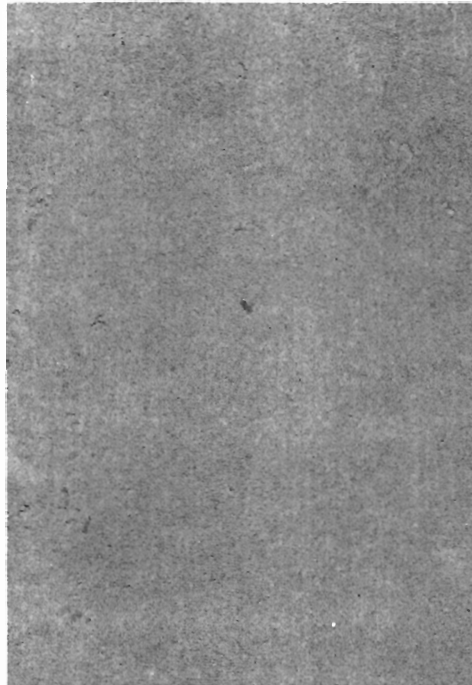
Fig. 20

Fig. 21
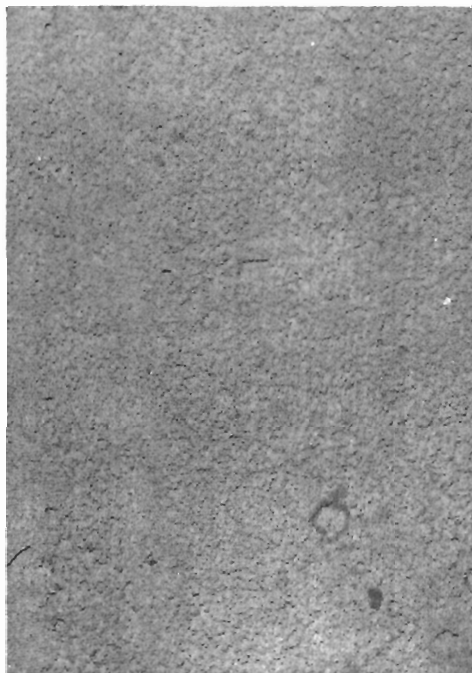
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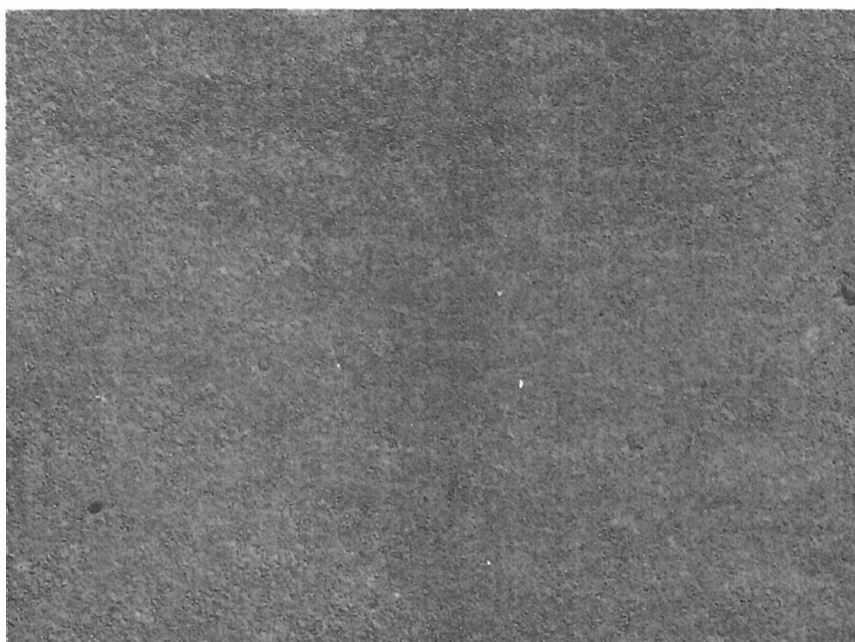
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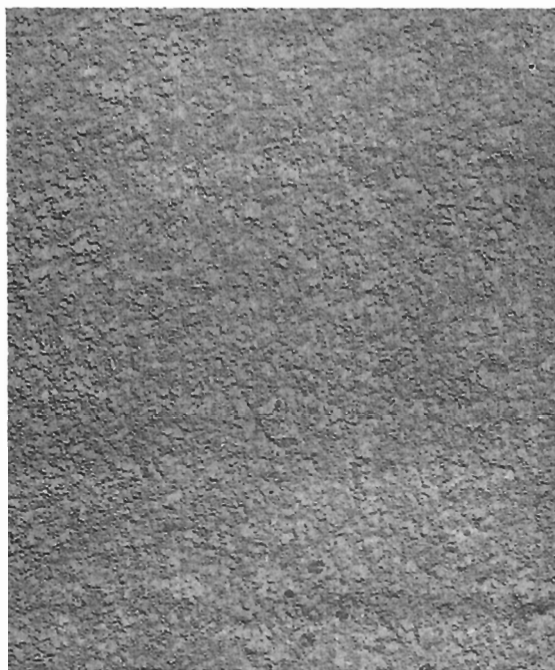
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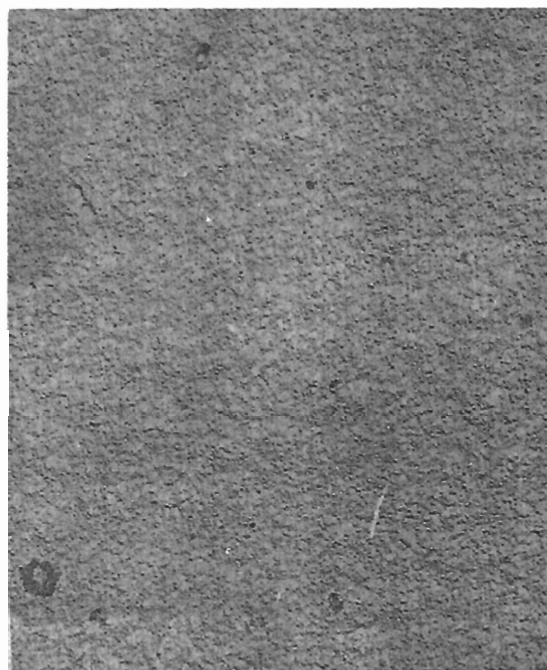
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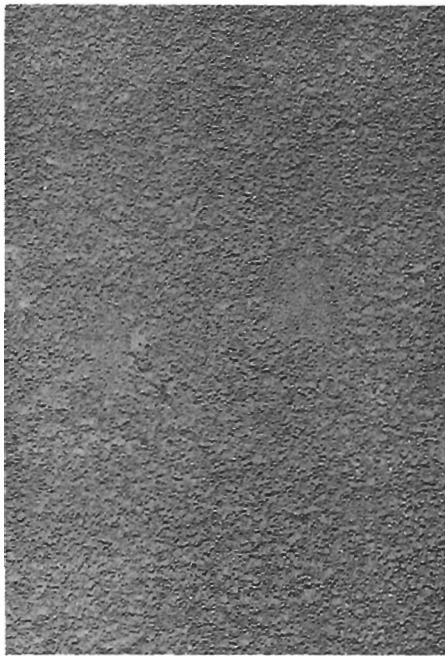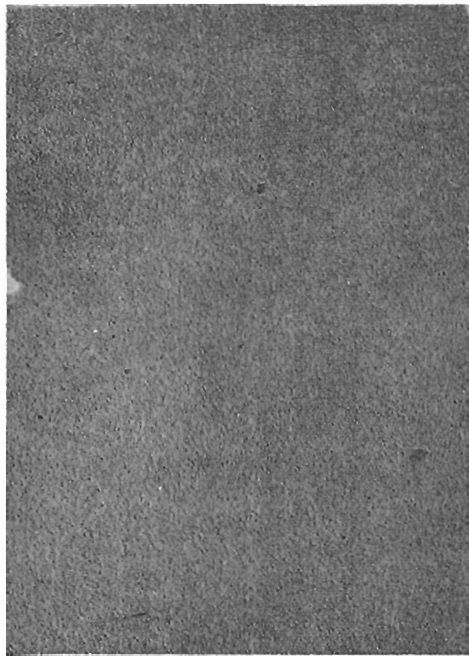
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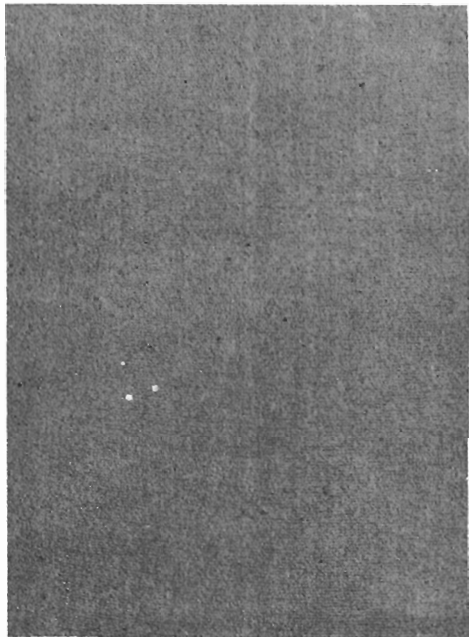
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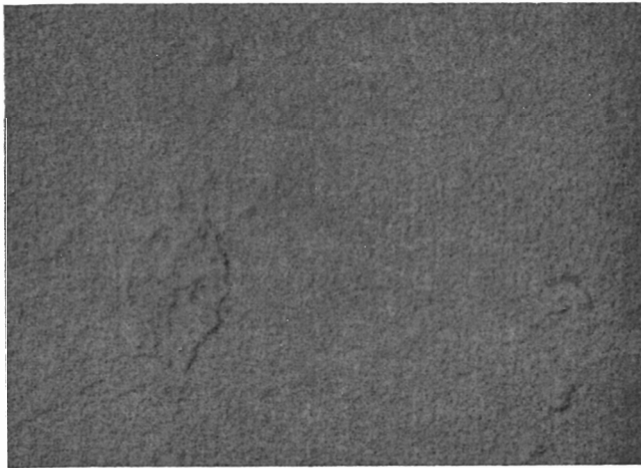
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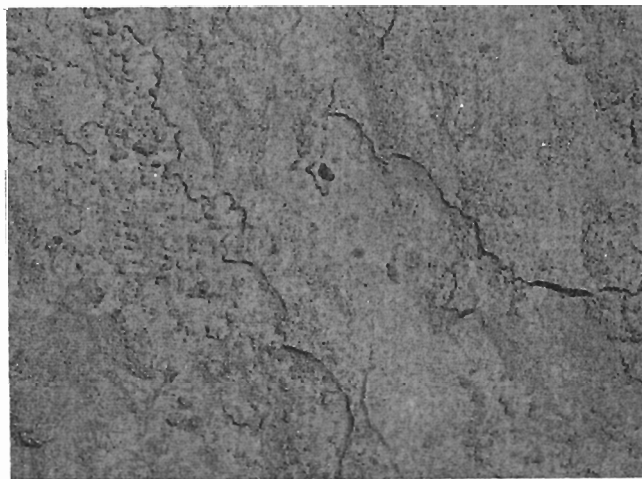
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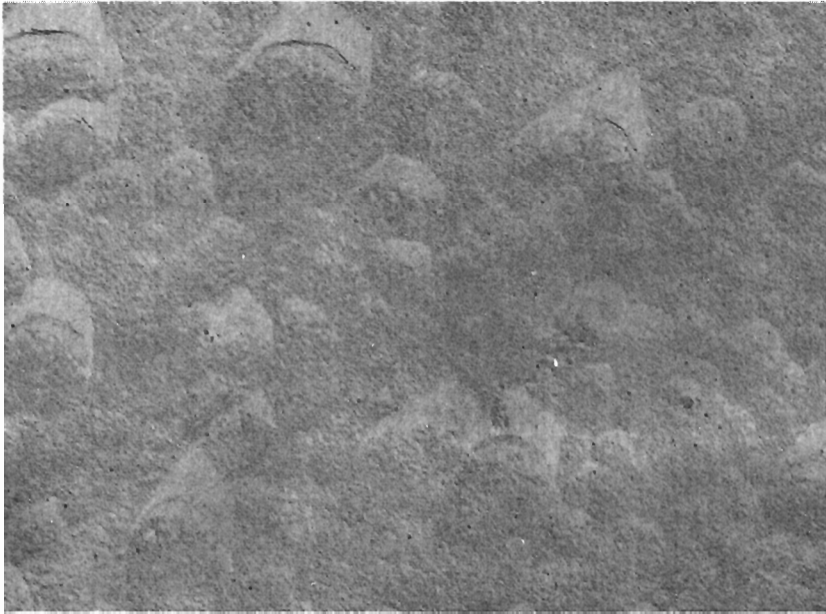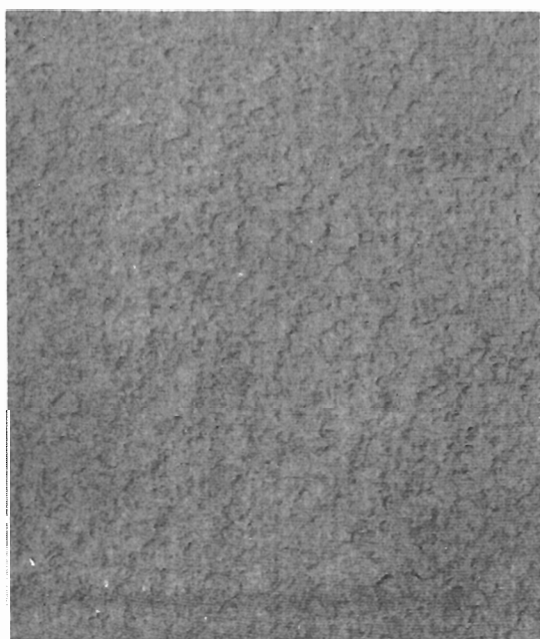
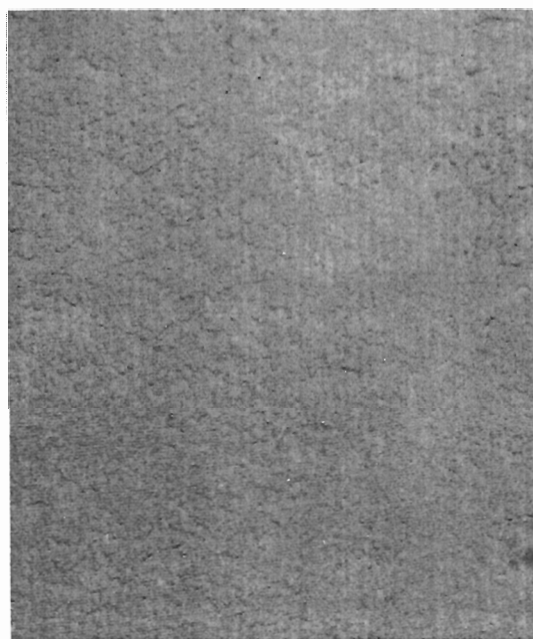Fig. 32

Fig. 33

Fig. 34
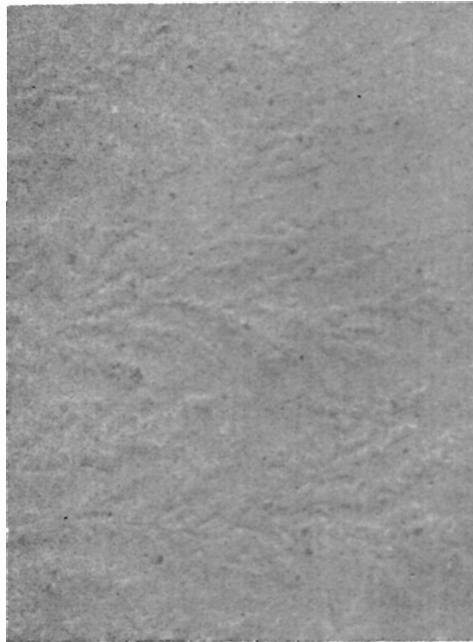
Fig. 35-36a.

Fig. 36b.

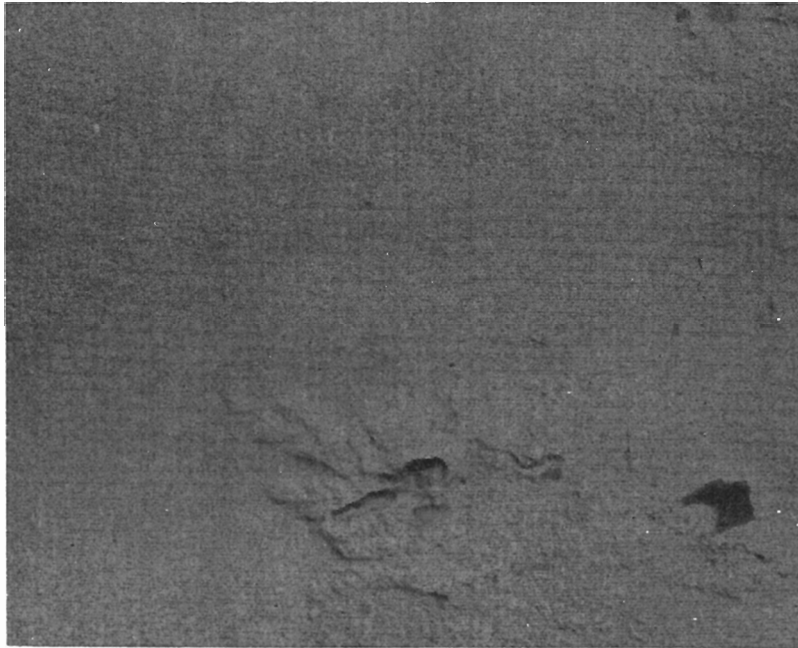Fig. 37

Fig. 38

Fig. 39   Fig. 40

Fig. 41