THE EFFECT OF PRODUCTS OF COMBUSTION UPON CERAMIC WARE; WITH PARTICULAR REFERENCE TO THE ACTION OF MANUFACTURED GAS UPON RAW GLAZES

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I. INTRODUCTION

The direct firing of ceramic products in a furnace or kiln without a muffle offers an opportunity for obtaining a distinct economy in the production of high-fired glazed, enameled, and other types of wares.

Glazed and enameled wares produced by high-firing are advantageous because such wares are more durable and harder, and have other properties which increase their ability to resist wear in the various capacities for which they may be used. Temperatures required for such products are obtained readily only in direct firing.

Direct firing is of interest in the general manufacture of ceramic ware because economies may be realized from (1) heat savings by removing the dead load of muffles and saggers; (2) from a lowered investment in construction and a lowered cost of maintenance compared with that of a muffled furnace; and (3) from decreased fuel cost due to the shorter firing time required.

Coal, wood, and oil were used early in the commercial development of the ceramic industry, and it was soon found that muffle type firing was required to prevent an exceptional amount of rejected loads or "rejects" with such fuels. Proponents of gas firing[1] claim that this possesses the following advantages over coal, wood, or oil firing: (1) even temperature rise, without flash heating as with certain coals; (2) more readily controlled temperature rise; (3) better control of atmosphere composition (the maintenance of uniform gas composition and uniform firing conditions in turn maintains an approximately constant ratio of constituents); (4) absence of free carbon in the atmosphere, as contrasted with the smoking period of coal firing; (5) freedom from muffle breakage and from the dirt occurring in such deterioration; (6) economy in operating costs and cleanliness resulting from the elimination of ash removal or solid fuel conveying; (7) economy of space for the same reasons; (8) heat economy in that both the gas and air feed may be preheated by the flue gases; and (9) economy in labor requirements.

Direct firing with gas has not become widespread in the ceramic industry, perhaps in part because of the early difficulties experienced with coal firing. While it is true that many defects in ceramic products, especially glazed ware, can be traced to atmospheric conditions, there is perhaps insufficient basic information of the

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1. For discussion of the economics and advantages of direct gas firing, see the following references- G 6; H 6; M 1; M 9; M 19; O 1; R 1; R 2; V 3; W 3; W 6. Gas fired kilns are frequently described in the literature and some examples may be found in C 2; M 2; S 9; T 5.

behavior of ceramic ware available. Combustion products at high temperatures are among the least known of a large number of factors which may produce imperfect ceramic goods; consequently the defects are often attributed to these.

A few of the other causes[2] of ceramic defects may be (1) the direct impingement of the flame, (2) the rate of heating, (3) the duration of heating, (4) the aging of the slip, and similar conditions. "Scumming" or the deposit of water-soluble salts[3] upon the surface of the ware is another defect that may occur without the influence of an injurious atmosphere.

The determination of the existence of the defects mentioned and their degree have been reported, in general, by descriptions and, occasionally, by photographs. This may, in some cases, cause variation in agreement among investigators.

In the investigation here presented, an effort is made to control or eliminate such causes of the defects and discrepancies mentioned. While it was not possible to simulate industrial practice, such practice is considered in planning the experiments. The material

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2. Many of the suggestions as to causes are based on opinions of experienced operators of ceramic kilns and have not in every case been checked by laboratory work. See D 5; I 1; H 1; W 2; W 8.

3. See the discussion and bibliography in C 4 and I 5.

studied is a Bristol type glaze (not fritted) of simple composition and analysis, in order that the reproduction of such a glaze might be easy and the addition of coloring agents might not require serious variations in its development. This glaze is subjected to an atmosphere of combustion products of manufactured gas and some of the components that are believed to cause defects are varied to determine the minimum or mazimum values necessary to attain a glazed product equivalent to air firing. The results of the investigation will be reported in various ways to show relative values.

The literature does not contain an extensive amount of data upon glazes of any type. A review of the action of combustion products upon all types of ceramic products, that is, glazes, glasses, enamels and clay ware, is made.

II. HISTORICAL

A. INTRODUCTORY

The action of combustion gases upon ceramic substances was early recognized by glass makers and pottery producers. The glass makers noted a blue-gray deposit, "bloom", as an indication of well fired glass. Likewise, pottery makers have described processes by which reducing atmospheres were produced to obtain certain surface characteristics and colors. Early records and observations of manufacturers began to appear in the French and German periodicals about the middle of the 19th Century, and were found in the English and American journals when these began publication. The early publications recognized occurring defects and gave practical methods for decreasing or eliminating them. To J. W. Mellor, an English ceramist, must be credited early alignment of industrial observations and laboratory results. His reports extend from the first issue of the "Transactions of the English Ceramic Society" until recent years.

The work dealing with the influence of combustion gases upon ceramic products, has been of two general types, (a) the observation and industrial control of defects having economic importance, and (b) the laboratory investigation of some particular ceramic product without extended consideration of the general field.

The industrial reports and observations as a whole, appear to be lacking in specific data. This makes the reproduction of the effect difficult or at least uncertain. Very often the material examined is indicated only by name and no mention made of its composition or ingredients. Further, in noting the atmosphere to which the defect is attributed, the writers often state what they believe may be present but seldom give an analysis. Thus, it is found impossible to catalogue, except in a very general manner, this data either according to the cause or to the material on which the defect was noted.

The laboratory experiments offer similar difficulties in interpretation. However, in these, more data is usually available in regard to the analytical composition of the atmospheres and of the materials used. The gases used in the laboratory have usually been substantially pure and few attempts have been made to determine the effect of diluting a particular component of an atmosphere to concentrations similar to that occurring in direct firing. Modern experiments are tending to be more complete but, in general, at present, do not appear to be sufficient in number to indicate more than general opinions and trends.

In succeeding pages, the literature will be reviewed with particular emphasis on the effects of combustion products on ceramic wares. Special attention will be given those gases whose presence in combustion products is common. The formation of these defects as well as the methods of determining and expressing the data obtained will be discussed.

The exact terminology used by an author in describing the various defects varies. However, some commonly accepted trade meaning is usually implied by the words used by ceramists. The following definitions will be used in this work.

"Spitting-out" or "spit-out" consists, in glaze or enamel, of a bursted bubble whose edges have not healed. "Pinholing" refers to tiny holes in glazes or enamels appearing as pin pricks that may have resulted from spit-outs that have healed partially. "Pockmarked" refers to larger defects than are inferred by spit-out. "Blistering" is used to describe ceramic ware in which there are unbroken bubbles formed. In unglazed ware, a bubble may be described as "bloated".

"Crazing and "shivering" are terms used to describe hair line cracks produced in the glaze or enamel by difference in coefficients of expansion and contraction of the body and the covering. It is quite common usage to make no differentiation between these effects but to call either "crazing".

"Scumming" is an effect for which there is some controversy. With "scumming", are confused "sulfuring", "starring", "efflorescence", "bloom" and "iridescence". "Sulfuring" may be considered a general term covering all the effects that may be produced by sulfur compounds in the gaseous products of combustion.

Although the remaining terms are often used to indicate the observer's opinion of the influence of sulfur compounds, the present use of them will be to describe certain physical appearances after firing. "Starring" is an effect due to the formation of crystals upon the surface of the glaze or enamel. "Iridescence" is attributed to a metallic sheen or luster. "Scumming" is a dullness of the surface, of which "bloom" and "efflorescence" are different magnitudes of scumming in order of decreasing intensity. "Bloom" is often referred to in the literature as scumming upon glass. Statements in the literature indicate that all the above defined terms may be due to water-soluble sulfates, but no such statement will be affirmed in the present investigation.

B. THEORY OF ACTION OF COMBUSTION PRODUCTS

In scientific literature, the action of combustion products upon ceramic bodies frequently has been discussed. The difficulties of determining the action of multicomponent systems consisting of clay bodies, glazes or glasses, and combustion gases, are innumerable. To represent systems of more than three variables in a graphic analysis[4] is difficult or impossible. Ceramic substances may range from two components to an extremely large number. In view of the many variables, experimentation in the present study was undertaken somewhat on a trial and error basis rather than as a scientific investigation of the equilibrium of multicomponent phases. From the experiments, the cause of a definite effect was indicated and a possible theory for such action from known reactions was developed.

Among the general theories[5] presented for the development of defects in ceramic bodies are what may be termed the sulfuric acid theory, the gas absorption theory, and the carbon absorption theory. The sulfuric acid theory has attained popularity and is accepted by many observers at the present time.

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[4] See Findlay, pg. 275, The Phase Rule, Longmans, Green and Co. New York, 1935.

[5] For an excellent resume see M 17.

The sulfuric acid theory was expounded by Mellor (M 7), and other investigators[6] have made only slight changes to account for the particular reaction that they were studying. The basis of this theory is that in fuels there are certain elements and compounds which upon burning yield acidic gases. Of these gases, sulfur dioxide or sulfur trioxide may be considered the stronger, since by solution in water sulfuric acid is formed. This acid may then act upon the basic constituents in the ceramic body, such as the alkalies, the alkaline earths, and certain metals that occur in the clays (i.e. chromium,. iron) or with metallic materials added to improve or change the properties of the body, e.g. salts or oxides of cobalt, tin, lead, and the like. The sulfates thus formed may cause defects in several ways. Mellor[7] cites examples to show that the sulfates which are insoluble or undecomposed in the ceramic substance may crystallize on the surface. Other investigators[8] think that the water-soluble sulfates present originally in the materials or formed from the gases in contact with the ware, may come to the surface, thus causing scumming.

Investigations of glazes have given support to similar theories concerning the crystallization of the

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[6] See also references J 7; L 6; M 6; and A 15; G 1 (brief resume)

[7] See M 7; M 8.

[8] See L 6; C 4; T 3.

sulfates[9] and the scum formation from water-soluble sulfates[10]. Ortman (O 1), however, proposes the theory that the sulfates, either formed from the gases or those originally present, may prevent proper maturity, color, or texture by (1) being decomposed by heat or by reducing conditions, (2) being displaced by silica, (3) displacing weaker acids, or (4) reacting with coloring oxides and fluxes, thus explaining both spit-out and scumming. This theory is supported by observations of many independent investigators[11].

In experiments upon glass,[12] sulfates entering as impurities or formed from sulfur dioxide, have a definite influence upon alkali loss or solubility. M. W. Travers (T 4) in investigating the action of combustion products upon glass, proposed a theory for the action of sulfur dioxide based upon the partial pressures of the solids as sodium carbonate, sulfate, and sulfite whose gaseous decomposition products are present in combustion gases. He found by using Nernst's Heat Equation,[13] that the calculated pressures over the solids at 600°-700° C would be too high for the carbonates

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[9] See M 10; M 11; D 2.

[10] See S 1; W 7.

[11] See Z 1; D 2; S 5; B 30 as a few examples.

[12] See P 12; E 4.

[13] M. Travers recognized that the Nernst Heat Equation could not be solved but by comparing values obtained by the equation and by experiment at lower temperatures assumed that the magnitude of the values was correct.

and sulfites but would be within the range of sulfate formation from the estimated trioxide present in the gases.

At the same time that J. W. Mellor (M 7) proposed the application of the sulfuric acid theory to glazes, A. Hopwood and W. Jackson (H 9) proposed a similar theory for the coloration of iron bearing clays, in which they agree with Ortman (O 1) that the sulfates formed from the gas-solid reaction are decomposed, resulting in liberating iron oxide. Other investigators[14] accept the explanation of the mechanism of the formation of sulfates in clay and wares but do not believe that the sulfates are decomposed but instead that they cause noticeable surface defects that cause scumming and related effects upon the later applied glazes.

The theory of absorption of non-reactive gases into the ceramic ware has not received general acclaim, although some of the more recent investigations consider it among the possible actions taking place in the kiln. The theory early proposed by H. C. S. Deville and L. Troost (D 3) held that spit-out was induced by the absorption of gases at high temperatures and subsequent ejection at lower ones. This opinion was supported by

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[14] See P 2; J 6; L 4; C 1; S 6.

other investigators[15] who found that ceramic bodies were porous to hot gases and that there is absorption in the bodies.

Studies upon glazes[16] have supported this theory and indicated that it is the absorption of water which may cause the majority of such defects. The subsequent rapid heating for decorating or other purposes causes superheating of the water and thereby fast volume expansion resulting in spit-out.

The absorption of carbon theory[17] may be taken to include (1) the deposition of carbon and combustible gases in the crevices and cavities of the ware, and (2) the carbonaceous matter in the raw materials. These combustible materials in the body will burn because ceramic bodies are permeable to hot gases; particularly to oxygen,[18] producing carbon dioxide and water. If these gases are not permitted to escape before fusion or vitrification of the ware, blistering and similar defects may occur. With the improvement of combustion processes with regard to completeness of burning and temperature regulation, this theory seems gradually to have disappeared from the investigations. There is,

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[15] See H 2; B 7; B 3; B 14; E 4; D 1; M 4.
[16] See C 7; M 16; R 5.
[17] See M 5; V 5; M 17 and B 4 (resumes).
[18] See B 7 and B 14.

however, one exception; that is, in the study of refractories[19] in which carbon is often deposited from the intensely reducing atmospheres used for metallurgical purposes.

Although enamels may be considered as having essentially the same composition as glazes and glasses, the theories[20] as to the cause of their defects, have not been discussed in this presentation because the reaction of the metal and the enamel, the enamel and metal composition, and the condition of the surface are, in general, deemed prime factors in such theories.

There are a few theories which are quite different. Among the most interesting is one discussed by A. E. J. Vickers and L. S. Theobald (V 2) in 1925 and by W. A. Wezl and A. G. Pincus (W 5) in 1938. According to this, water is the reactant.[21] Its action is held to be due to (1) the apparent reducing action which it shows at high temperatures and (2) its effect as a strong acid. Mellor (M 17), however, suggests that it is not the action of water itself which causes

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[19] See H 13 (good bibliography).

[20] See P 11; C 3; R 9. The consideration of enamel defects, bonding and the like, have received considerable attention and many articles are to be found in recent literature.

[21] This is also in agreement with experiments by Morey and Fenner (M 18) and by Firth, Hadkin, Parkin and Turner (F 1).

the reduction but the displacement of oxygen.

Another unusual theory was one developed by H. B. Henderson (H 5) from observations on kiln firing of bricks and ceramic ware. He expressed the opinion that hard graphic carbon was deposited by firing under intensely reducing conditions (natural gas). When high temperatures were reached, this carbon reduced the silicon dioxide of the clay, causing silicon to volatilize and condense in the cooler portions of the kiln. Oxidation of the silicon may take place, he believes, either before or after condensation.

Although the theories postulating the absorption of non-reactive gas or carbon, and the few unusual theories just mentioned are well supported by experimental data and industrial experience, they are useful only in specific cases. The absorption of gas at high temperatures and rejection at lower temperatures seems difficult to visualize. The defects of ceramic ware developed by absorption of moisture and other gases upon standing and subsequent refiring, are encountered in two or three-firing practice, however, only one-firing is applied in the case of the majority of ceramic products. Likewise, the carbon theory necessitates the assumption of incomplete combustion, and of improper heating. Although these may occur, the conditions constitute a problem of control and not a property of the ware. The exceptional theories are applicable only to and are formulated only for specific cases. The sulfuric acid theory, however, seems to remain as an explanation having considerable weight in the arguments against direct firing.

C. ACTION OF FIRING ATMOSPHERES

Examination of the data upon which the preceding theories were based showed that the effects of combustion products vary widely in type and degree, depending upon the materials, the gaseous atmospheres, and the methods used.

The experimental results are based on determinations from direct fired and muffled commercial and laboratory kilns and tube furnaces. The atmospheres used range from pure gases to actual products of combustion. Likewise, the materials studied vary considerably, ranging from simple glazes to complex fritted glazes and natural occurring clays. In many cases, however, the composition of neither the atmosphere nor the materials used were given and the name or type of ceramic ware or glaze tested only was indicated.[22]

While ceramic literature was first developing and scientific investigations of ceramic problems were initiated, the industry was using coal, then in the final stages of replacing wood as fuel. The burning was

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[22] Appendix I gives a summary of (1) types of furnaces used, (2) the nature of the atmosphere studied, and indicates whether or not the compositions of the ceramic materials or the atmospheres were given in the references cited.

generally made in direct-fired kilns where the fire box was in the side or bottom of the kiln and the combustion gases had free access to the ware. These gases were found to cause defects[23] in the development of glazes[24] such as blistering, spit-out, roughening, and color variations of the surface. With glasses,[25] enamels,[26] and other clay products,[27] scumming and color changes were the chief difficulties, but the defects noted with glazes were also experienced. The color changes were, for the most part, attributed to an oxidizing or reducing action, and the scumming attributed to the sulfur content in the atmosphere.

In order to remove this enormous dead-load in heating and rejection costs, the ceramic industry developed the muffle kiln to keep the ware out of contact of the flue gases. This apparently brought about an economical reduction in heavy ceramic products and clay wares,[28] because very few difficulties with the products were later reported. However, with glazes[29]

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[23] See AppendixIIfor a detailed review of causes and effects of various atmospheres.

[24] See A 13; B 2; C 6; G 2; H 17; P 4; M 16; M 17 (oil);S 2;B6.

[25] See A 7; L 2; P 3 (oil); S 3; W 1; W 5.

[26] See Q 8.

[27] See A 16; B 9; B 11; C 1; H 5 (natural gas); H 7; H 8; H 10; J 6 (natural gas); L 4; L 5 (natural gas); P 1; P 2; P 7; R 2; R 4.

[28] See B 1 where experiments on various atmospheres in commercial kilns were made but were not reported as actual operating difficulties.

[29] See A 6; A 8; C 7; E 5; F 2; W 7; O 1.

and enamels,[30] scumming, pinholing, and spit-out persisted. As in direct firing, the experimenters or operators, found that colors were affected by the state of the muffle atmosphere, and again attributed pinholing and spit-out to the action of sulfur in the muffle. The presence of these gases in the muffles is found to be derived from several sources, (1) the gases generated by the ware, (2) leakage through broken or otherwise faulty muffles, and (3) diffusion through the muffles. H. E. Ebright and co-authors (E 2) and recently G. H. Spencer-Strong and L. J. McMahon (S 7) have conducted experiments showing that water vapor with air atmospheres alone will cause scumming and sometimes blistering.

With the introduction of gas producers and other sources of cheap and efficient fuel gases, the economy of direct-firing appealed to the industry. Manufactured and by-product gases can be supplied free of many of the factors associated with coal firing which theory and commercial observation deemed responsible for uneconomical operation. This was shown to be true by observations on both glazes[31] and enamels,[32] and

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30. See A 9; E 2; R 3; S 7.
31. See G 7; M 4; R 5; W 3; W 4; W 8.
32. See A 1; A 14; G 7; G 8; P 9.

likewise on heavy clay products[33]. Reducing conditions, flame impingement, and overheating, were found to be the chief difficulties associated with direct gas firing and they were readily solved by proper furnace design. However, it was noticed that variations in oxygen and sulfur content of the gases had an effect upon the color and texture of the surfaces. This was particularly evident with glasses[34] and was also reported by Grady (G 7) and Andrews (A 1) upon glazes and enamels.

Laboratory tests followed commercial kiln observations. The purpose of those experiments reported in the literature as indicated above was to determine (1) the effect of the components of combustion gases, (2) the maximum concentrations permissible without giving noticeable effects, and (3) the influence of factors such as composition, temperature, and time. Some investigators[35] hold, in agreement with the industrial results, that there is no reaction when gas is burned under oxidizing condition. More[36] find, however, that a deposit or color is formed on the surface of glazes and glasses. All agree that reducing conditions are

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[33] See H 6.
[34] See M 14; Z 2.
[35] See L 3; W 2.
[36] See C 3; D 2; D 4; M 14; T 2; T 4; W 5.

unfavorable, and that all types of ceramic products will be attacked under reducing conditions. An exception is made, however, by M. W. Travers (T 5), and W. A. Weyland and A. B. Pincus (W 5), who find for glass that reducing conditions will lessen the action of combustion products.

The reported investigations attributed the formation of defects in oxidizing atmospheres to the presence of either sulfur dioxide or sulfur trioxide. When relatively pure sulfur dioxide gas is passed over ceramic ware, defects have been reported ranging from complete destruction to pinholes and color changes[37]. With dilute sulfur dioxide gas, as in combustion products or in air, efflorescence, feathering, pock-marks, pinholes, color changes, and scumming have been observed[38]. Such a wide variation of effects (even assuming different compositions of the materials)

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[37] See Footnotes 35 and 36 and A 4; A 5; B 13; C 7 M 12.
[38] See B 4; C 8; G 3; K 1; K 2; N 1; P 3; P 6; V 3.
(1) For Glazes, see B 8; G 5; J 6; M 10; W 2.
(2) For Glasses, see C 8; D 4; T 1.
(3) For Enamels, see A 2; A 3; A 4; A 5; K 3.
(4) For Miscellaneous Clay Products, see H 9; S 5.

warranted further experimentation, particularly because these facts do not agree with observations noted in industrial gas firing. Determinations of the minimum sulfur concentration required to cause defects on glazes ranged from three hundred and eleven (311) to thirty-five hundred (3500) grains sulfur dioxide per one hundred (100) cubic feet of gas products, on enamels from three (3) to twelve (12) grains of sulfur dioxide per one hundred (100) cubic feet; on glass two and five tenths (2.5) to twelve hundred and fifty (1250) grains sulfur dioxide per one hundred (100) cubic feet; and on miscellaneous claywares about six hundred (600) grains sulfur dioxide per one hundred (100) cubic feet.

If one neglects the concentration of sulfur dioxide that will be harmful to enamels, the remaining minimum concentrations, although varying considerably, are much above that which will ordinarily occur in producer, or other manufactured gases. This leads to the possibility of another factor operating; for example, the oxygen content of the gas. As has been discussed[39], the oxidizing or reducing power of combustion products influences the final state of the ceramic product to a

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[39] See page 41 and reference B 12 on type of analyses required, i.e. complete, not just O_2 and CO_2.

marked extent. Experiments made by varying the oxygen[40] content (in agreement with practical observations) show that (1) for glazes four (4) to ten (10) percent oxygen should be present, (2) for enamels seven (7) to twenty-one(21) percent oxygen, and (3) for miscellaneous clay ware three (3) to six (6) percent excess oxygen.

In the firing of ceramic ware in an oxidizing atmosphere, the two products of combustion in largest proportions are carbon dioxide and water. According to most authors, atmospheres of carbon dioxide, or of carbon dioxide mixed with neutral gases, produced blistering and pitting.[41] When admitted with oxygen, however[42], there is no apparent effect. E. E. Geisinger and K. Berlinghof (G 3), and also A. Pfaff (P 5) on the other hand find no effect with carbon dioxide atmospheres.

Water vapor, too has a definite effect on ceramic processes[43]. It causes blistering, bubbles, darkening and color changes similar to reducing

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[40] See Al; A 14; H 6; K 3; L 5; P 9; V 3; W 3; W 4.

[41] See A 2; A 3; A 4; B 1; B 4; C 5; E 2; H 11; N 1; P 6; P 9; R 7; V 3; W 2.

[42] Recommended: five (5) percent oxygen with eleven (11) percent carbon dioxide, for glazes and seven and three tenths (7.3) percent oxygen with seven (7) percent carbon dioxide for enamels.

[43] See B 1; B 15; C 1; D 7; E 1; E 2; G 3; K 1; K 2; M 16; R 5; V 3; W 2.

atmospheres, to which its action is often attributed, either by reduction of the oxygen content or by dissociation. It is well to remember, however, that the amounts of water used in these determinations are, in many cases, above that normally found in combustion products. Water, also, increases the activity of sulfur dioxide attack; this may be deemed a support for the sulfuric acid theory. H. E. Ebright and G. H. McIntyre (E 1) recommend for enameling furnaces, that the water vapor content be kept below one (1) percent, and in a later article, the same authors in collaboration with J. I. Irwin (E 2) find that three and one-half ($3\frac{1}{2}$) percent water vapor with the acidic gases of about one-half ($\frac{1}{2}$) percent will cause blistering and scumming. W. E. Badger (B 1) finds that a water vapor atmosphere aids the vitrification of ceramic ware, in spite of its reducing action on colored ware.

The effects of many other volatile or gaseous substances have been noted[44]. Some of these are hydrocarbons, carbon monoxide, nitrogen, various acids, and those substances which may be used for vapor glazing, or may be included in the combustion products

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[44] A discussion of some of these effects may be found in investigations by A. P. Watts (W 2) E. E. Geisinger and K. Berlinghof (G 3), A. F. Green and F. H. Clews (G 8), A. E. J. Vickers (V 3), H. L. Longnecker (L 4), A. E. Badger (B 1) and S. M. Phelps (P 7).

of fuels. These materials are not commonly found in combustion products, nor has their action been investigated beyond pure atmospheres.

D. METHOD OF EXPRESSING RESULTS

Ceramic wares are glazed for decoration, to decrease chemical activity and porosity, and to increase durability to abrasion and other mechanical attack. The tests made upon the finished product have been designed to determine the degree to which these ends have been attained. As the early ceramic industries were concerned with pottery, dishware, and decorative tile, the first tests made were visual and later photographic. With the advent of greater demand for uniformity in colors, tints, and other surface appearances, the science of physics began to be applied to the problems, resulting in many types of color matching methods such as visual inspection, the use of various tintometers, and the analysis of reflected light. As the industry entered the construction fields, demands for mechanical performance arose and suitable instruments for the measurement of various phases of such performance were developed.

For ceramic ware designated for the general public use, such as china and porcelain ware, enamel objects, and facing bricks, the method usually employed has been visual and the expression of the observations by word pictures continues. Such reports have been illustrated in a very high percentage of the citations reviewed in earlier sections of this dissertation. The practice is common in both industrial and laboratory reports. It is evident that this method will be dependent upon the vocabulary, the eyesight and other human characteristics of the examiner. In addition, this type of test fails in the determination of small differences and, for the reasons given, often to convey the desired knowledge to other investigators. The use of photographs[45] is one answer but often requires either a large amount of space (as do descriptions) or special equipment, (i.e. for photomicrographs), and expense, particularly in color work.[46]

The investigation of lead poisoning from glazes introduced solubility tests[47] for sulfates and other soluble substances as well as for lead compounds. With the exceptions of legal requirements upon lead, there is no standatdization of solubility tests, each investigation or industrial concern using individual standards.

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45. See references B13; E 5; G 3; M 10; and R 9, for the photographic expressions in the literature, and references E 3 and P 8 for those using photomicrographs.
46. See P 6 for color prints.
47. See C 8; G 4; K 2; M 11.

The determination of porosity has been standardized and methods may be found among the tests suggested by the American Society for Testing Materials.[48] Glazed and enameled wares, in the glazing or enameling process, have their porosity decreased to a negligible amount; accordingly, porosity is not usually determined upon this type of ceramic product.

Durability[49] has become an important consideration in the selection of ceramic ware for construction purposes and in the development of tableware of lasting qualities. One method of examination is known as "metal marking".[50] It is a measure of the susceptibility of glazes (or enamels) to marking with various metals and alloys. Care must be exercised that scratching of the surface is not interpreted as a metal mark, which consists of leaving a thin film of the metal on the ware.

A number of methods[51] for the determination of

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48. See D 116-34; C 20-33; C 4-24; and others in their publications.
49. For impact resistance, see R 8.
50. See A 17; G 4.
51. The following methods have appeared only recently in the literature and refer in general to treatment of glasses and enamels. The discussion upon light reflectivity is derived from articles on paper and varnishes and are included because, in the opinion of the writer of this dissertation, they may afford some information on glazes and enamels.

abrasive hardness, as a measure of durability, have been developed. Of these, there are in use, (1) the abrasive wheel, (2) the sand blast, (3) cylinder rotation, (4) needle scratching, and (5) a resistance to free-falling sand. The first three of the above mentioned methods are difficult to standardize and offer no guarantee of equal forces upon the test piece throughout the run. The fourth method, that of scratching, depends upon the sharpness of the point, the pressure on the point, and the manner in which the point is applied; the scratch is not easily analyzed for depth of penetration. The method depending on the resistance to wear of falling sand may be measured by decrease in weight or by the changing in amount of reflected light (which will be discussed later). This method, however, is dependent upon the humidity and the wear of the sand grains.

Changes in the surface characteristics, either in smoothness[52] or color may be measured by changes in amount of reflected light. The equipment recommended for such results is too expensive for plant control

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52. See A 10; A 12, on enamels and H 14; H 15, and H 16 on the general theory of refectivity studies. An excellent bibliography is found in H 15 upon this subject.

work, but substantially equivalent equipment could be constructed readily. J. Konarzewski and A. E. J. Vickers (K 1) used a simple Lovibond Tintometer to express colors, while other investigators[53] have suggested highly developed photoelectric arrangements for precision color determination.

Although verbal descriptions are verbose and space consuming, they are the general method of reporting results of action of gaseous atmospheres upon ceramic processes. They are often supplemented by solubility data and by photographs. Various mechanical testing methods have been developed for clay ware and commercial products as a whole, e.g. such finished products as porcelain insulators, enameled ware, glass and tableware, but few have been suggested for use upon a glazed or enamel surface independent of the body properties. A recent development in the field of paints and varnishes, the determination of blemishes and colors by reflected light, has already entered the enamel field but it has apparently not been applied very much in investigations of enamels or glazed ware.

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53. See M 15; R 6; S 8; V 1.

III. EXPERIMENTAL

A. INTRODUCTORY

The foregoing review indicates (1) that the data upon the action of combustion atmospheres upon ceramic ware is limited; (2) that the reproduction or intercomparison of most, if not all, of the experiments would be difficult because (a) the compositions of either the ware or the atmospheres used were unknown or (b) the majority of the results was obtained upon industrial installations; (3) and that the methods used for the expression of the effects are subject to variations due to the observer, particularly his eyesight and his command of descriptive rhetoric.

The work herein described was undertaken primarily in the hope of determining the effect of combustion products upon ceramic ware with some regard to chemical conditions that might be found in industrial atmospheres, and secondly, of suggesting a simple, rapid, and reproducible method for determining such an effect. Three possible methods of expressing the results of such experimentation are compared.

In order that the work may be reproduced, or compared with other work, the composition of the materials and the analysis of the furnace atmospheres employed are given.

Of the fuels used in published studies,[54] gaseous fuels appeared advantageous in that their composition is fairly uniform and the products of combustion at all stages of firing are substantially constant. Analyses made upon the gas supplied did show some variations over the period of experimentation. Such variation is encountered in most manufactured gases, however, and it was therefore not deemed necessary to control these variations further.

The ceramic ware tested was raw glazes (of the Bristol type) maturing at 1200° C., chosen to represent glazes maturing at a temperature for which direct firing would be profitable and in the temperature range toward which modern trends are approaching.

The test used for determination of sulfur present was chosen because of its rapidity. The results are indicative of the magnitude of the concentration present.

Several devices were studied for the combustion of

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[54] Although the apparatus was designed for the burning of manufactured gas, similar tests may be run with-variations only in the combustion chamber for the use of coal or oil.

the gas in a confined space so that the composition would not change before it came in contact with the ware. Some of these included metallic chambers; chambers connected with rubber tubing; and entire glass apparatus. The glass chambers were considered the most satisfactory because analysis of the products showed that these gave results agreeing with theoretical considerations. Several methods for the removal and analysis of sulfur dioxide from the combustion products were tried. The method selected was found to be reproducible and rapid.

B. APPARATUS

The determination of the effect of combustion of manufactured gas upon glazed ware may be divided into two parts: first, the production of a glaze under an atmosphere of the combustion products, and second, the measurement of the effect of changes in the atmosphere upon the glaze produced.

Reports upon the production of a glaze under an atmosphere of combustion products in the laboratory are not common. Dettmer (D 2) and A. P. Watts (W 2) use conditions[55] similar to those developed for these experiments. The present tests are, however, distinctive in the fact that care is exercised in preventing the admittance of uncontrolled air.[56] By having all connections of tightly fitting glass between the combustion chamber and the firing chamber for the ware, no air was allowed to enter and the combustion products were not changed by reaction with

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[55] See Figures 1 and 2 for schematic diagram and pictures of apparatus.

[56] A. P. Watts (W 3 and W 4) developed a large size kiln for the direct firing of glazed wares suitable for heating with gas alone in which the entrance of air and gas was controlled.

metal surfaces. The combustion chamber was equipped with an inlet for secondary air, with a connection for the entrance of the spark coil lead (the second lead being through the blast lamp)[57]. In addition, a connection was made for a manometer near the outlet, and an explosion head was provided by a thin sheet of aluminum foil. (Figure 3).

The explosion head was very efficient. Several trials were made by admitting explosive mixtures of gas and air into the chamber and igniting with a spark. Explosions resulting would rip the foil away but would not injure any of the apparatus.

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57. The design was a modification of the U. S. Bureau of Standards (Drehschmidt) method; discussion of which may be found in the Bureau of Standards Circular No. 48 (1916) and pages 351-355, L. M. Dennis and M. L. Nichols, "Gas Analysis", The Macmillen Company, New York, 1929.

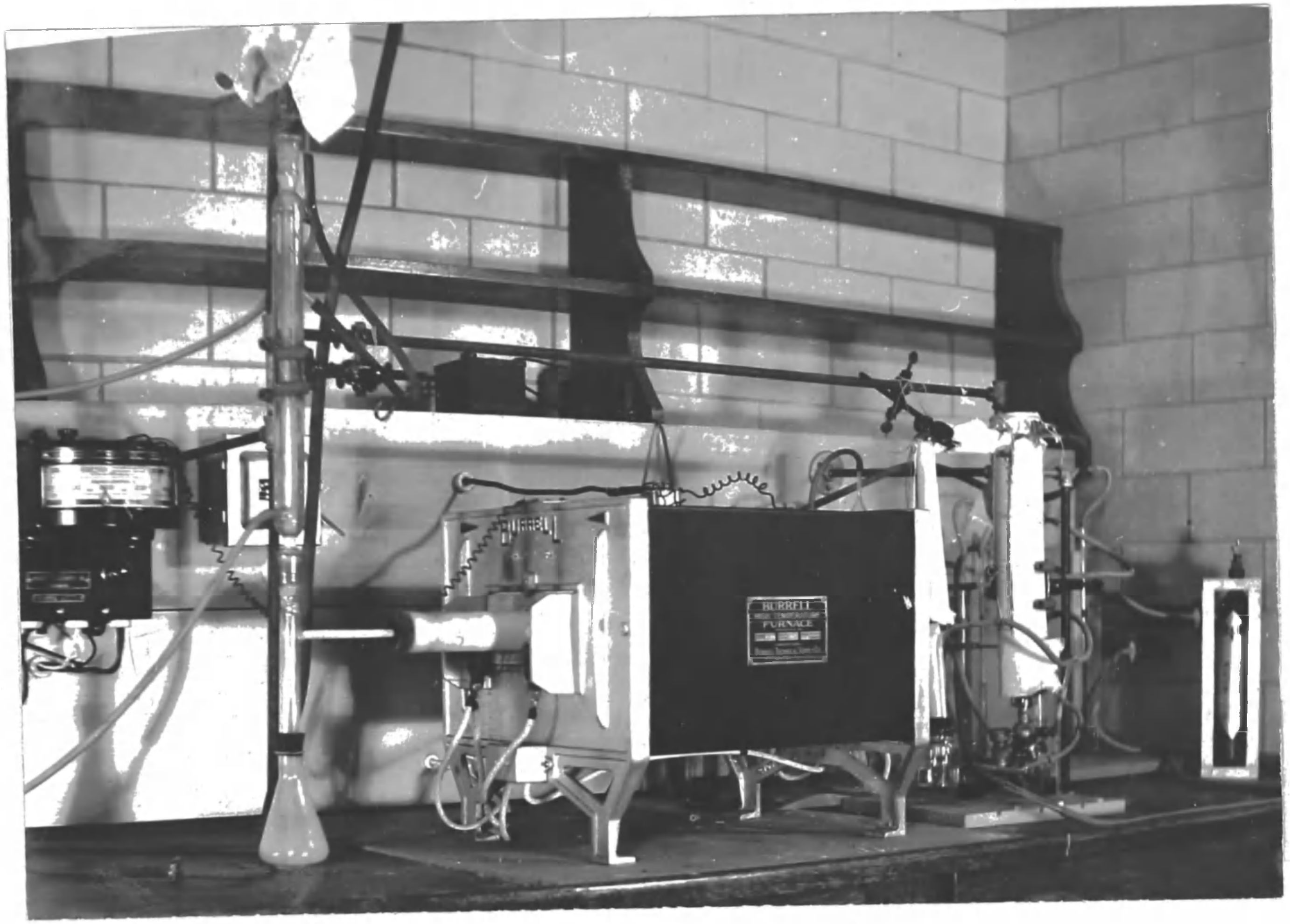
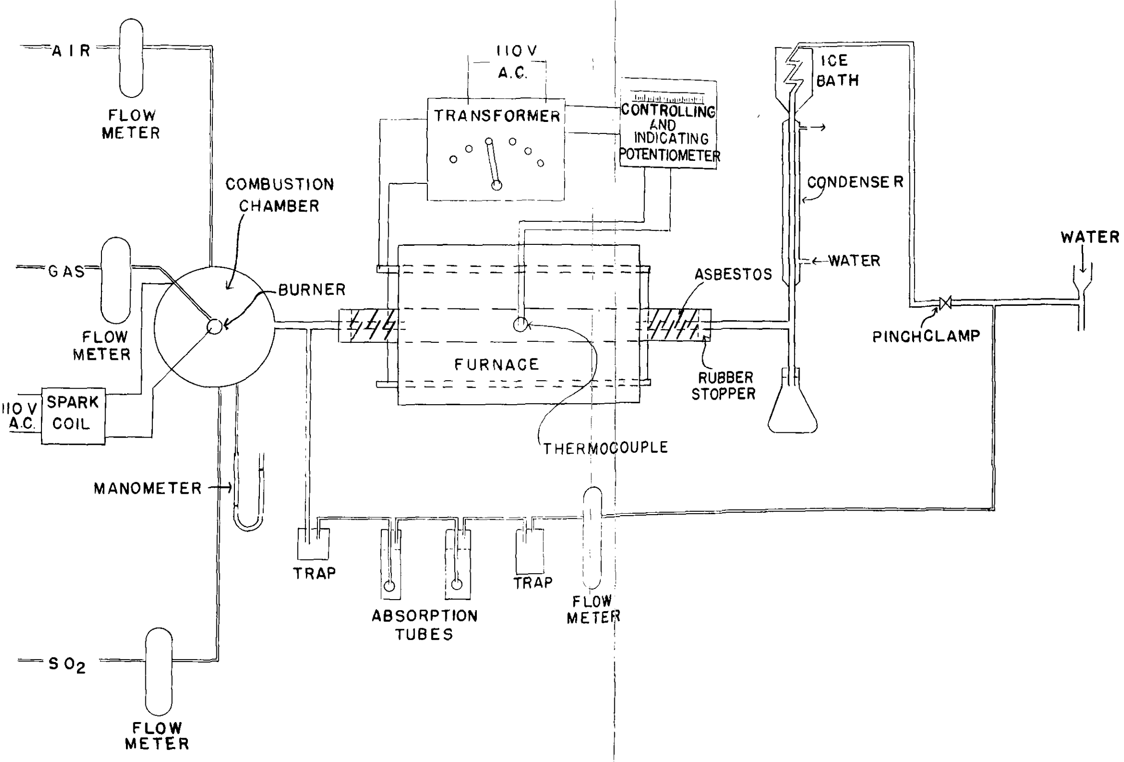


Figure 1.
GENERAL VIEW OF APPARATUS USED FOR CONTROL OF FURNACE ATMOSPHERES, TEMPERATURE, AND GAS VELOCITY

FIGURE 2 -

SCHEMATIC DIAGRAM OF APPARATUS



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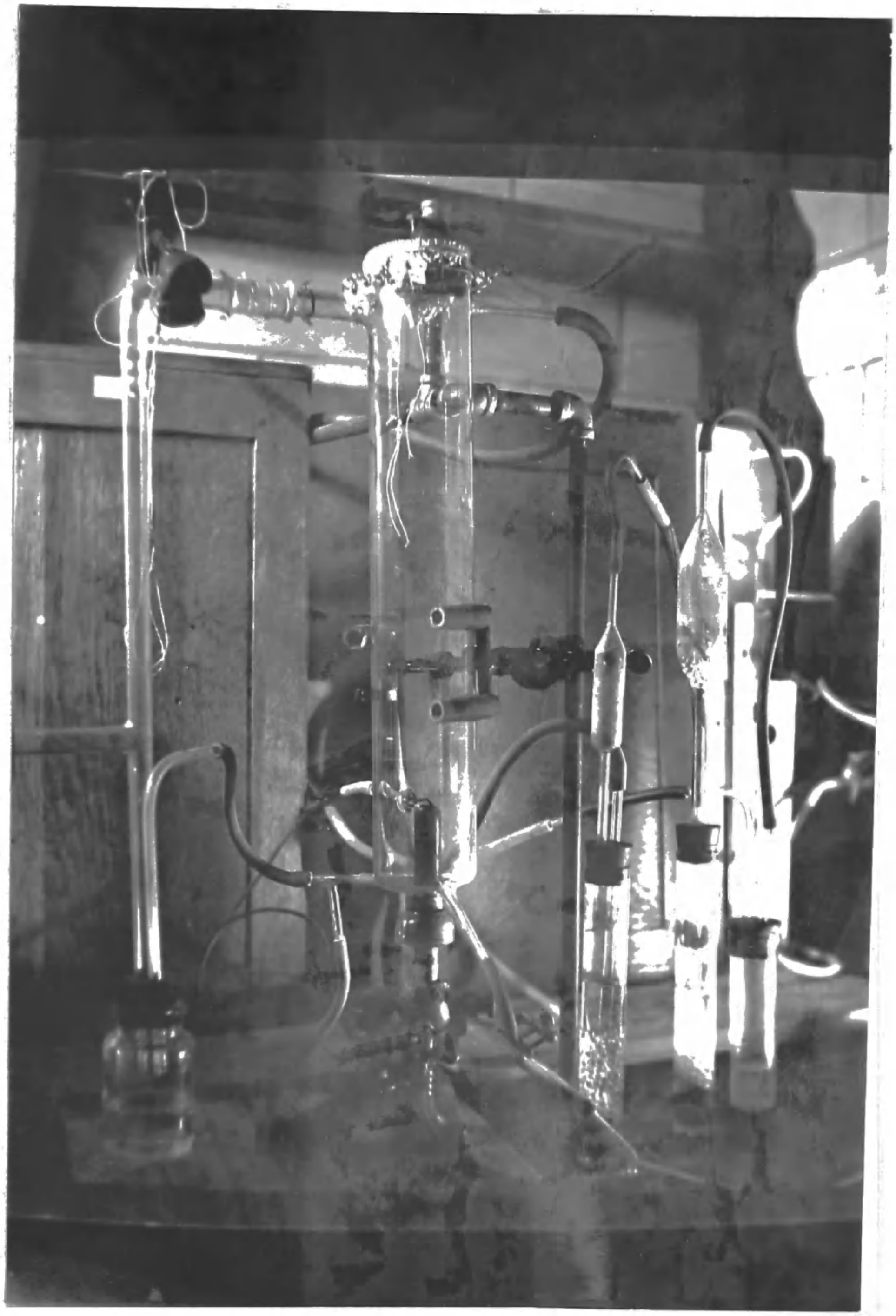

Figure 3.

COMBUSTION CHAMBER AND

ABSORPTION TRAIN

In order to insure as complete combustion as possible, a fine mesh copper screen was placed over the burner opening. The resulting flame cone did not exceed an inch in height. The chamber was insulated with asbestos to avoid chilling of the gases and consequent shifting of their equilibria. To check the degree of combustion, complete analyses were made before and after the combustion products had passed through the firing zone (when the temperature was at 1200°C.) (Table 1). The results showed that essentially all the combustion was taking place in the combustion chamber under the various conditions of firing employed.

The pressure was maintained at approximate atmospheric pressure by means of suction. The variations were not greater than a half inch of Meriam Red Oil[58](or 0.42 inches of water) under the extreme conditions.

The admission of air and city gas was controlled by wall cocks, other gases by pressure valves from tanks. The streams were passed through calibrated flow meters (note Table 2 and Graph 1) and into the

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[58] Meriam Red Oil was obtained from the Meriam Company, Columbus, Ohio with a specific gravity of 1.181.

combustion chamber to be burned or mixed as the case required.

The flow meters were of the U-bend type across the ends of which were orifices drawn from Pyrex glass capillary tubing. In general, the flow meters were capable of showing a difference in head of about a foot. The orifices were joined to the flow meters by rubber tubing, and were so drawn that the range of volumes of gases desired could be obtained. The indicating liquid was Meriam Red Oil.

TABLE 1

GAS ANALYSIS

Subject	CO_2	Ill.	O_2	H_2	CO	CH_4	C_2H_6	N_2	% Theor Air
City									
Gas (1)	2.3	1.6	0.6	30.7	15.3	36.4	1.6	11.5	0
(2)	2.3	1.5	1.0	31.3	14.2	36.5	1.2	12.0	0
Average	2.3	1.5	0.8	31.0	14.8	36.4	1.5	11.7	0
<u>Combustion</u> <u>Products</u>									
A- (a)[59]	9.0	-	6.3	0.5	0.3	-	-	83.9	137.1
(b)	9.2	-	5.7	-	0.3	-	-	84.8	132.3
Average	9.1	-	6.0	0.3	0.3	-	-	84.3	135.2
B- (a) (1)	11.7	-	1.7	-	-	-	-	86.6	108.2
(2)	12.1	-	0.9	-	-	-	-	87.0	104.2
(b)	12.2	-	1.2	-	-	-	-	86.3	105.7
Average	12.0	-	1.3	-	-	-	-	86.7	106.2
C[60] (a)(1)	11.2	-	1.3	1.6	1.3	0.3	-	84.3	97.1
(2)	11.6	-	0.7	2.2	1.5	0.4	-	83.6	91.5
(b)	11.5	-	0.6	1.3	1.0	0.2	-	85.4	95.6
Average	11.4	-	0.8	1.7	1.3	0.3	-	84.4	94.4
D[60] (a)(1)	10.3	0.2	1.4	3.2	3.0	0.3	-	81.6	87.8
(2)	10.3	-	1.5	3.1	2.9	0.5	-	81.3	89.3
(b)	11.2	-	0.3	3.0	2.8	0.2	-	82.5	87.6
Average	10.8	0.1	1.1	3.1	2.9	0.3	-	81.8	88.2
E[60] (a) (1)	7.1	-	1.3	6.4	6.6	0.6	-	78.0	75.8
(2)	6.2	0.1	0.2	7.3	7.8	1.4	-	77.0	65.1
(b)	7.9	0.2	0.3	6.0	5.9	0.4	-	80.3	74.4
Average	7.1	0.1	0.6	6.6	6.8	0.8	-	78.0	71.6

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[59] (a) and (b) refer to samples taken before and after passage through firing zone at 1200°C.

[60] Carbon was deposited.

TABLE 2

CALIBRATION OF FLOW METERS

Manometer No.	Material		Temperature	Scale Reading (left) cms.	Time sec.	Amt. water measured cc.	Rate of flow (cu. ft./hr.)
	Used	Tested					
1	air	gas	70	zero (50.6)	-	1000	-
				53.0	30.6		
					30.6		4.15
				54.0	24.4	1000	
					26.3		
					25.0		5.05
				54.5	23.0	1000	
					22.5		
					22.0		5.65
				55.0	20.8	1000	
					21.4		
					22.0		5.95
				58.1	15.1	1000	
					15.3		
					14.9		8.40
2	gas	gas	70	zero (41.9)	-	-	-
				43.9	289.2	1000	
					288.5		
					289.0		0.44
				45.5	185.0	1000	
					187.0		
					185.8		0.685
				47.9	125.0	1000	
					130.0		
					126.8		1.00
				50.1	104.0	1000	
					105.8		
					108.0		1.20
				55.9	78.4	1000	
					78.8		
					78.2		1.62

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61. Cubic feet per hour = $\frac{3600}{(t(sec)\text{per liter})(28.32)} = \frac{127.1}{t(sec)\text{ per liter}}$

TABLE 2 (CONT'D.)

Manometer No.	Material		Temperature	Scale Reading (left) cms.	Time sec.	Amt. water measured cc.	Rate of flow (cu. ft./hr.)
	Used	Tested					
3	SO_2	Air	70°	zero (16.9)	-	-	-
					1138.0	10	
				18.5	1204.5		
					1131.5		1.10×10^{-3}
					514.4	10	
				20.5	630.8		
					523.8		2.43×10^{-3}
					333.8	10	
				22.5	335.4		
					336.4		3.80×10^{-3}
					174.4	10	
					175.5		
				27.4	171.8		7.29×10^{-3}
					133.4	10	
				30.6	133.8		
					130.5		9.60×10^{-3}
4	C.P.[62]	Air	70°	zero (73.3)			
					57.2	1000	
				74.3	58.8		
					57.4		2.20
					39.2	1000	
				75.2	40.4		
					38.9		3.22
					24.5	1000	
				77.4	25.2		
					24.5		5.13
					19.3	1000	
				79.7	18.2		
					19.2		6.72
					15.5	1000	
				83.2	13.8		
					13.6		8.91

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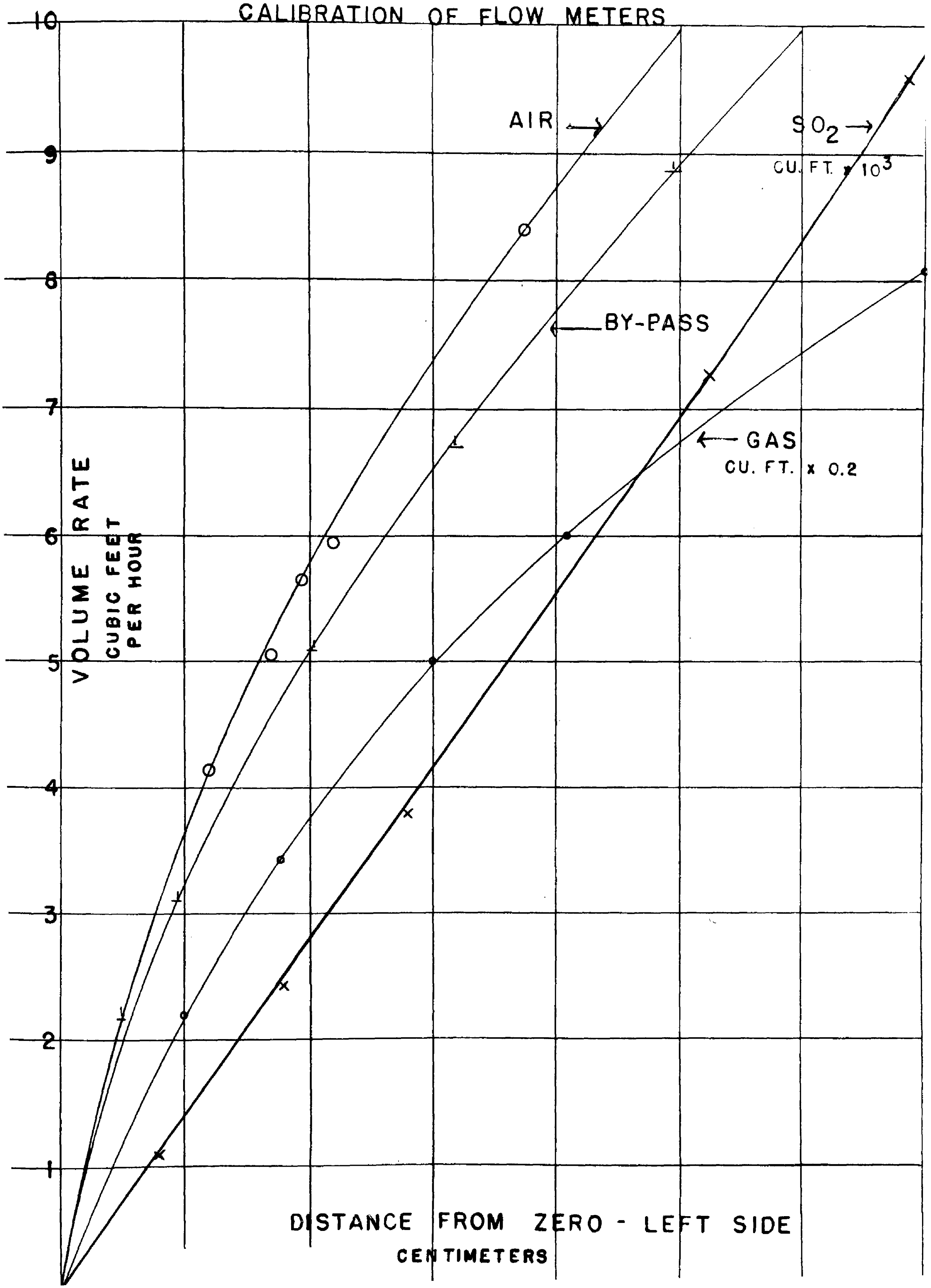
[62] By-pass flow meter for combustion products.



CALIBRATION OF FLOW METERS

The flow meters were calibrated with the gas to be measured. The gas was allowed to flow through the orifice and displace water in a jar. The volume of displaced water was measured under known pressure conditions and the time for a definite volume to flow was observed. The reproducibilities for small and large flow meter readings were not all that might be desired but for intermediate readings the flows (varying with the orifices used) checked within plus or minus two-tenths (± 0.2) second. The meter readings were constant during calibration but varied slightly[63] during the experimental studies for several causes, such as fluctuations in suction and burner pressures.

The firing chamber consists of a dual element Globar type furnace with a one and seventy-five hundredths (1.75) inch inside diameter non-porous high temperature McDaniel combustion tube. There is a central six (6) inch zone of uniform heating[64]. A Platinum-Platinum 13% Rhodium thermocouple, located in the center of the heated zone, controls the power input through an indicating-proportioning controller warranted to maintain temperatures within ± five (5)°C.

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[63] See Table 3.

[64] By thermocouple exploration.

TABLE 3

VARIATION IN FLOW METERS

Flow Meter Setting (Cms.)		Average		Deviation[65]		Average[66] Deviation		Deviation of Setting (cms.)	Av. Deviation of setting (cms.)	Av. Deviation of volume (cu.ft./hr.)
		One liter Time (sec.)	Volume (cu.ft./hr.)	Time (sec.)	Volume (cu.ft./hr.)	Time (sec.)	Volume (cu.ft./hr.)			
				plus or minus	plus or minus	plus or minus		plus or minus	plus or minus	plus or minus
Air	53.0	30.6[5]	4.15	0.2	0.02			0.1		
	54.0	25.2	5.05	0.7	0.14			0.1		
	54.5	22.5	5.65	0.5	0.13			0.1		
	55.0	21.4	5.95	0.6	0.17			0.1		
	58.1	15.1	8.40	0.2	0.09	0.4	0.11	0.2	0.1	0.09
Gas	43.9	288.9	0.44	0.5	0.00			-		
	45.5	185.9	0.69	0.7	0.01			-		
	47.9	127.3	1.00	1.8	0.02			-		
	50.1	105.9	1.20	1.6	0.02			0.5	0.5	0.05
	55.9	78.5	1.62	0.2	0.01	1.0	0.01	-		
SO_2	18.5	1158x10^2	1.10x10^{-3}	31x10^2	0.03x10^{-3}			0.3		
	20.5	556.3x10^2	2.43x10^{-3}	50x10^2	0.33x10^{-3}			0.2		
	22.5	335.2x10^2	3.80x10^{-3}	0.9x10^2	0.02x10^{-3}			0.2	0.2	0.28x10^{-3}
	27.4	174.2x10^2	7.29x10^{-3}	1.6x10^2	0.05x10^{-3}			-		
	30.6	132.6x10^2	9.60x10^{-3}	1.3x10^2	0.10x10^{-3}	17x10^2	0.11x10^{-3}	-		
By-Pass	74.3	57.8	2.20	0.7	0.03			0.2		
	75.2	39.5	3.22	0.5	0.04			0.2		
	77.9	24.8	5.13	0.3	0.06			0.2		
	79.7	18.9	6.72	0.5	0.17			0.2		
	83.2	14.3	8.91	0.8	0.48	0.6	0.16	0.2	0.2	0.22

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65. Deviation = (mean - observed)

66. Average deviation = $\frac{\text{Summation of deviations}}{\text{Number of observations}}$

The ends of the firing tube are sufficiently removed from the furnace for the use of hard rubber stoppers. The stoppers are protected by asbestos guards to prevent heating by radiation and contact with the combustion products.

The outlet of the tube is connected to a condenser and cooling coil in which the water of combustion is condensed. The gases leaving the coil are saturated at $15^{o}C$.

Suction for drawing the atmosphere through the furnace was first obtained by an air-pump, but after preliminary tests, when some failures were experienced, a water pump was substituted and is found satisfactory. In order to maintain an approximately constant rate of flow in the firing zone, the gas stream is divided into two parts. A constant volume is allowed to go through the furnace. By determining the total volume, subtracting the constant volume and adjusting a by-pass line through a flow meter to read the remainder, this adjustment is readily made. By varying both the suction applied and the open cross section area of the line leading from the furnace, (See Figure 2) the pressure within the furnace is maintained at atmospheric pressure.

The by-passed gases are relieved of their excess water vapor by passage into a cooled trap. Then, by means of a series of absorption tubes equipped with diffusion balls emersed in slightly alkaline solution, the readily water soluble gases are absorbed and the remaining gases measured by a calibrated flow meter. (See Table 1).

When atmospheres containing controlled moisture content are desired, a water scrubber is inserted in an air line which by-passes the combustion chamber described above. By regulating the temperature of such a scrubber, the amount of water contained in the air can be regulated. When relatively dry atmospheres are desired, two calcium chloride drying towers are inserted in place of the water scrubber. The result of such action is an atmosphere which allows no condensation in the cooling system previously described; such an atmosphere shall be referred to as a dry atmosphere in later discussion.

The effect of combustion products of different compositions and of other atmospheres is recorded by descriptions and by photomicrographs.[67] In addition,

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[67] A Bausch and Lomb Microscope with a camera of fixed-focus attachment. See Figure 4. The power used was 50x.

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---

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a rough reflectometer was constructed (Figures 5 and 6 with Table 4). This consists essentially of an incandescent lamp, a two-inch square tube for the passage of the light, and a holder for the test specimens so that readings at normal and about sixty-seven (67°) degrees to the normal might be observed. The reflected light values are measured by a copper oxide photoelectric cell and read from a direct current ammeter connected therewith[68]. The reproducibility of the readings depends primarily upon the reproducibility of the voltage applied to the light source.

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[68] Knight-Beeche Foundation Meter; D. C.-Volt-Ohm Microammeter 20,000 ohms per volt Number A 2333.

TABLE 4

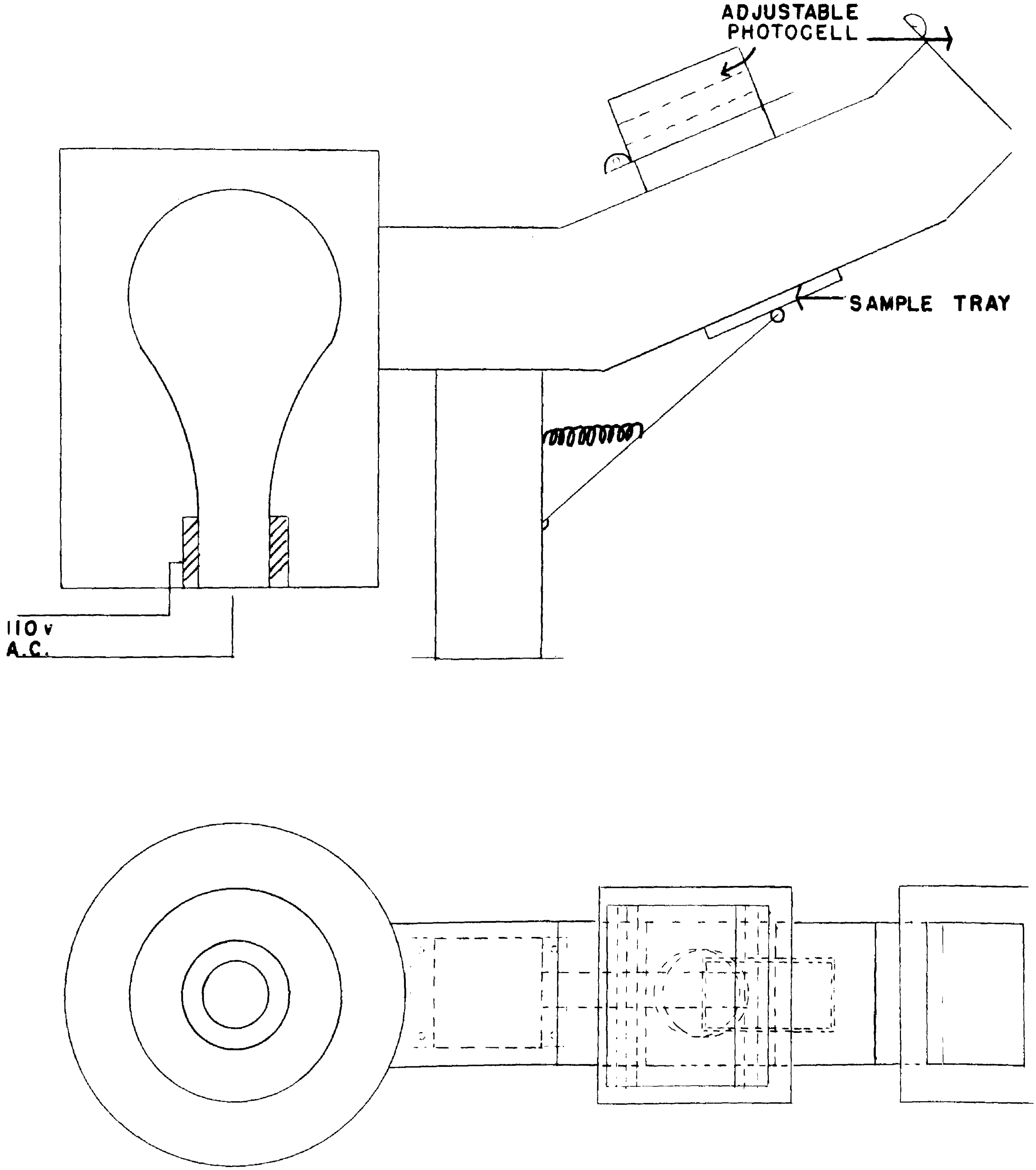
REFLECTOMETER DIMENSIONS

A 1 -	Light Source to Sample	5½ inches
2 -	(a) Sample to Receptor (angular)	4 inches
	(b) Sample to Receptor (perpendicular)	2½ inches
3 -	(a) Diameter of Source	2 inches
	(b) Diameter of Receptor	1½ inches
4 -	(a) Angle of Incidence	67.5°
	(b) Angle of View	67.5°
5 -	Area Illuminated (Sample)	1¾ x 7/8"
B 1 -	Light - Incandescent Lamp (frosted)	150 watts
	Receptor - Weston Cell No. 548	

Figure 4.

PHOTOGRAPH OF MICROSCOPE AND CAMERA

FIGURE 5.-
SKETCH OF REFLECTOMETER



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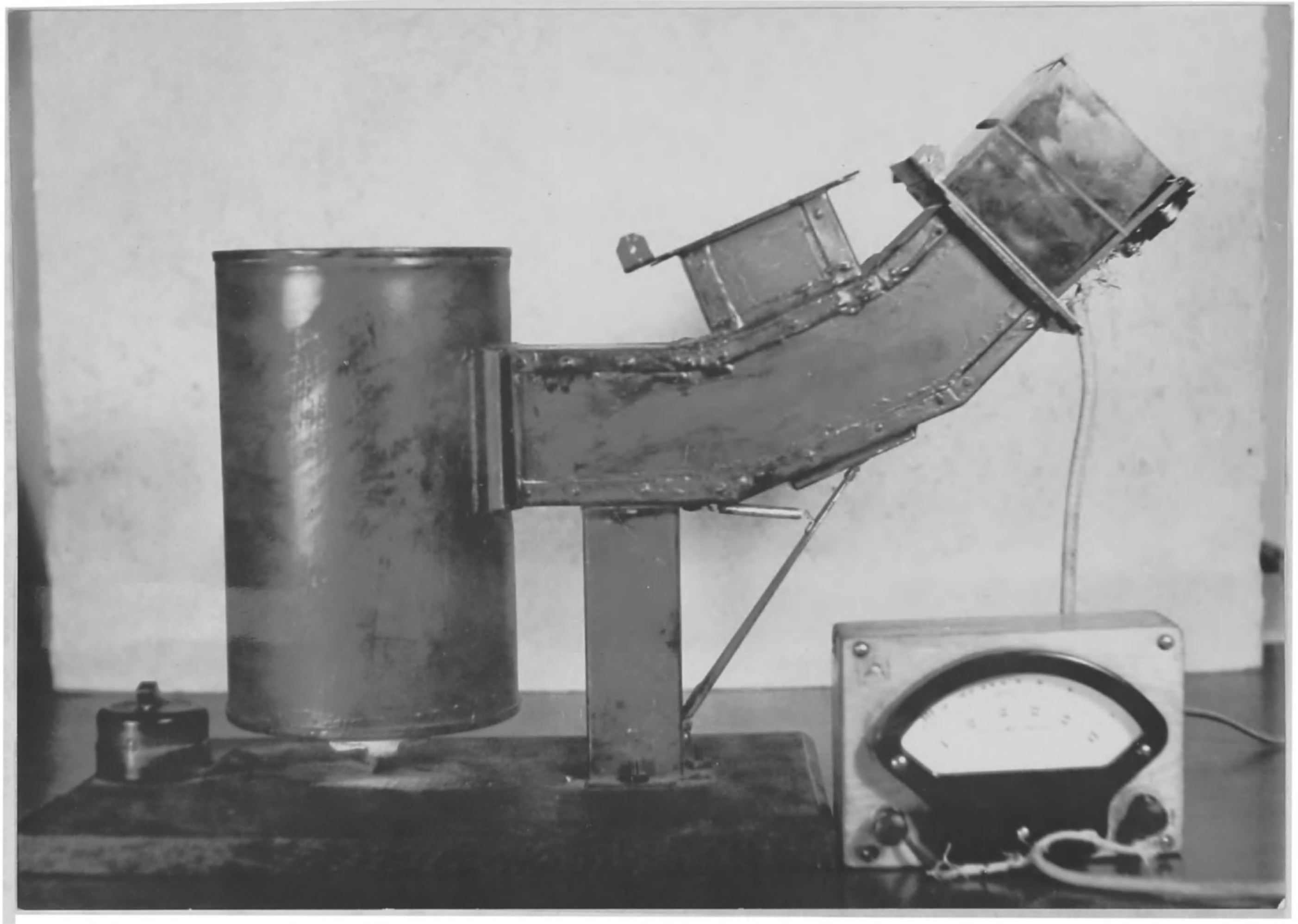

Figure 6.

PHOTOGRAPH OF REFLECTOMETER

C. MATERIALS

The raw materials for the production of the glazed ware desired are obtained for the most part from "C.P" chemicals.[69] The body, however, was not developed in the laboratory but consists of a white unglazed flooring tile with dimensions of 2 x 1 x $\frac{1}{4}$ inches.

In the preliminary work, the composition of neither the body nor the glazes used was known. The only data available were that they were fired at 940°C for a white glaze and at 1200°C for the blue-green glaze.[70]

The glazes for the later experiments are compounded from the raw materials. Only the composition of the acceptable glazes was reported. The formulae[71] are simple in order that possible variations in composition can be made and their effects noted. From the fundamental white glaze (Ca-10), substitutions and additions of metals, commonly used for coloring and

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[69] Analysis and composition of the raw materials and body used is given in Appendix III .

[70] The glazes described were commercial glazes and were not run through the series of tests used.

[71] See Table 5 for the batch weights and formula of the glazes used.

other properties, are made. All the resulting glazes were fired at 1200°C. Although this may not be the best maturing temperature, all the colors and surfaces obtained in air firing are fair and are taken as the standard.

The materials[72] are weighed, water added, and mixed in a pebble mill to break up lumps and insure uniformity. The mixtures are stored in tightly closed jars to prevent evaporation of water. Before the glaze is applied to the tiles, the jar is placed upon a set of rollers and allowed to roll for about twelve (12) hours.

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[72] The raw materials were all ground to pass a 200 mesh screen.

TABLE 5

GLAZE COMPOSITIONS

Key	Formula						Batch Weight	
							Substance	.Weight (grams)
Sn - 7	K_2O	0.15						
	CaO	0.56	Al_2O_3	0.37	SiO_2 SnO_2	3.52 0.13	Flint	87.8
	ZnO	0.29					Feldspar	58.5
							Kaolin	40.7
							Whiting	38.1
							Zinc Oxide	16.5
							Tin Oxide	13.5
								255.1
							Water 250 cc	
Ca - 10	CaO	0.65						
	K_2O	0.15	Al_2O_3	0.25	SiO_2	2.85	Flint	87.8
	ZnO	0.20					Feldspar	66.0
							Kaolin	20.4
							Whiting	51.8
							Zinc Oxide	12.9
								238.9
							Water 200 cc	
Pb - 11	PbO	0.65						
	K_2O	0.15	Al_2O_3	0.40	SiO_2	4.56	Flint	87.8
	ZnO	0.20					Feldspar	38.7
							Kaolin	29.9
							Basic Carbonate	77.9
							Zinc Oxide	7.6
								241.9
							Water 250 cc	

TABLE 5 CONT'D.

Key	Formula						Batch Weight	
							Substance	Weight (grams)
Co - 1	CaO	0.65						
	K_2O	0.15	Al_2O_3	0.22	SiO_2	2.50	Flint	87.8
			Co_2O_3	0.29				
	ZnO	0.20					Feldspar	83.5
							Kaolin	18.1
							Whiting	65.1
							Zinc Oxide	16.3
							Cobaltic Oxide	46.1
								316.9
							Water 250 cc	
Cr - 2	CaO	0.65						
			Al_2O_3	0.22				
	K_2O	0.15			SiO_2	2.50	Flint	87.8
			Cr_2O_3	0.10				
	ZnO	0.20					Feldspar	83.5
							Kaolin	18.1
							Whiting	65.1
							Zinc Oxide	16.3
							Chromic Oxide	15.2
								286.0
							Water 250 cc	

TABLE 5 CONT'D.

Key	Formula						Batch Weight	
							Substance	Weight (Grams)
Mn - 1	CaO	0.65						
	K_2O	0.15	Al_2O_3	0.22	SiO_2	2.50	Flint	87.8
	ZnO	0.20	Mn_2O_3	0.25			Feldspar	83.5
							Kaolin	18.1
							Whiting	65.1
							Zinc Oxide	16.3
							Manganese Carbonate	28.7
								299.5
							Water 250 cc	
Ni - 1	CaO	0.54						
	K_2O	0.12	Al_2O_3	0.18	SiO_2	2.04	Flint	87.8
	ZnO	0.17						
	NiO	0.17					Feldspar	83.5
							Kaolin	18.1
							Whiting	65.1
							Zinc Oxide	16.3
							Nickelic Oxide	15.2
								286.0
							Water 250 cc	
Fe - 5	CaO	0.41						
	K_2O	0.09	Al_2O_3	0.22	SiO_2	2.50	Flint	87.8
	ZnO	0.13						
	Fe	0.37					Feldspar	46.0
							Kaolin	28.5
							Whiting	35.9
							Zinc Oxide	9.0
							Ferric Oxide (red)	25.4
								232.6
							Water 165 cc	

TABLE 6

GLAZE COMPOSITIONS

Glaze in Percentages

Material	Sn-7	Ca-10	Pb-11	Co-1	Cr-2	Mn-1	Ni-1	Fe-5	Av.
Flint	34.5	36.8	36.3	27.8	30.7	29.3	30.7	37.7	33.0
Feldspar	22.9	27.6	16.0	26.3	29.2	27.9	29.2	19.8	24.9
Kaolin	15.9	8.5	12.4	5.7	6.3	6.1	6.3	12.3	9.2
Whiting	14.9	21.7		20.5	22.8	21.7	22.8	15.4	17.4
Zinc Oxide	6.5	5.4	3.1	5.2	5.7	5.5	5.7	3.9	5.1
Tin Oxide	5.3								10.4 (colors)
Basic Lead Carbonate			32.2						
Cobaltic Oxide				14.5					
Chromic Oxide					5.3				
Manganese Carbonate						9.6			
Nickelic Oxide							5.3		
Ferric Oxide (red)								10.9	

D. PROCEDURE

The general procedure follows:

1. The dipped tile is supported upon thin wires and allowed to air dry (if it shows bubbles or a non-uniform surface, it is discarded). After this, it is dried at a hundred and ten (110°) degrees centigrade in an electric dryer. It is then set upon heavy chromel wire supports and slid into the tube until it is in the uniform heating zone. (Usually two samples, either of different glazes or duplicates, are placed in the furnace for each run. It was found that the relative position in the tube makes no noticeable difference in the results). To secure maturity, care is taken to see that the ware is well within this zone.

2. The apparatus is tested for leaks by admitting air. The air then is adjusted to a desired rate and the suction varied until the manometer on the furnace shows that this is at atmospheric pressure. If the air is to be used with minimum moisture content it is passed through two absorption tubes containing calcium chloride. When this is done, no water is condensed. If the run is to be made with other gases, they are then admitted at controlled rates. If city

gas or water vapor are to be used, it is necessary to start the condenser and fill the cooling coil with ice so that there will be no loss in the water vapor measurement.[73] When manufactured gas is to be burned, the spark coil is started and the spark adjusted to jump from the lead wire to the screen in the burner. The gas is then admitted slowly until a flow of about one and two tenths (1.2) of a cubic foot per hour is obtained.

3. For the combustion products, adjustment of the suction and the flow of by-pass gases is then made. (As the temperature in the furnace increases, the adjustment of the suction must be made continually to correct for the increase in volume).

4. The furnace is started cold, or below 100°C, in all cases. The temperature is slowly increased according to the curve in Graph 2 and data in Table 7.[74] When the temperature reaches 1200°C, samples of the combustion products are taken and analysis made. In the preliminary experiments, simple Orsat analysis

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[73] With other gases and air, this may be adjusted after the heating has started, the small loss in the period of time of starting is not important. Air usually yields about one to two grams of water in four or five hours.

[74] Several longer heating schedules were tried in the preliminary tests. They were from this same curve but the time axis was shifted and condensed without changing the general outline of the curve.

for oxygen and carbon dioxide was made but was deemed unsatisfactory. Complete analysis was made on a Bureau of Mines modification of the Orsat. Analyses are not made in every case. Several analyses on different runs, using the same flowmeter settings, showed that the conditions are reproducible.

5. After the maximum temperature is reached, the temperature is allowed to decrease according to the curve cited. When 590°C[75] is reached, the current and gas are shut off, and the glazed ware and furnace allowed to cool to 100°C.

6. The ware is then removed, observed, subjected to the reflectivity test, and photographed.

7. In the determination of the sulfur compounds present in the products of combustion, the alkaline solution is removed from the tubes in the absorption train and titrated, using a tetrahydroxyquinone method.[76] As with the analysis of the combustion products, a

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[75] From literature study, it was noted that most glazes were solidified by the time this temperature is reached.

[76] See Appendix IV for detailed directions.

number of observations are obtained and when a constant value[77] is found, no further tests are run.

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[77] After a period of several weeks, a test would be made to determine whether the constancy still existed. This was found to be true in every case.

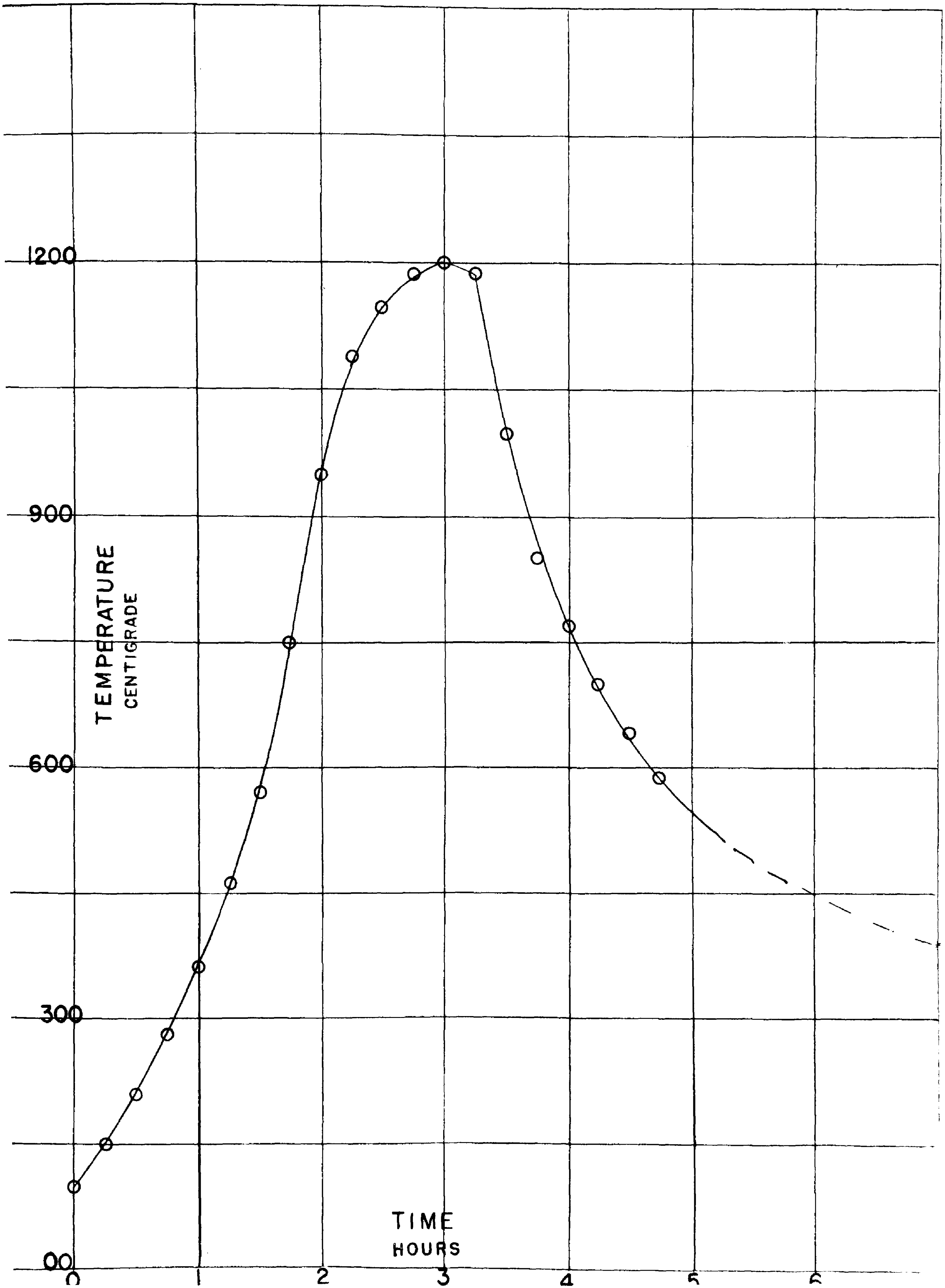
TABLE 7

HEATING RATE

Time (hours)	Temperature (^{o}C)
0	100
0.25	150
0.50	210
0.75	280
1.00	360
1.25	460
1.50	570
1.75	750
2.00	950
2.25	1090
2.50	1160
2.75	1190
3.00	1200
3.25	1190
3.50	1000
3.75	850
4.00	770
4.25	700
4.50	640
4.75	590

GRAPH 2.-

HEATING CURVE



E. DATA

In general, each of the different glazes is subjected to a pre-determined atmosphere before changing to another. For comparison, the results on each glaze have been grouped. The data upon the experiments are given in Table 8 and that upon the reflectivity measurements in Table 9.

TABLE 8

EXPERIMENTAL TESTS[78]

DATA

Number[79] of Glaze		Volumes per Hour Air Meter	cu. ft.	Gas Meter	cu. ft.	SO_2 Meter (10+3)	cu. ft.	By-pass Meter	cu. ft.	Water (H_2O) Gms.	Titration $BaCl_2$ Soln. cc.	
Sn-7	1	53.0	4.15	50.1	1.2	-	-	73.5	0.6	58.5	1	1.2
	2	54.0	5.05	50.1	1.2	-	-	73.9	1.5	60.9	-	-
	3	54.5	5.65	50.1	1.2	-	-	74.1	1.9	61.3	-	-
	4	55.0	5.95	50.1	1.2	-	-	74.3	2.3	63.5	1	2.5
	5	58.1	8.4	50.1	1.2	-	-	76.4	4.4	16.2	1	4.6
	6	54.75	5.8	-	-	-	-	74.3	2.3	4.0	1	0.5
	7	55.0	5.95	50.1	1.2	17.5	0.4	74.3	2.3	68.3	3	4.45
	8	55.0	5.95	50.1	1.2	18.3	0.95	74.3	2.3	68.2	3	8.6
	9	55.0	5.95	50.1	1.2	19.1	1.5	74.3	2.3	54.1	3	15.2
	10	55.0	5.95	-	-	-	-	74.3	2.3	dry	-	-
	11	55.0	5.95	-	-	17.5	0.4	74.3	2.3	dry	-	-
	12	55.0	5.95	-	-	-	-	74.3	2.3	55.1	-	-
Ca-10	1	53.0	4.15	50.1	1.2	-	-	73.5	0.6	58.4	1	1.6
	2	54.0	5.05	50.1	1.2	-	-	73.9	1.5	60.9	1	3.5
	3	54.5	5.65	50.1	1.2	-	-	74.1	1.9	61.3	1	2.3
	4	55.0	5.95	50.1	1.2	-	-	74.3	2.3	63.5	1	1.5
	5	58.1	8.4	50.1	1.2	-	-	76.4	4.4	56.4	1	3.5
	6	54.75	5.8	-	-	-	-	74.3	2.3	3.9	-	-
	7	55.0	5.95	50.1	1.2	17.5	0.4	74.3	2.3	68.3	-	-
	8	55.0	5.95	50.1	1.2	18.3	0.95	74.3	2.3	63.7	-	-
	9	55.0	5.95	50.1	1.2	19.1	1.5	74.3	2.3	54.1	-	-
	10	55.0	5.95	-	-	-	-	74.3	2.3	dry	-	-
	11	55.0	5.95	-	-	17.5	0.4	74.3	2.3	dry	-	-
	12	55.0	5.95	-	-	-	-	74.3	2.3	55.1	-	-
Pb-11	1	53.0	4.15	50.1	1.2	-	-	73.5	0.6	58.4	1	2.6
	2	54.0	5.05	50.1	1.2	-	-	73.9	1.5	62.0	1	2.9
	3	54.5	5.65	50.1	1.2	-	-	74.1	1.9	71.3	1	3.1
	4	55.0	5.95	50.1	1.2	-	-	74.3	2.3	55.5	1	4.0
	5	58.1	8.4	50.1	1.2	-	-	76.4	4.4	56.4	1	2.3
	6	54.75	5.8	-	-	-	-	74.3	2.3	3.9	-	-
	7	55.0	5.95	50.1	1.2	17.5	0.4	74.3	2.3	64.3	-	-
	8	55.0	5.95	50.1	1.2	18.3	0.95	74.3	2.3	63.7	-	-
	9	55.0	5.95	50.1	1.2	19.1	1.5	74.3	2.3	67.6	-	-
	10	55.0	5.95	-	-	-	-	74.3	2.3	dry	-	-
	11	55.0	5.95	-	-	17.5	0.4	74.3	2.3	dry	-	-
	12	55.0	5.95	-	-	-	-	74.3	2.3	52.9	-	-

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[78] Based upon a 4.75 hour run, see heating curve page. 65.

[79] Rearranged into groups of glazes studied, see Appendix V. for order of testing.

TABLE 8 CONT'D.

Number of Glaze		Volumes per Hour Air Meter	cu. ft.	Gas Meter	cu. ft.	SO_2 Meter	cu. ft.	By-pass Meter	cu. ft.	Water (H_2O) Gms.	Titration $BaCl_2$ soln. cc.	
						(10+3)						
Co-1	1	53.0	4.15	50.1	1.2	-	-	73.5	0.6	64.5	1	1.1
	2	54.0	5.05	50.1	1.2	-	-	73.9	1.5	54.2	-	-
	3	54.5	5.65	50.1	1.2	-	-	74.1	1.9	63.9	-	-
	4	55.0	5.95	50.1	1.2	-	-	74.3	2.3	54.4	1	4.6
	5	58.1	8.4	50.1	1.2	-	-	76.4	4.4	21.6	1	4.3
	6	54.75	5.8	-	-	-	-	74.3	2.3	4.0	-	-
	7	55.0	5.95	50.1	1.2	17.5	0.4	74.3	2.3	71.4	-	-
	8	55.0	5.95	50.1	1.2	18.3	0.95	74.3	2.3	61.6	-	-
	9	55.0	5.95	50.1	1.2	19.1	1.5	74.3	2.3	61.4	-	-
	10	55.0	5.95	-	-	-	-	74.3	2.3	dry	-	-
	11	55.0	5.95	-	-	17.5	0.4	74.3	2.3	dry	-	-
	12	55.0	5.95	-	-	-	-	74.3	2.3	55.0	-	-
Cr-2	1	53.0	4.15	50.1	1.2	-	-	73.5	0.6	54.7	1	1.3
	2	54.0	5.05	50.1	1.2	-	-	73.9	1.5	63.1	-	-
	3	54.5	5.65	50.1	1.2	-	-	74.1	1.9	66.7	-	-
	4	55.0	5.95	50.1	1.2	-	-	74.3	2.3	59.0	1	5.3
	5	58.1	8.4	50.1	1.2	-	-	76.4	4.4	50.1	1	5.1
	6	54.75	5.8	-	-	-	-	74.3	2.3	4.0	-	-
	7	55.0	5.95	50.1	1.2	17.5	0.4	74.3	2.3	67.7	-	-
	8	55.0	5.95	50.1	1.2	18.3	0.95	74.3	2.3	66.4	-	-
	9	55.0	5.95	50.1	1.2	19.1	1.5	74.3	2.3	56.9	-	-
	10	55.0	5.95	-	-	-	-	74.3	2.3	dry	-	-
	11	55.0	5.95	-	-	17.5	0.4	74.3	2.3	dry	-	-
	12	55.0	5.95	-	-	-	-	74.3	2.3	54.6	-	-
Mn-1	1	53.0	4.15	50.1	1.2	-	-	73.5	0.6	54.7	1	1.5
	2	54.0	5.05	50.1	1.2	-	-	73.9	1.5	62.0	1	2.6
	3	54.5	5.65	50.1	1.2	-	-	74.1	1.9	71.3	-	-
	4	55.0	5.95	50.1	1.2	-	-	74.3	2.3	55.5	1	2.5
	5	58.1	8.4	50.1	1.2	-	-	76.4	4.4	50.1	1	3.1
	6	54.75	5.8	-	-	-	-	74.3	2.3	4.0	-	-
	7	55.0	5.95	50.1	1.2	17.5	0.4	74.3	2.3	64.3	-	-
	8	55.0	5.95	50.1	1.2	18.3	0.95	74.3	2.3	68.2	-	-
	9	55.0	5.95	50.1	1.2	19.1	1.5	74.3	2.3	67.6	-	-
	10	55.0	5.95	-	-	-	-	74.3	2.3	dry	-	-
	11	55.0	5.95	-	-	17.5	0.4	74.3	2.3	dry	-	-
	12	55.0	5.95	-	-	-	-	74.3	2.3	52.9	-	-
Ni-1	1	53.0	4.15	50.1	1.2	-	-	73.5	0.6	54.7	1	1.4
	2	54.0	5.05	50.1	1.2	-	-	73.9	1.5	54.2	-	-
	3	54.5	5.65	50.1	1.2	-	-	74.1	1.9	63.9	-	-
	4	55.0	5.95	50.1	1.2	-	-	74.3	2.3	54.4	1	4.4
	5	58.1	8.4	50.1	1.2	-	-	76.4	4.4	50.1	1	4.5

TABLE 8 CONT'D.

Number of Glaze		Volumes per Hour Air Meter	cu. ft.	Gas Meter	cu. ft.	SO_2 Meter	cu. ft.	By-pass Meter	cu. ft.	H_2O Gms.	Titration $BaCl_2$ Soln.	cc.
Ni-1	6	54.75	5.8	-	-	(10+3) -	-	74.3	2.3	4.0	-	-
	7	55.0	5.95	50.1	1.2	17.5	0.4	74.3	2.3	71.4	-	-
	8	55.0	5.95	50.1	1.2	18.3	0.95	74.3	2.3	61.6	-	-
	9	55.0	5.95	50.1	1.2	19.1	1.5	74.3	2.3	61.4	-	-
	10	55.0	5.95	-	-	-	-	74.3	2.3	dry	-	-
	11	55.0	5.95	-	-	17.5	0.4	74.3	2.3	dry	-	-
	12	55.0	5.95	-	-	-	-	74.3	2.3	55.0	-	-
Fe-5	1	53.0	4.15	50.1	1.2	-	-	73.5	0.6	57.1	1	1.3
	2	54.0	5.05	50.1	1.2	-	-	73.9	1.5	63.1	-	-
	3	54.5	5.65	50.1	1.2	-	-	74.1	1.9	66.7	-	-
	4	55.0	5.95	50.1	1.2	-	-	74.3	2.3	59.0	1	3.2
	5	58.1	8.4	50.1	1.2	-	-	76.4	4.4	21.7	1	4.6
	6	54.75	5.8	-	-	-	-	74.3	2.3	4.2	-	-
	7	55.0	5.95	50.1	1.2	17.5	0.4	74.3	2.3	67.7	-	-
	8	55.0	5.95	50.1	1.2	18.3	0.95	74.3	2.3	66.4	-	-
	9	55.0	5.95	50.1	1.2	19.1	1.5	74.3	2.3	56.9	-	-
	10	55.0	5.95	-	-	-	-	74.3	2.3	dry	-	-
	11	55.0	5.95	-	-	17.5	0.4	74.3	2.3	dry	-	-
	12	55.0	5.95	-	-	-	-	74.3	2.3	54.6	-	-

TABLE 9

REFLECTANCE DATA AND RESULTS

Subject		Reading		Computations[80]	
Glaze	Ref.[81] No.	Normal	Angular	Reflectivity	Specular Gloss
Std.Glass	0	18.5	105.0	91.0	5.64
Sn-7	1	18.5	105.0	91.0	5.64
	2	18.0	108.0	88.8	5.80
	3	18.0	108.0	88.8	5.80
	4	18.5	108.0	91.0	5.80
	5	18.5	105.0	91.0	5.64
	6	18.5	106.0	91.0	5.69
	7	19.0	105.0	93.6	5.64
	8	19.0	102.0	93.6	5.48
	9	19.0	103.0	93.6	5.54
	10	20.0	110.0	98.4	5.90
	11	20.5	104.0	100.9	5.58
	12	20.5	105.5	100.9	5.66
Ca - 10	1	18.0	76.0	88.8	4.08
	2	18.0	80.0	88.8	4.39
	3	17.5	100.0	86.1	5.36
	4	18.0	100.0	88.8	5.36
	5	18.0	92.0	88.8	4.94
	6	18.0	100.0	88.8	5.36
	7	18.5	99.0	91.0	5.31
	8	18.5	92.5	91.0	4.96
	9	18.5	92.0	91.0	4.94
	10	19.5	108.5	96.0	5.82
	11	19.5	99.0	96.0	5.31
	12	18.0	109.0	88.8	5.85
Pb - 11	1	16.0	74.0	78.7	3.97
	2	16.0	80.0	78.7	4.29
	3	18.0	98.0	88.8	5.26
	4	19.0	102.0	93.6	5.47
	5	18.0	92.0	88.8	4.94
	6	18.0	104.0	88.8	5.58
	7	18.5	90.0	88.8	5.40
	8	18.0	99.5	88.8	5.34
	9	18.0	100.5	91.0	4.83
	10	20.0	100.0	98.4	5.36
	11	20.0	82.0	98.4	4.40
	12	20.0	97.5	98.4	5.23

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80. See Calculations, page 84 .

81. See Appendix V to key to actual test number.

TABLE 9 CONT'D.

Glaze	Subject Ref. No.	Reading		Computations.	
		Normal	Angular	Reflectivity	Specular Gloss
Co - 1	1	8.0	80.5	39.4	4.33
	2	8.5	100.0	41.8	5.37
	3	8.5	102.0	41.8	5.49
	4	8.5	100.0	41.8	5.37
	5	8.5	100.0	41.8	5.37
	6	8.5	108.0	41.8	5.81
	7	9.0	100.0	44.3	5.37
	8	9.0	101.0	44.3	5.44
	9	8.5	90.0	41.8	4.84
	10	9.0	115.5	44.3	6.20
	11	9.0	103.0	44.3	5.53
	12	9.0	104.0	44.3	5.58
Cr - 2	1	9.0	72.0	44.3	3.86
	2	10.0	70.5	49.2	3.78
	3	11.5	100.5	56.6	5.40
	4	11.0	100.0	54.1	5.36
	5	11.0	100.0	54.1	5.36
	6	11.0	108.0	54.1	5.80
	7	11.0	98.0	54.1	5.26
	8	11.0	96.5	54.1	5.18
	9	11.0	91.0	54.1	4.89
	10	12.0	100.0	59.0	5.36
	11	12.0	94.0	59.0	5.04
	12	12.0	97.5	59.0	5.23
Mn - 1	1	18.0	101.0	88.8	5.41
	2	18.5	97.5	91.0	5.23
	3	18.0	98.5	88.8	5.29
	4	10.0	107.0	49.2	5.75
	5	10.0	112.0	49.2	6.00
	6	9.5	108.0	46.8	5.80
	7	10.0	109.0	49.2	5.85
	8	10.0	105.0	49.2	5.64
	9	11.5	95.0	56.6	5.10
	10	9.5	110.0	46.8	5.90
	11	10.0	94.5	49.2	5.07
	12	9.5	104.0	46.8	5.58

TABLE 9 CONT'D.

Glaze	Subject Ref. No.	Reading Normal	Reading Angular	Computations Reflectivity	Specular Gloss
Ni - 1	1	10.0	78.0	49.2	4.19
	2	10.0	86.0	49.2	4.61
	3	12.5	90.0	61.5	4.84
	4	14.0	97.0	68.9	5.21
	5	12.0	90.5	59.0	4.86
	6	13.0	94.0	64.0	5.05
	7	13.5	92.0	66.5	4.94
	8	13.0	91.5	64.0	4.91
	9	14.0	86.0	68.9	4.62
	10	15.0	98.0	73.8	5.26
	11	15.0	93.0	73.8	4.99
	12	15.0	100.5	73.8	5.40
Fe - 5	1	7.5	100.0	36.9	5.37
	2	8.0	103.0	39.4	5.53
	3	7.5	108.5	36.9	5.83
	4	8.0	107.0	39.4	5.75
	5	8.5	103.0	41.8	5.53
	6	8.0	101.5	39.4	5.45
	7	8.5	110.5	41.8	5.94
	8	7.5	100.0	36.9	5.37
	9	8.0	90.0	39.4	4.84
	10	9.0	104.0	44.3	5.59
	11	9.0	89.5	44.3	4.80
	12	8.5	97.0	41.8	5.21

TABLE 10

REFLECTANCE STANDARD

From Henry A. Gardner Laboratory, Washington, D. C.

Reflection Sample No. 521

% Reflectance MgO = 100%

Green (Reflectivity)	Blue	Amber
91.0%	90.8%	90.3%

Specular gloss 5.64

Instrument - Hunter Multipurpose Reflectometer[82]

---

[82] This instrument has a 45° viewing - incident arrangement. The reflectivity is read at 90 deg. to the sample.

F. CALCULATIONS

The following discussions are sample calculations from the preceding data:

1. Determination of organic sulfur in manufactured gas used for the tests.[83]

(a) Standardization of $BaCl_2$ solutions[84]
(Illustrated by solution number 1)

(1)
$$\text{cc of } Na_2SO_4 \text{ solution} \quad \text{grams } Na_2SO_4 \text{ per cc} \quad \frac{1}{\text{cc } BaCl_2 \text{ soln.}} = \text{gms. } Na_2SO_4/\text{ cc } BaCl_2$$

$$(0.5)\left(\frac{2.5}{250}\right)\left(\frac{1}{7.50}\right) = 0.00232 \text{ grains S/cc } BaCl_2$$

(2)
$$\text{gms. } Na_2SO_4 \text{ per cc } BaCl_2 \quad \frac{\text{Mol. Wt. Sulfur}}{\text{Mol. Wt. } Na_2SO_4} \quad \frac{1}{453.6} \quad (7000) = \text{grains S/cc } BaCl_2$$

$$(0.000667)\left(\frac{32}{142}\right)\left(\frac{1}{453.6}\right)(7000) = 0.00232 \text{ grains S/cc } BaCl_2$$

(b) Titrations[85] (for example, an A atmosphere)

(1)
$$\begin{aligned} \text{grains S/25 cc sample} &= (\text{cc } BaCl_2 \text{ used})(\text{grains S/cc}) \\ &= (3.5)(0.00232) \\ &= 0.00812 \end{aligned}$$

(2) total grains S per By-Pass gas =(total grains S per 25 cc sample $\frac{\text{total vol. of sample}}{25}$

$$\begin{aligned} &= (0.00812)\left(\frac{100}{25}\right) \\ &= 0.03248 \end{aligned}$$

---

[83] A qualitative test gave no indication of hydrogen sulfide.

[84] See Table 11 for data and summary.

[85] See Table 8 for data and Table 12 for summary, the values used were average data readings.

(3) total grains S per 100 cubic feet = (total grains S in By-Pass

$$\frac{100}{\text{Vol of by-pass gas}}$$

$$= (0.03240)\left(\frac{100}{(4.4)(4.75)}\right)$$

$$= 0.155$$

(4) grains S per 100 cu.ft. of mfg. gas = grains S per 100 cu. ft. of combustion product

$$\frac{\text{Vol. of comb. products}}{\text{Vol. of gas used}}$$

$$= (0.155)\ \frac{(8.0)}{(1.2)}$$

$$= 1.03$$

TABLE 11

STANDARDIZATION OF $BaCl_2$ SOLUTIONS

DATA AND CALCULATION

Number		$BaCl_2$ Soln. cc. used	Standard[86] Na_2SO_4 Soln. cc. used	1 cc $BaCl_2$[87] equiv. to grains S
1		7.55	0.50	0.00232
		7.45		
		7.50		
	average	7.50		
2		3.65	1.00	0.00939
		3.70		
		3.70		
	average	3.70		
3		3.10	3.00	0.0343
		3.00		
		3.05		
	average	3.05		

---

[86] From C. P. Chemicals, 2.500 grams Na_2SO_4 in 250 cc. of water.

[87] For calculations see page 74.

TABLE 12

SUMMARY OF SULFUR ANALYSIS

Atmosphere Ref.	cc $BaCl_2$ Av.	Grains S per 100 cu.ft. Combustion product		Grains S per[88] 100 cu. ft. manufactured gas	
		(computation)	(analysis)	(computation)	(analysis)
A	3.5	0.155		1.03	
B	2.9	0.246		1.25	
C	2.5	0.258		1.17	
D	2.2	0.286		1.16	
E	1.0	0.326		1.14	
B (1)[89]	4.45	4.62	5.60	23.47	28.5
B (2)	8.6	10.63	10.82	54.05	55.1
B (3)	15.2	16.65	19.10	84.75	97.3

---

[88] The accuracy is not as great as the values indicate; in any particular determinations the individual titrations check, but the repetition of a given atmosphere may cause 50% or more variation in any of the titrations from the tests.

[89] The values are the sum of the atmosphere B above and sulfur dioxide added through the flow meter given by computation and single titration checks.

The average organic sulfur determination[90] indicates that an assumption of two (2) grains of sulfur per 100 cubic feet of city gas is sufficiently accurate. The analysis upon gases of higher concentrations of sulfur compounds agrees essentially with that calculated from flow meter readings in which sulfur dioxide is added to increase the sulfur content since in combustion of organic sulfur, sulfur dioxide results.

2. Determination of the firing atmosphere[91] and its relation with theoretical combustion.[92]

(a) Theoretical Combustion

Component (by analysis)	O_2	+ N_2	yields CO_2	+ H_2O	+ N_2
2.3 CO_2	-	-	2.3	-	-
1.5 III(C_2H_4)	4.5	16.9	3.0	3.0	16.9
0.8 O_2	(-0.8)	(-3.1)	-	-	-
31.0 H_2	15.5	58.3	-	31.0	58.3
14.8 CO	7.4	27.8	14.8	-	27.8
36.4 CH_4	72.8	273.9	36.4	72.8	273.9
1.5 C_2H_6	5.3	19.9	3.0	4.5	19.9
11.7 N_2	-	-	-	-	11.7
100.0 Gas	-104.7 O_2	393.7 N_2	59.5 CO_2	111.3 H_2O	408.5 N_2

---

[90] See Table 12 for summary of calculations of sulfur analyses.

[91] The analysis as determined by the Bureau of Mines Orsat apparatus does not account for the water vapor which would be an active component under the temperatures used.

[92] See Table 1 for data and Tables 13 and 14 for summary of calculations.

Summarizing, 1 part gas requires 4.984 parts air yielding a product which would have the analysis 10.3% CO_2; 19.3% H_2O;70.4% N_2.

(b) Determination of the percent theoretical air[93] and of the analysis.

(1) The data (Table 13) for case A atmosphere gives on an hourly basis 1.2 cubic feet of gas being burned in 8.4 cu. feet of air.

(a) From theoretical combustion calculations

$$\frac{1.0 \text{ gas}}{4.98 \text{ air}} = \frac{1.2 \text{ gas}}{x \text{ air}}$$

x air = 5.98 cubic feet/ hour of air.

(b) Then, % theoretical air $= \frac{8.4}{5.98} \times 100 = 140.5\%$

(2) Likewise the analysis may be calculated.

$CO_2 = \frac{0.595}{1} \times 1.2 = 0.715$ cu. ft. per hr.

$N_2 = \frac{4.085}{1} \times 1.2 = 4.900$ " " " "

$H_2O = \frac{1.118}{1} \times 1.2 = 1.338$ " " " "

Excess Oxygen = (8.4 - 5.98) x 0.21 = 0.509

Excess Nitrogen = (8.4 - 5.98) x 0.79 = 1.91

from which the analysis would be on the percentage basis 7.6% CO_2; 5.4% O_2; 14.3% H_2O; and 72.7% N_2.

(c) The firing atmosphere from the complete gas analysis[94]

---

[93] Summary found in Table 14; analysis cannot be calculated theoretically under reducing conditions.

[94] Data found in Table 1 for manufactured gas composition and combustion product analysis upon the dry basis.

for case <u>A</u>.

(1) % air

(a) Ratio of N_2/C in original gas = 11.7/59.5 = 0.197

(b) Carbon in product x 0.197 = 9.3 x 0.197 = 1.83 N_2 from gas

(c) N_2 in product - N_2 from gas = 83.9 - 1.83 = 82.1 N_2 " air

(d) N_2 from air x $\frac{0.21}{0.79}$ = 82.1 x $\frac{0.21}{0.79}$ = 21.8 O_2 from air

(e) O_2 present[95] - O_2 needed[96] = 6.3 - 0.25 - 0.15 = 5.9 O_2 available.

(f) % theoretical air = $\frac{+\ O_2 \text{ from air}}{O_2 \text{ from air} - O_2 \text{ available}}$ x 100 =

$\frac{21.8}{211.8-5.9}$ x 100 = 137.1%

(2) The correction for the water content

(a) Average weight of water condensed = 4.5 gms. in 4.75 hrs. through the furnace.

(b) Total volume of combustion gases = $\frac{\text{In volume actual}}{\text{In volume theoretical}}$ (Outlet Volume Theoretical) + Free Air

$$= \frac{1.2 + 5.98}{5.984}\ \underline{\ 4.68\ } + 2.42$$

$$= 8.04 \text{ cubic feet per hour}$$

(c) total amount of H_2O per hour = $\frac{\text{wt. measured}}{\text{(Time)(Furnace Vol.)}}$[97] (total vol.)

Amt. of water = $\frac{45}{(4.75)(7.5-4.4)}$ 7.5 = 22.9 gms./ hr.

(d) Moles water per hr. = $\frac{\text{weight per hr.}}{\text{Mol. weight}}$ = $\frac{22.9}{(454)(18)}$ = 0.0028 moles/ hr.

---

[96] The oxygen required to reduce all in completely burned products, such as carbon monoxide.

[97] Volume furnace = Volume Total - Volume by-pass.

[95] The oxygen from the gas is negligible.

(e) Cu. ft. per hour = moles x 359 = (0.0028) (359)
= 1.008

(f) Percentage of water vapor = $\frac{\text{cubic feet water}}{\text{total volume gases}} \times 100$

$= \frac{1.008}{8.04} \times 100$

= 12.5% increase in the total volume (dry basis)

(g) then upon recalculation upon wet basis

$CO_2 = 9.0 \times \frac{100}{112.5} = 8.0\ \%$

$O_2 = 6.3 \times \frac{100}{112.5} = 5.6\ \%$

$H_2 = 0.5 \times \frac{100}{112.5} =, 0.5\%$

$CO = 0.3 \times \frac{100}{112.5} = 0.3\%$

$H_2O = 12.5 \times \frac{100}{112.5} = 11.1\%$

$N_2 = 83.9 \times \frac{100}{112.5} = 74.5\%$

TABLE 13

COMBUSTION DATA

Subject Atmosphere	Gas Rate cu.ft. per hr.	Air Rate cu.ft. per hr.	H_2O[98] Condensed (grams)	By-pass cu.ft. per hr.	Calculated[99]		
					Combustion Tot. Vol.	Vol. thru tube	Products Velocity ft./hr.
A	1.2	8.4	45.0	4.4	8.0	3.6	215.5
B	1.1	5.95	61.8	2.3	5.6	3.3	197.5
C	1.2	5.65	62.2	1.9	5.4	3.5	209.5
D	1.2	5.05	60.1	1.5	4.8	3.3	197.5
E	1.2	4.15	60.5	0.6	4.2	3.6	215.5
					Average	3.46	207.1

---

[98] Water carried out below 15°C is neglected, it partially accounts for the water added by the entering air and gas. The figures are average of the tests in Table 8.

[99] See Calculations, page 74

TABLE 14

FURNACE ATMOSPHERES

COMPARISON OF CALCULATIONS OF THEORETICAL COMBUSTION AND ANALYSIS

Gas Rate	Air Rate										
Cu.Ft.per hr.		Subject	CO_2	Ill	O_2	H_2	CO	CH_4	H_2O	N_2	% Theor. Air[A]
-	-	Theoretical Combustion	10.3	-	-	-	-	-	19.3	70.4	100.0
1.2	8.4	Theoretical	7.6	-	5.4	-	-	-	14.3	72.7	140.5
		A Analysis	8.0	-	5.6	0.3	0.3	-	11.1	74.5	135.2
1.1	5.95	Theoretical	9.5	-	1.4	-	-	-	18.0	71.1	108.6
		B Analysis	10.2	-	1.1	-	-	-	14.7	74.0	106.2
1.2	5.65	C Analysis	9.8	-	0.7	1.5	1.1	0.3	14.2	72.4	94.4
		Theoretical[100]									94.4
1.2	5.05	D Analysis	9.3	0.1	1.0	2.7	2.5	0.3	14.4	69.7	88.2
		Theoretical[100]									84.3
1.2	4.15	E. Analysis	6.2	0.1	0.5	5.7	5.9	0.6	13.4	67.6	71.6
		Theoretical[100]									69.4

[A] from Table 1.

[100] Theoretical combustion products under reducing conditions can not be calculated.

Similar calculations were made for the other analyses, see Table 14. Under reducing conditions, for the calculation of theoretical air, carbon loss was neglected. While this is not the true condition, it was considered as a relative check on the theoretical air derived entirely from theoretical combustion calculations.

(3) Calculation of the reflectivity and specular gloss from reflectivity data.[101]

a. Reflectivity (R) of Number 1, Sn - 7 glaze

(1) $$R = \frac{\text{normal reading of sample}}{\text{normal reading of standard}}^{102} \text{ (R of Standard)}$$

$$= \frac{18.5}{18.5} \text{ (91.0\%)}$$

$$= 91.0\%$$

b. Specular gloss (S.G.) of Number 1, Sn - 7 glaze

(1) $$\text{Specular Gloss} = \frac{\text{Angular reading of sample}}{\text{Angular reading of Standard}} \text{ (S.G. Standard)}$$

$$= \frac{105.0}{105.0} \text{ (5.64)}$$

$$= 5.64$$

the results are summarized in Table 15, and illustrated by graphs 4 to 10 inclusive.

---

[101] See Table 9

[102] See Table 10 for data upon standard used.

G. RESULTS

The results are grouped into sections; first, a summary including description of the glaze and the calculated values of reflectivity and specular gloss, and second, the photomicrographs. Following these sections are graphs giving the expression of the calculated reflectivity and specular gloss against the variables, percent theoretical air, sulfur concentration, and water vapor content.

TABLE 15

SUMMARY OF EXPERIMENTAL RESULTS[103]

I Glaze Sn - 7

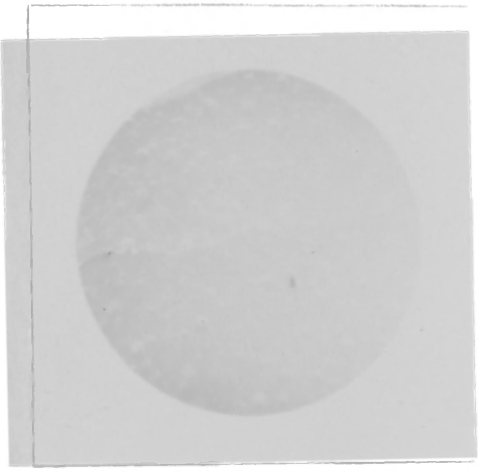
	Reference No.	Color	Texture	Var.[104] (% Theor. Air)	Reflectivity	Specular Gloss
A	1	yellow white	dull,rough	70	91.0	5.64
	2	yellow white	dull,rough	85	88.8	5.80
	3	White	bright,smoother	94	88.8	5.80
	4	whiter	brighter,smoothest	107.0	91.0	5.80
	5	White	bright,smoother	137.0	91.0	5.64
	6	white	dull,smooth	air	91.0	5.69
				(grains S / Av 100 cu.ft.)		
B	6	white	dull,smooth	. air	91.0	5.69
	4	whiter	bright,smooth	1	91.0	5.80
	7	whitest	brighter,smoother	5	93.6	5.64
	8	whitest	brighter,smoother	11	93.6	5.48
	9	white(dark)	bright,slightly rough	18	93.6	5.54
				(water vapor) (gm./cu.ft.)		
C	10	white(dark)	brighter,smoother	dry	98.4	5.90
	6	white	dull,smooth	1	91.0	5.69
	12	whitest	bright,smoothest	16	100.9	5.66
				(with sulfur)		
D	10	white(dark)	brighter,smoother	dry	98.4	5.90
	11	whitest	bright,smooth	dry + 5	100.9	5.58
	7	whiter	brighter,smoother	gas + 5 (1.1)	93.6	5.64

---

[103] See Tables 9,12 and 14.

[104] These values are given as the range in which the tests were made.

Figure 7.
Photomicrographs
I Glaze Sn-7
Varying Theoretical Air



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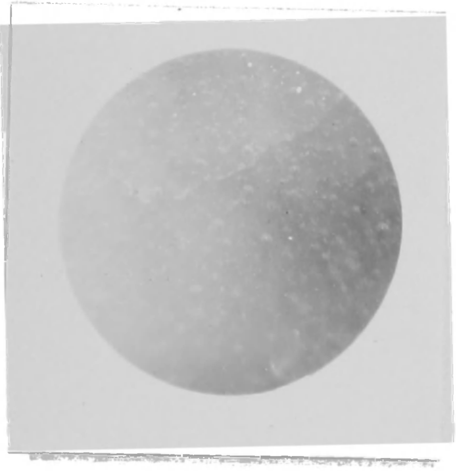

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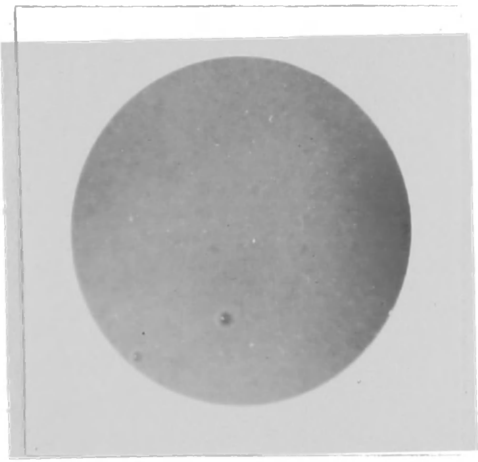

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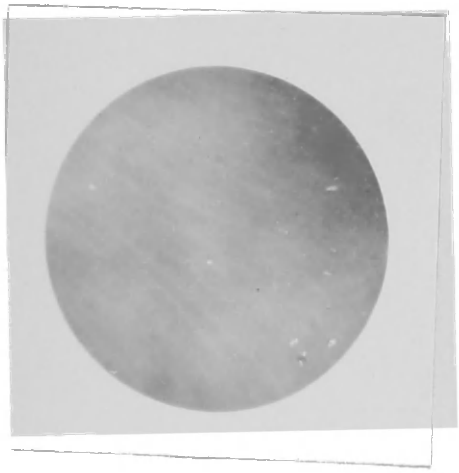

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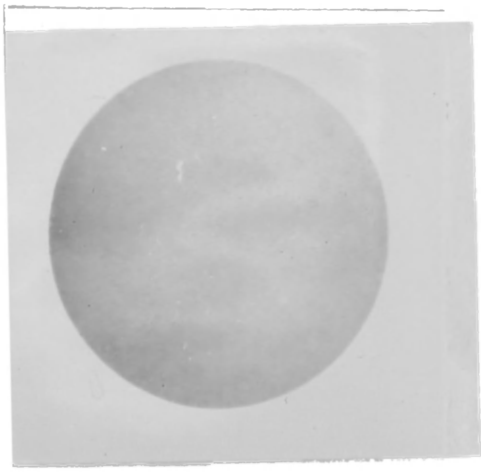

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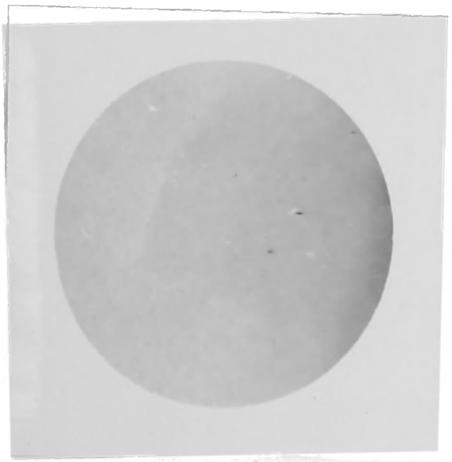
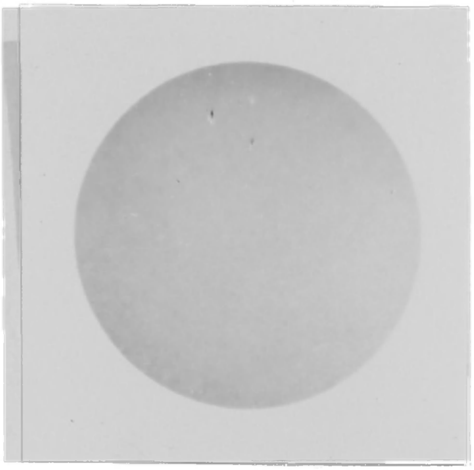


6.

Figure 8.
Photomicrographs
I Glaze Sn-7
Varying Sulfur Content.



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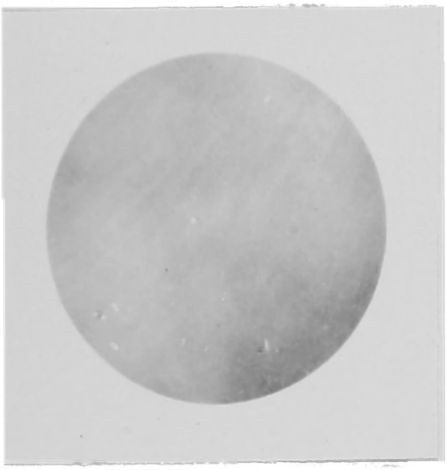

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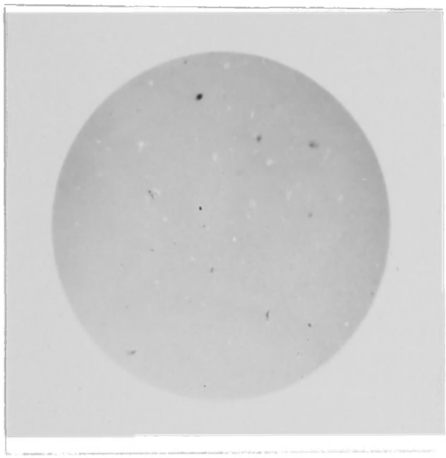

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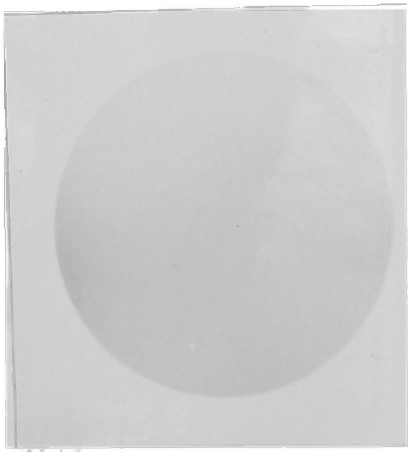

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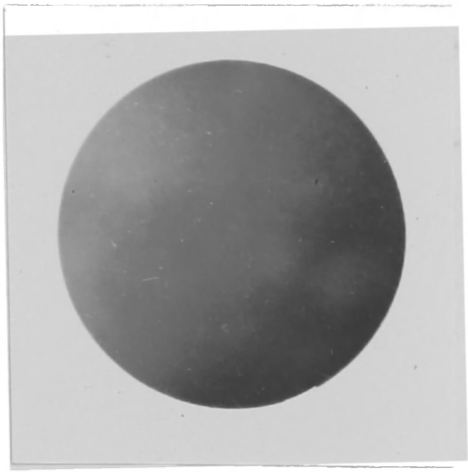
Figure 9.

Photomicrographs

I Glaze Sn-7

Varying Moisture Content

Without Sulfur



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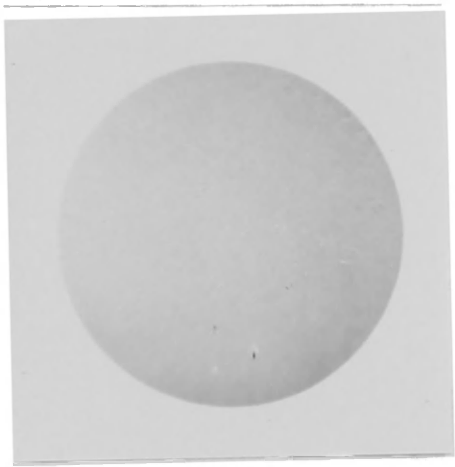

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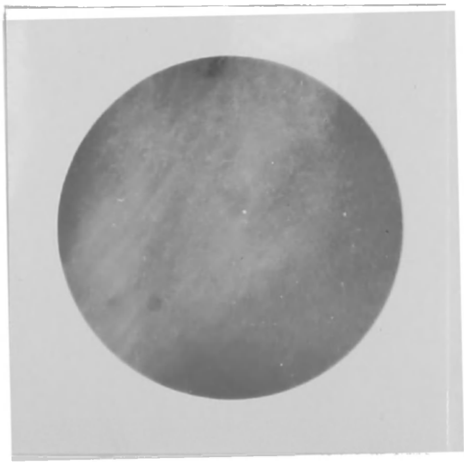

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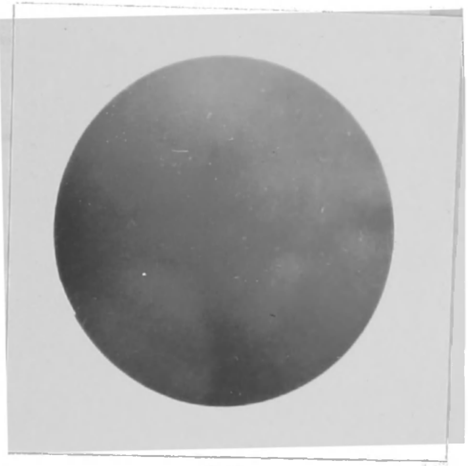
With Sulfur



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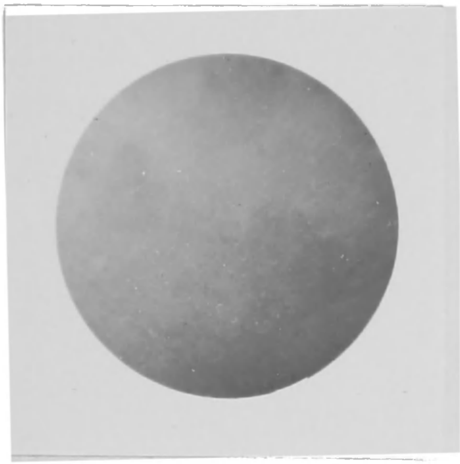


11.

7.

TABLE 16

SUMMARY OF EXPERIMENTAL RESULTS

II Glaze Ca - 10

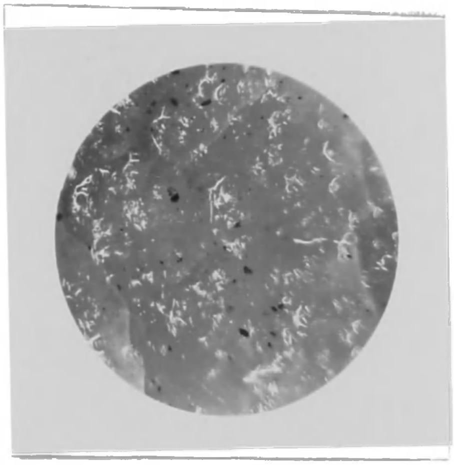
Reference	No.	Color	Texture	Var. (% Theor. Air)	Reflectivity	Specular Gloss
A	1	Clear white	dull,matte	70.0	88.8	4.08
	2	clear white	shiny,matte	85.0	88.8	4.39
	3	" "	brighter,wavy, crazing	94.0	86.1	5.36
	4	" "	" "	107.0	88.8	5.36
	5	" "	bright,pinholes, crazing	137.0	88.8	4.94
	6	" "	bright,pinholes, crazing	air	88.8	5.36
				(grains S) (av./100 cu.ft.)		
B	6	clear white	bright,pinholes, crazing	air	88.8	5.36
	4	clear "	brighter,wavy, crazing	1	88.8	5.36
	7	" "	dull,smoother crazing	5	91.0	5.31
	8	" "	duller,smoother crazing	11	91.0	4.96
	9	" "	dull,smooth crazing	18	91.0	4.94
				(water vapor) gm.cu.ft.		
C	10	clear white	brighter,pinholes crazing	dry	96.0	5.82
	6	" "	bright,pinholes crazing	1	88.8	5.36
	12	" "	brighter,wavy, crazing	16	88.8	5.85
				(with sulfur)		
D	10	clear white	dull,smoother, crazing	dry	96.0	5.82
	11	" "	duller,smoother, crazing	dry + 5	96.0	5.31
	7	" "	duller,smoother	gas + 5 (1.1)	91.0	5.31

Figure 10

Photomicrographs

II Glaze Ca-10

Varying Theoretical Air



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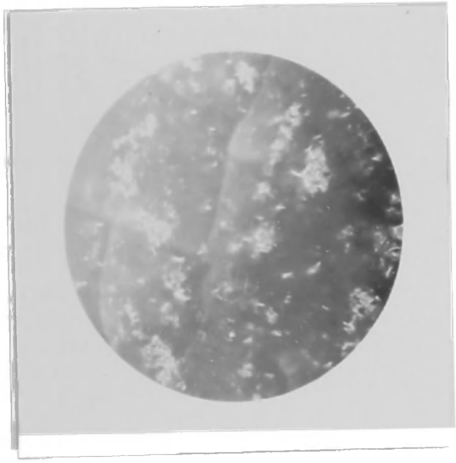

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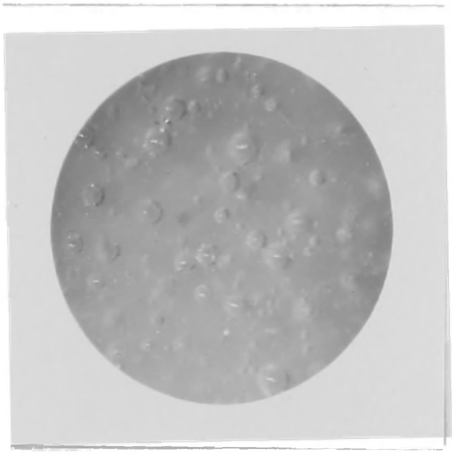

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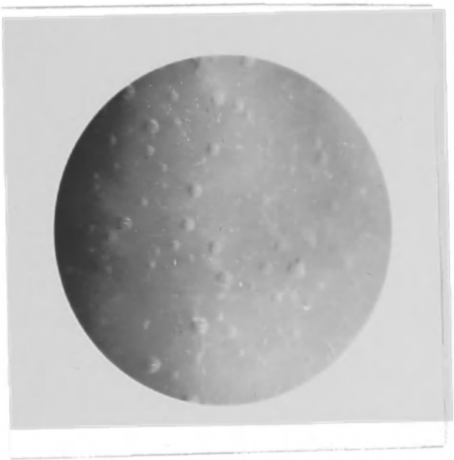

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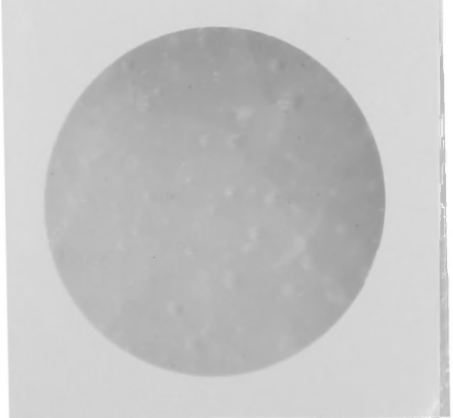

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6

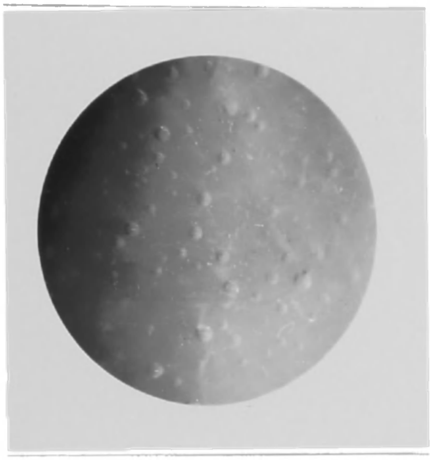
Figure 11

Photomicrographs

II Glaze Ca-10

Varying Sulfur Content

6



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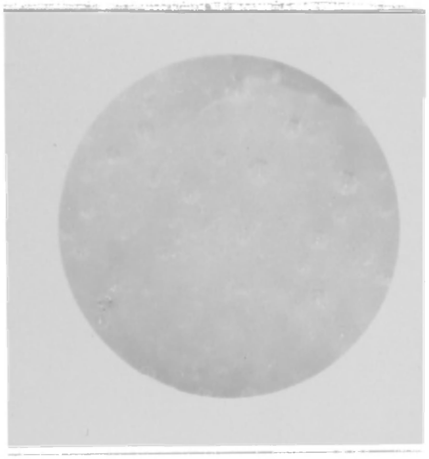

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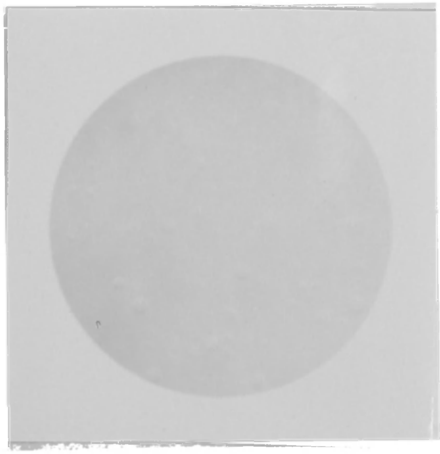

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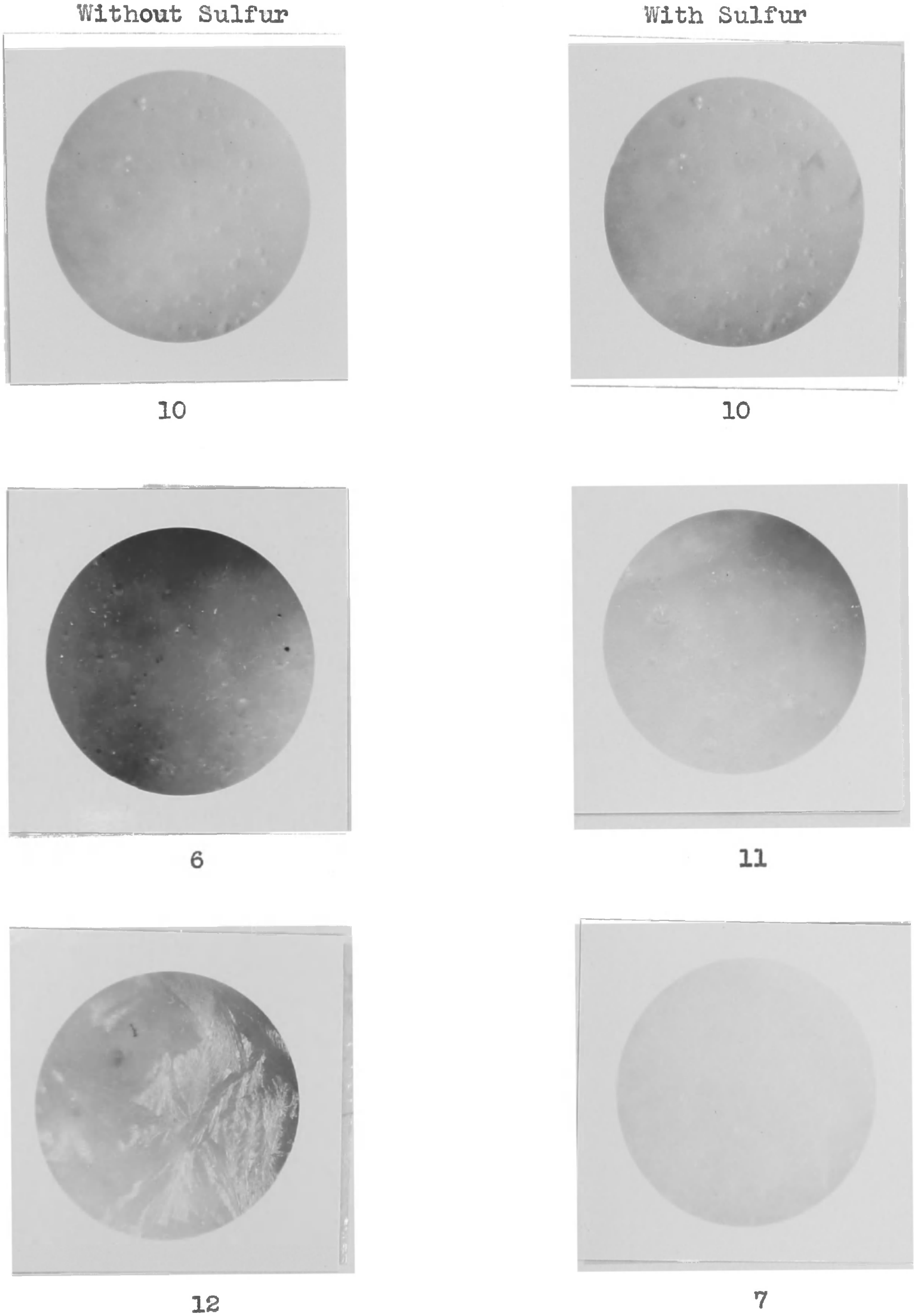
Figure 12

Photomicrographs

II Glaze Ca-10

Varying Moisture Content



Without Sulfur

With Sulfur

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TABLE 17

SUMMARY OF EXPERIMENTAL RESULTS

III Glaze Pb - 11

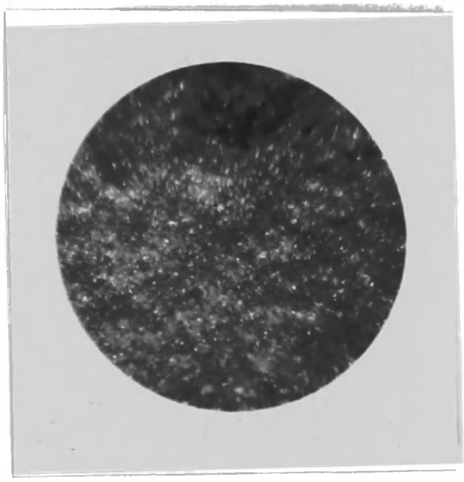
Reference	No.	Color	Texture	Var. (% Theor. Air)	Reflectivity	Specular Gloss
A	1	clear white	matte,shiny	70.0	78.7	3.97
	2	" "	matte,shiny	85.0	78.7	4.29
	3	" "	sl.rough,shiny, crazing	94.0	88.8	5.26
	4	" "	sl.rough,feels smooth	107.0	93.6	5.47
	5	" "	sl.rough,feels smooth	137.0	88.8	4.94
	6	" "	sl.rough,feels smooth	air	88.8	5.58
				(grains S) (av./100 cu.ft.)		
B	6	clear white	sl.rough,shiny	air	88.8	5.58
	4	" "	sl.rough,shiny	1	93.6	5.47
	7	clear yellowish white	rougher,shiny	5	88.8	5.40
	8	clear yellowish white	roughest,shiny	11	88.8	5.34
	9	clear yellowish white	roughest,shiny	18	91.0	4.83
				(water vapor) gm./cu.ft.		
C	10	clear white	deep pinholes bright	dry	98.4	5.36
	6	" "	sl.rough,shiny	1	88.8	5.58
	12	" "	very rough	16	98.4	5.23
				(with sulfur)		
D	10	clear white	deep pinholes bright	dry	98.4	5.36
	11	" "	very rough, shiny	dry + 5	98.4	4.40
	7	clear yellowish white	rougher,shiny	gas + 5 (1.1)	88.8	5.40

Figure 13

Photomicrographs

III Glaze Pb-11

Varying Theoretical Air



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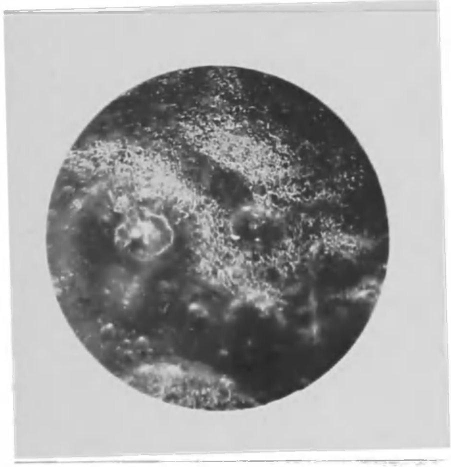

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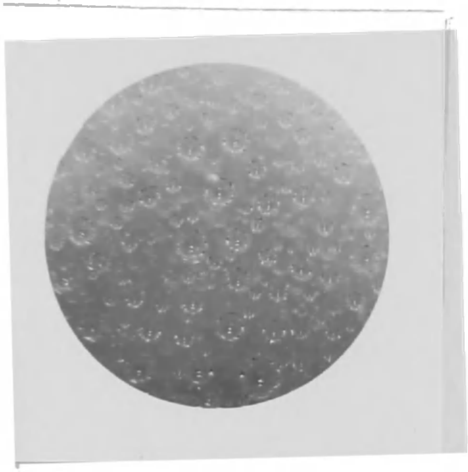

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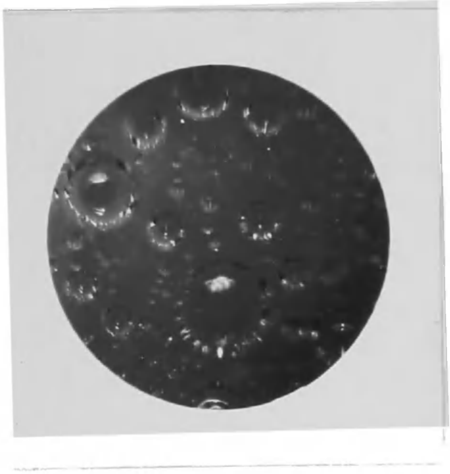

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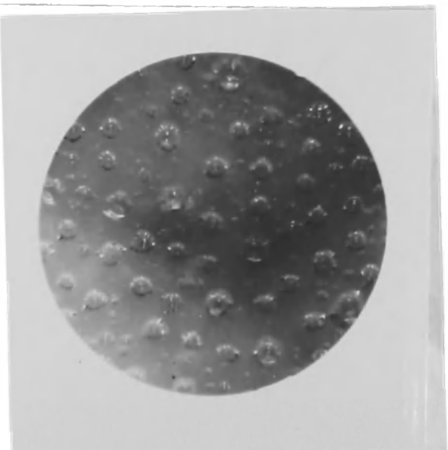

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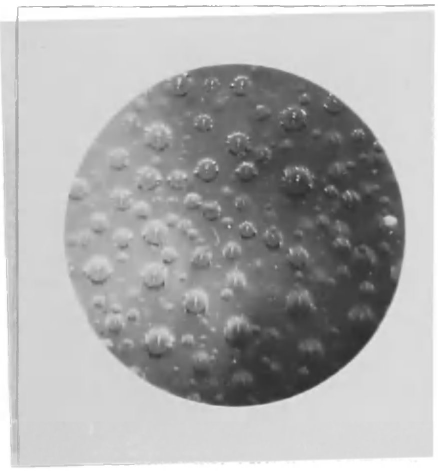

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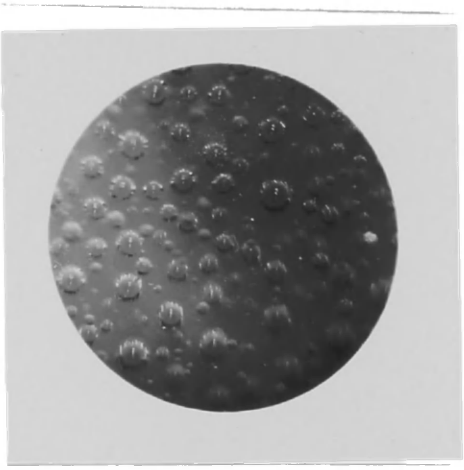
Figure 14

Photomicrographs

III Glaze Pb-11

Varying Sulfur Content



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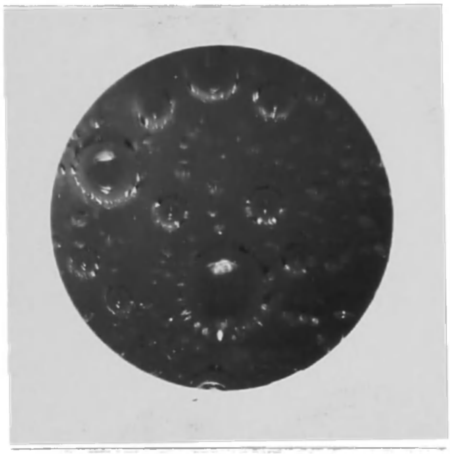

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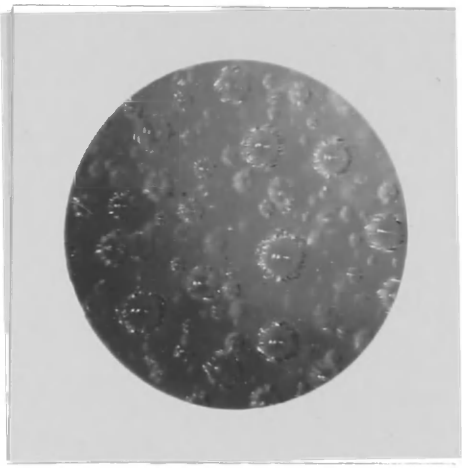

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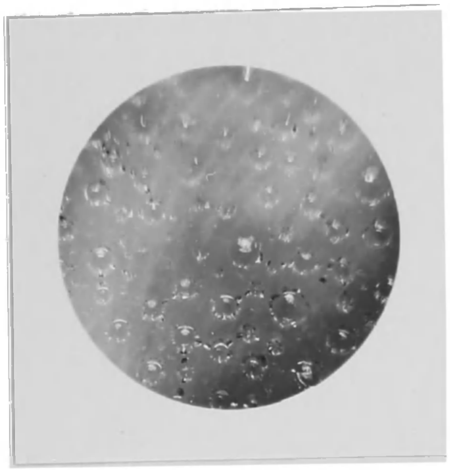

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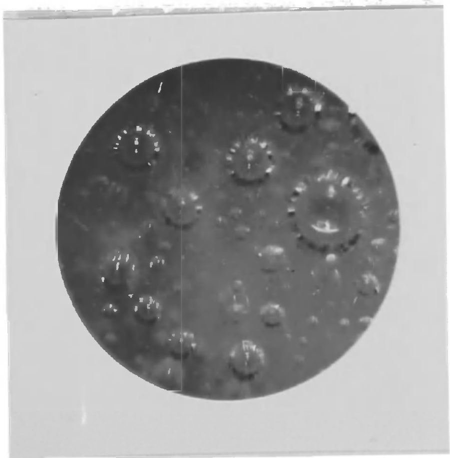

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Figure 15

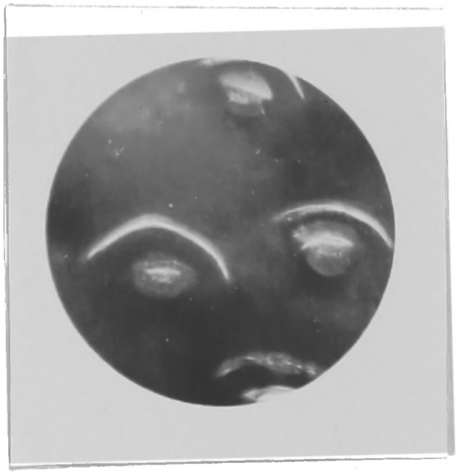
Photomicrographs

III Glaze Pb-11

Varying Moisture Content

Without Sulfur

With Sulfur



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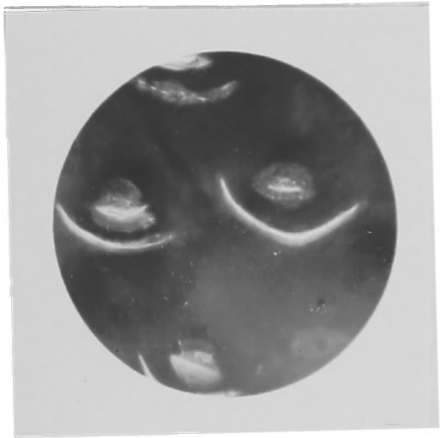

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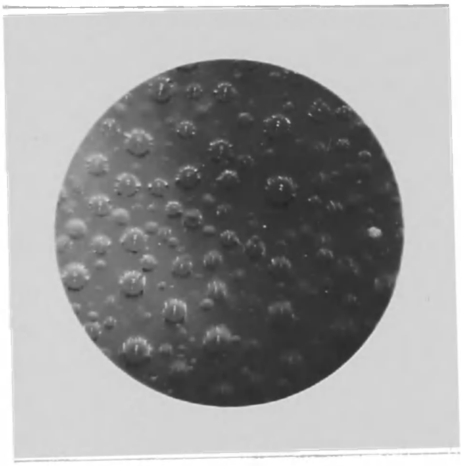

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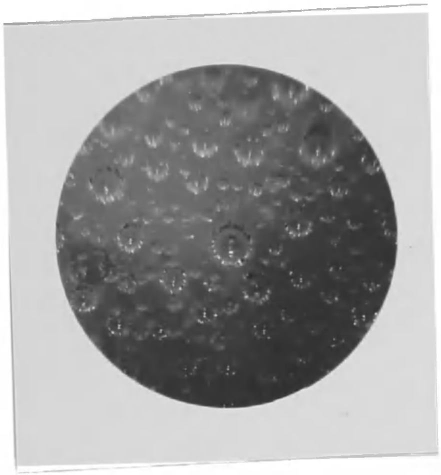

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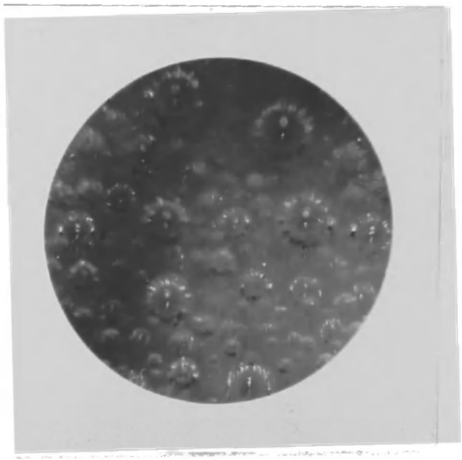

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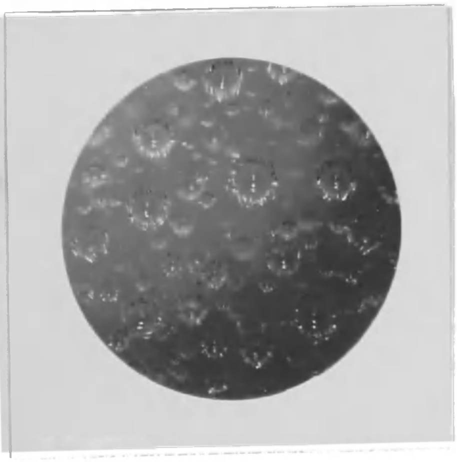

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TABLE 18

SUMMARY OF EXPERIMENTAL RESULTS

IV Glaze Co - 1

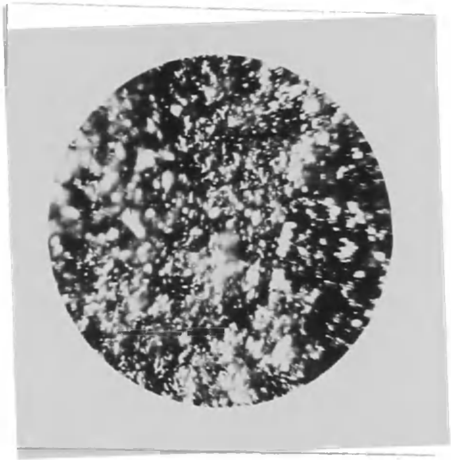
Reference	No.	Color	Texture	Var. (% Theor. Air)	Reflectivity	Specular Gloss
A	1	blue	very rough	70.0	39.4	4.33
	2	blue, copper spots	sl. rough	85.0	41.8	5.37
	3	blue, purple spots	smooth, pinholes	94.0	41.8	5.49
	4	blue, indefinite spots	smooth, faint pinholes	107.0	41.8	5.33
	5	tinge-green yellow	smooth, faint pinholes	137.0	41.8	5.37
	6.	blue	smooth, faint pinholes	air	41.8	5.81
				(grains S) Av./100 cu.ft.)		
B	6	blue	smooth pinholes	air	41.8	5.81
	4	blue, copper spots	smooth pinholes	1	41.8	5.33
	7	blue, brown scum	duller, some pinholes	5	44.3	5.37
	8	blue, light scum	duller	11	44.3	5.44
	9	blue, white scum, Cu spots	dullest, sl. rough	18	41.8	4.84
				(water vapor) (gm./cu.ft.)		
C	10	Blue(lt. copper tinge	sl. rough	dry	44.3	6.20
	6	blue	smooth, faint pinholes	1	41.8	5.81
	12	blue	bright, wavy	16	44.3	5.58
				(with sulfur)		
D	10	blue(lt. copper tinge	dull, some pinholes	dry	44.3	6.20
	11	blue, deep copper tinge	dullest, pinholes	dry + 5	44.3	5.53
	7	blue, brown scum	duller, some pinholes	gas + 5 (1.1)	44.3	5.37

Figure 16

Photomicrographs

IV Glaze Co-1

Varying Theoretical Air



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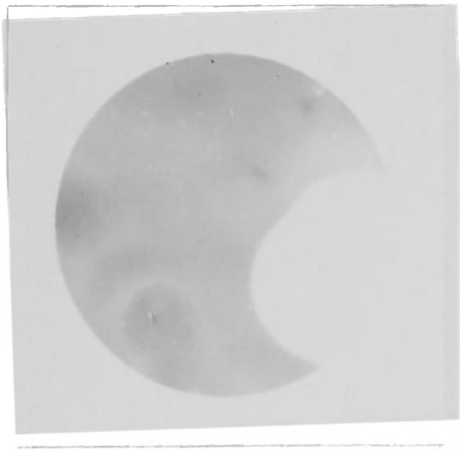

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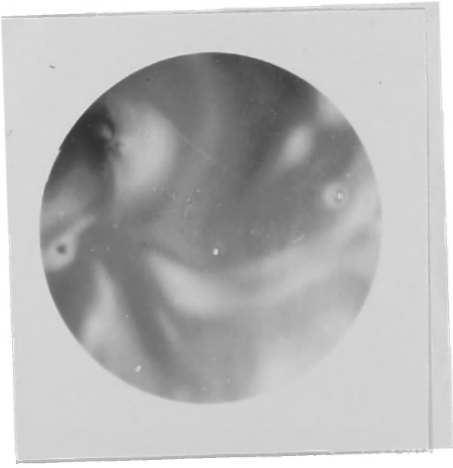

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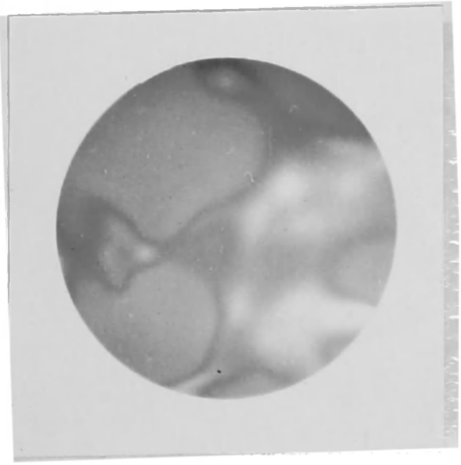

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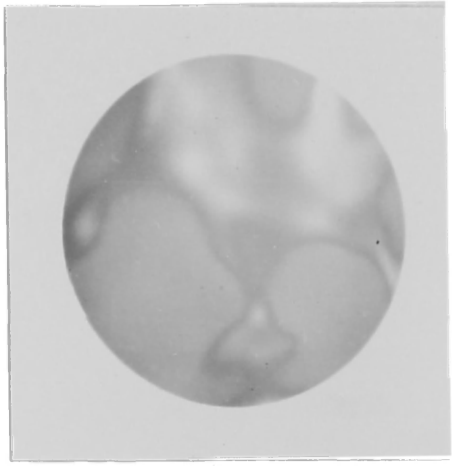
Figure 17

Photomicrographs

IV Glaze Co-1

Varying Sulfur Content



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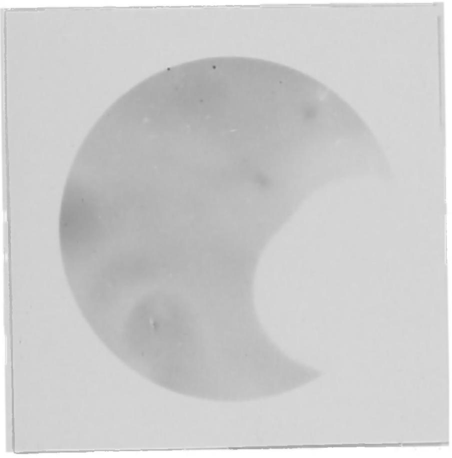

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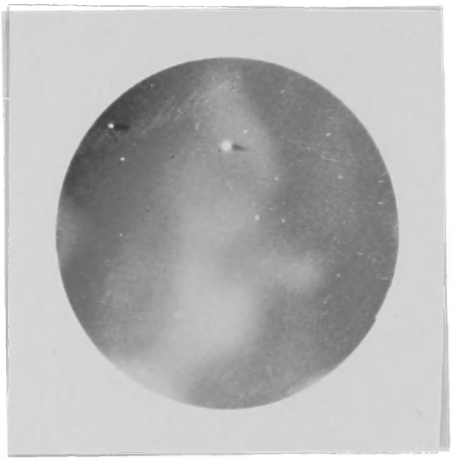

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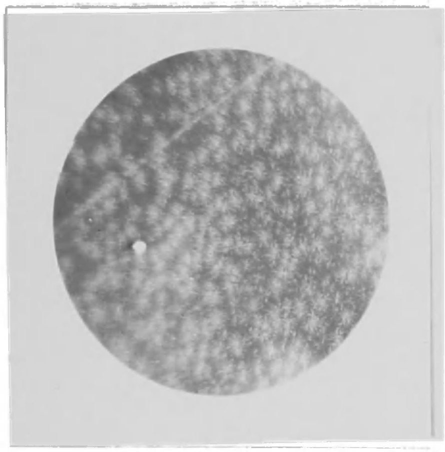

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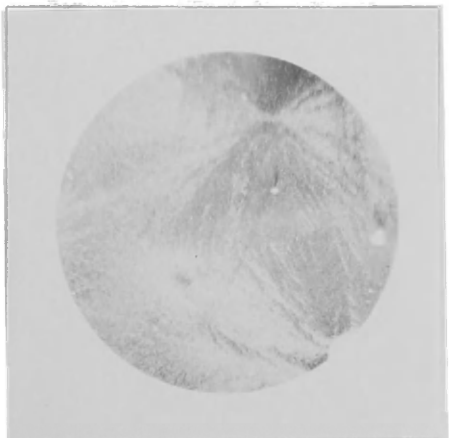

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Figure 18

Photomicrographs

IV Glaze Co-1

Varying Moisture Content

Without Sulfur

With Sulfur

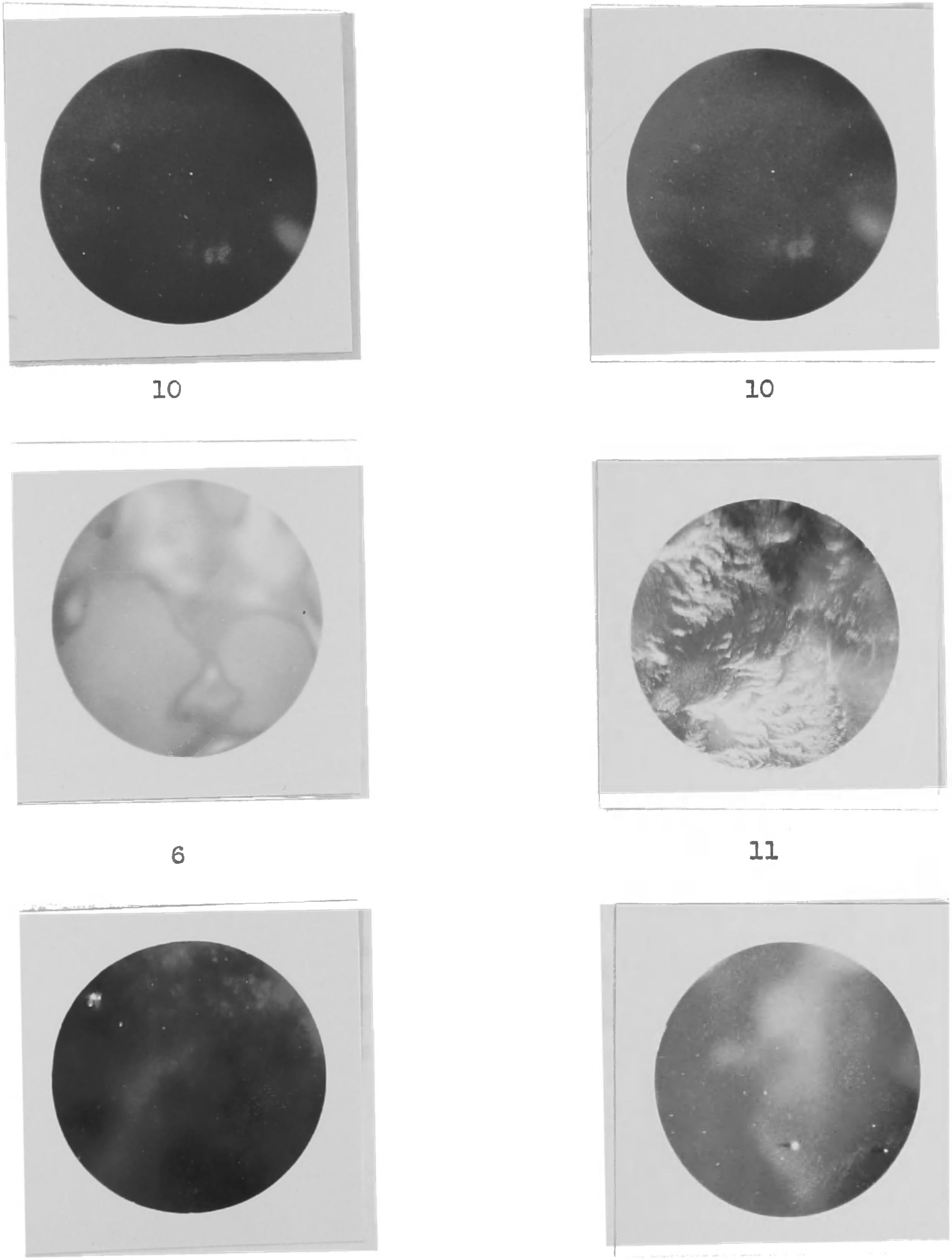

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TABLE 19

SUMMARY OF EXPERIMENTAL RESULTS

V Glaze Cr - 2

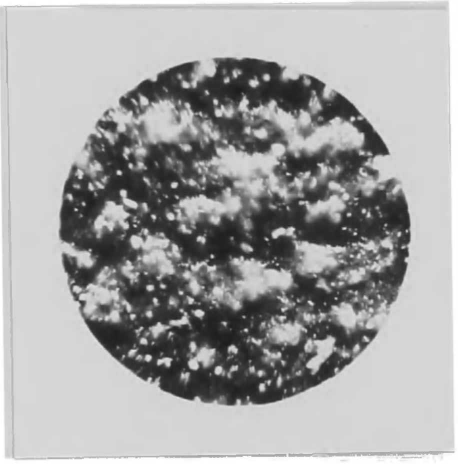
Reference	No.	Color	Texture	Var. (% Theor. Air)	Reflectivity	Specular Gloss
A	1	Green	bright,matte	70.0	44.3	3.86
	2	Green	matte	85.0	49.2	3.78
	3	Purplish Gray	bright,smooth	94.0	56.6	5.40
	4	Purplish Gray	duller,rougher	107.0	54.1	5.36
	5	Purplish Gray	dull,rough	137.0	54.1	5.36
	6	Purplish Gray	dull,rough	air	54.1	5.80
				(grains S) (Av./100 cu.ft.)		
B	6	Purplish Gray	dull,rough	air	54.1	5.80
	4	Purplish green spots	dull,rough	1	54.1	5.36
	7	Purplish green spots	dull,rough	5	54.1	5.26
	8	Purplish green spots	dull, sl.rough	11	54.1	5.18
	9	Purplish green spots	dull,smooth	18	54.1	4.89
				(water vapor) (gm./cu.ft.)		
C	10	Purplish gray spots	duller,sl.rough	dry	59.0	5.36
	6	Purplish gray	dull,rough	1	54.1	5.80
	12	Lt.Purplish gray spots	duller,sl.rough	16	59.0	5.23
				(with sulfur)		
D	10	Purplish gray,spots	dull,smooth	dry	59.0	5.36
	11	Purplish gray,spots	duller,smooth	dry + 5	59.0	5.23
	7	Purplish gray,spots	dull,sl.rough	gas + 5 (1.1)	54.1	5.26

Figure 19

Photomicrographs

V Glaze Cr-2

Varying Theoretical Air



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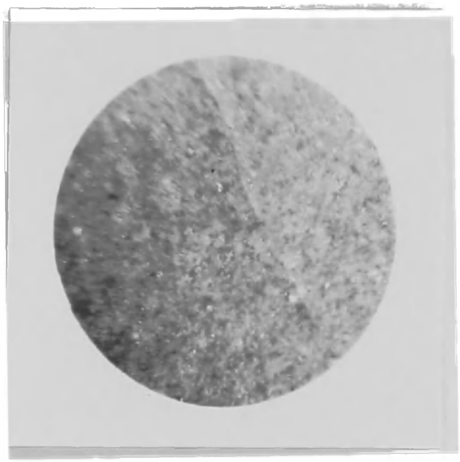

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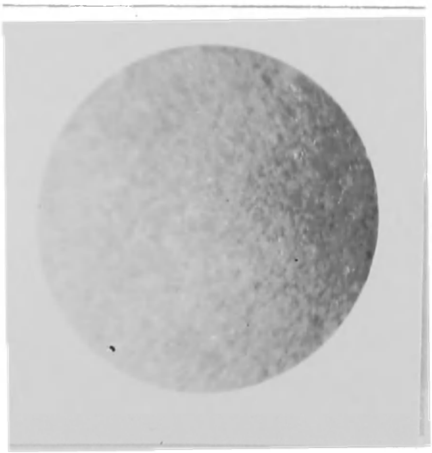

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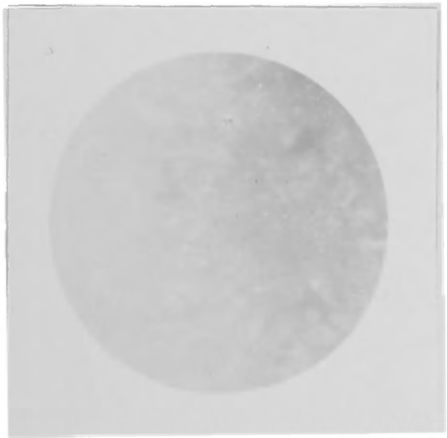

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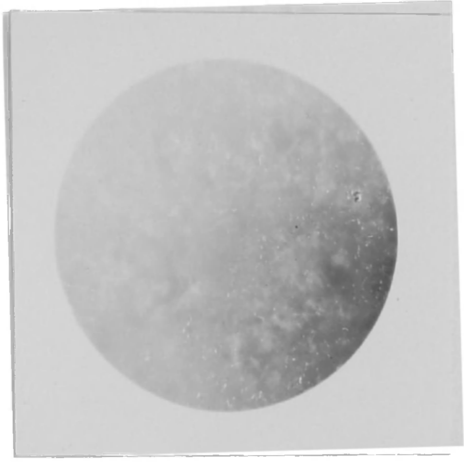
Figure 20

Photomicrographs

V Glaze Cr-2

Varying Sulfur Content



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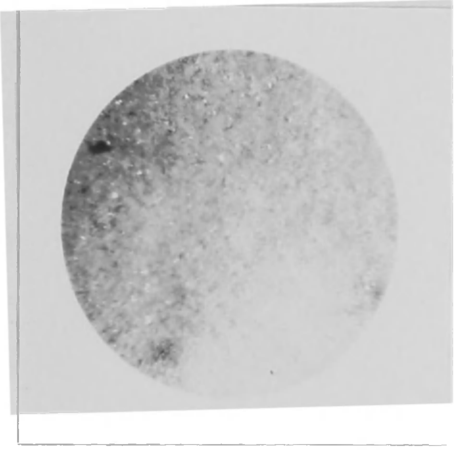

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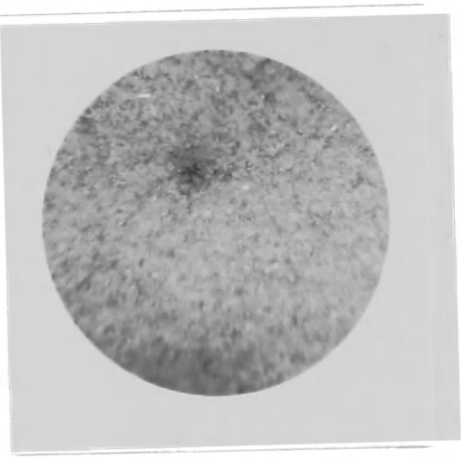

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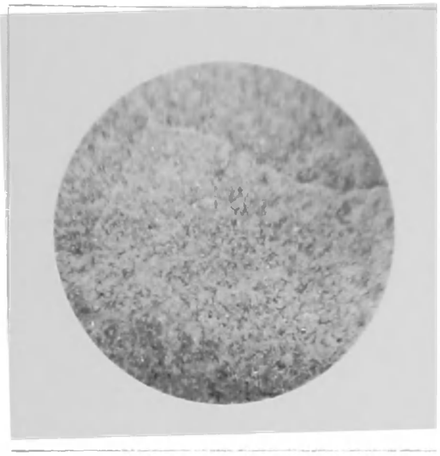

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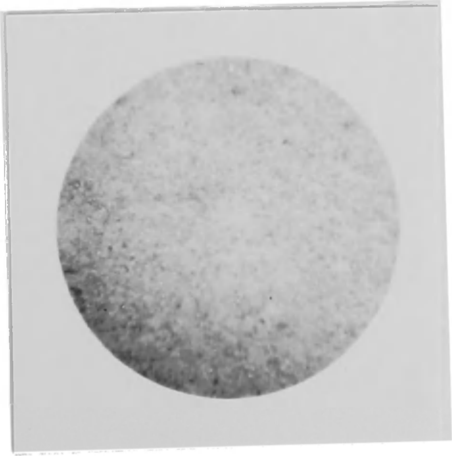

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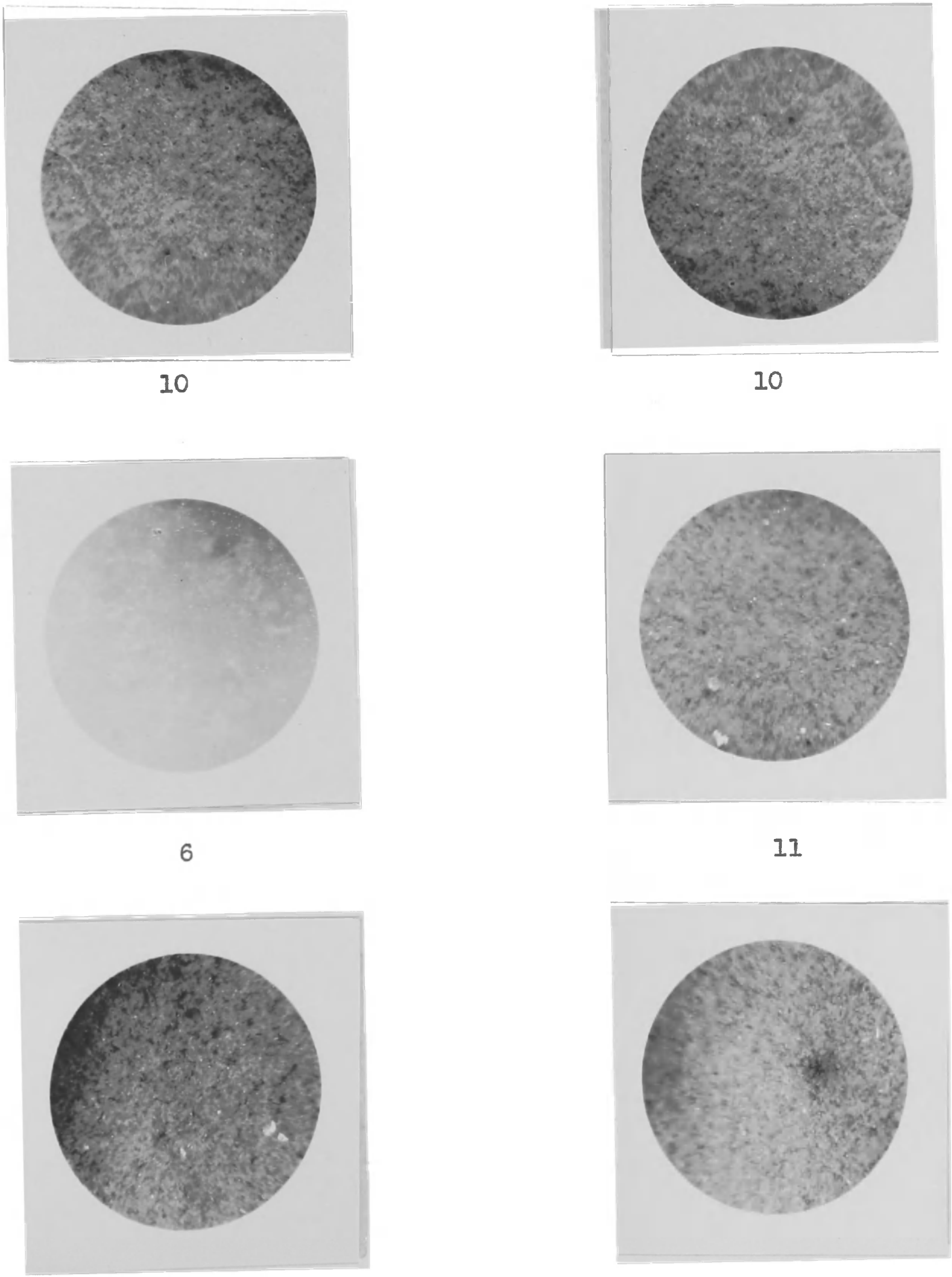
Figure 21

Photomicrographs

V Glaze Cr-2

Varying Moisture Content



Without Sulfur

With Sulfur

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TABLE 20

SUMMARY OF EXPERIMENTAL RESULTS

VI Glaze Mn - 1

Reference	No.	Color	Texture	Var. (% Theor. Air)	Reflectivity	Specular
A	1	White	dull[105]	70.0	88.8	5.41
	2	white	dull, wavy	85.0	91.0	5.23
	3	white, brown tinge	bright, wavy	94.0	88.8	5.29
	4	brownish purple	bright, wavy	107.0	49.2	5.75
	5	browner purple	bright, wavy	137.0	49.2	6.00
	6	Lt. brownish purple	bright, wavy	air	46.8	5.80
				(grains S) (av./100 cu.ft.)		
B	6	Lt. brownish purple	bright, wavy	air	46.8	5.80
	4	brownish purple	bright, wavy	1	49.2	5.75
	7	brownish purple	bright, light scum	5	49.2	5.85
	8	brownish purple	bright, faint pinholes	11	49.2	5.64
	9	Lt. brownish purple	dull, scum	18	56.6	5.10
				(water vapor) (gm./cu.ft.		
C	10	brownish purple	bright, smooth	dry	46.8	5.90
	6	Lt. brownish purple	bright, wavy	1	46.8	5.80
	12	brownish purple	bright, smooth	16	46.8	5.58
				(with sulfur)		
D	10	brownish purple	brighter, smooth	dry	46.8	5.90
	11	green tinge brown-purple	dull, feathering, smooth	dry + 5	49.2	5.07
	7	very light brownish purple	bright, lt. brown scum	gas + 5 (1.1)	49.2	5.85

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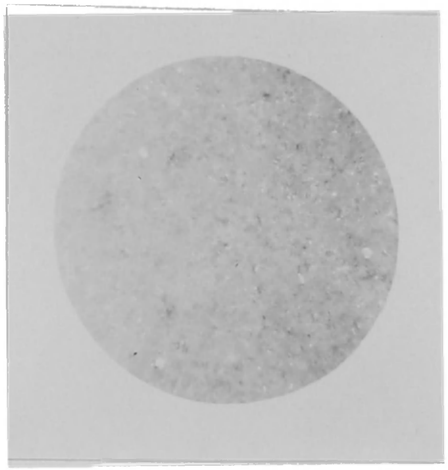
[105] Crazing in all cases.

Figure 22

Photomicrographs

VI Glaze Mn-1

Varying Theoretical Air



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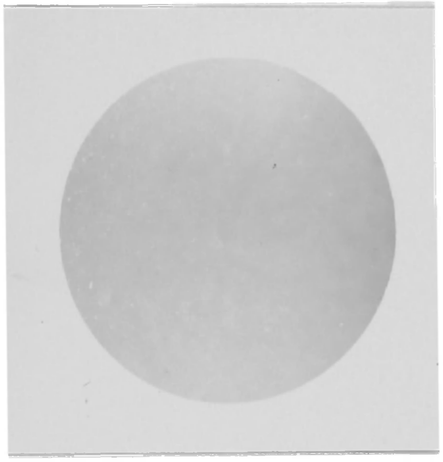

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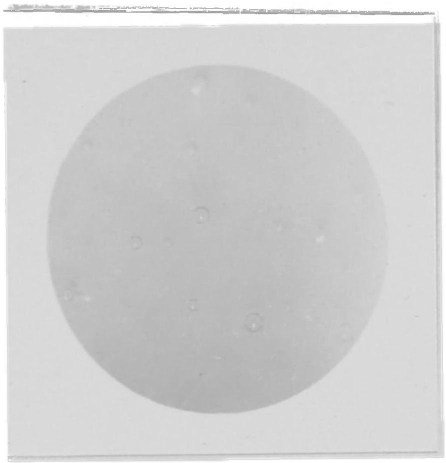

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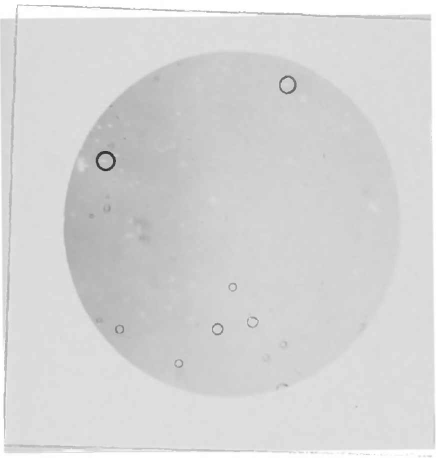

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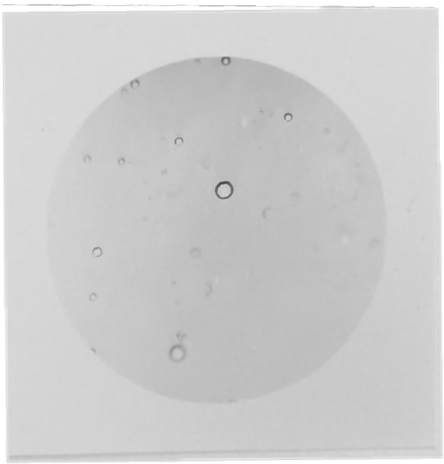

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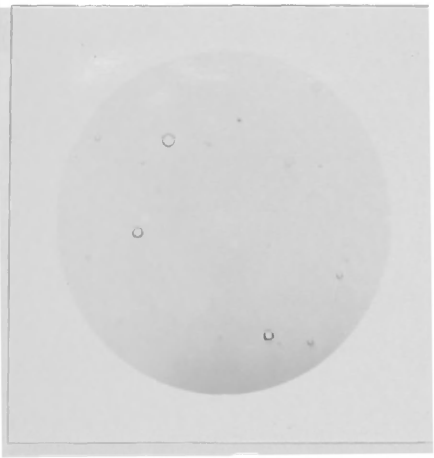

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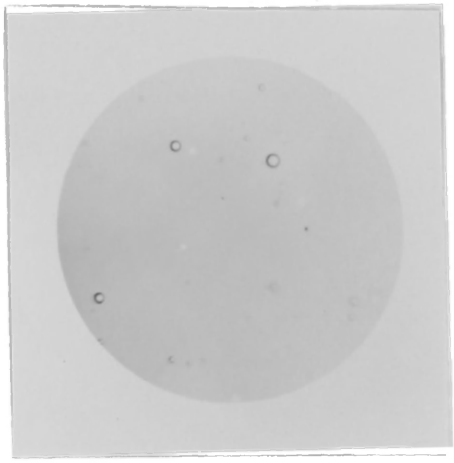
Figure 23

Photomicrographs

VI Glaze Mn-1

Varying Sulfur Content



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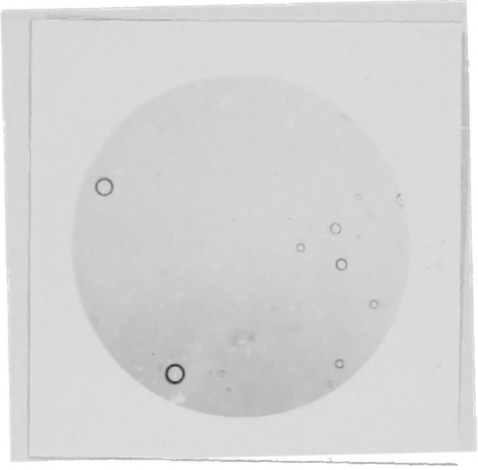

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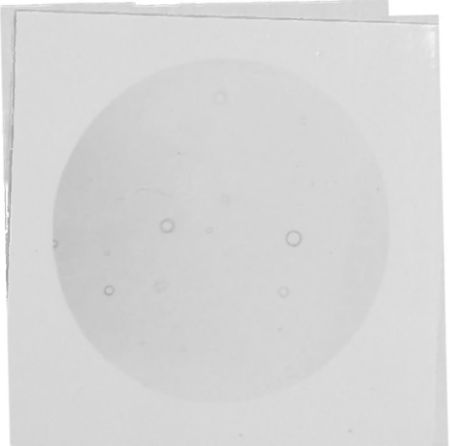

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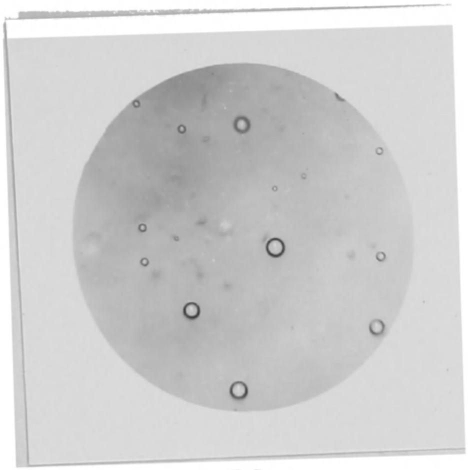
Figure 24

Photomicrographs

VI Glaze Mn-1

Varying Moisture Content

Without Sulfur



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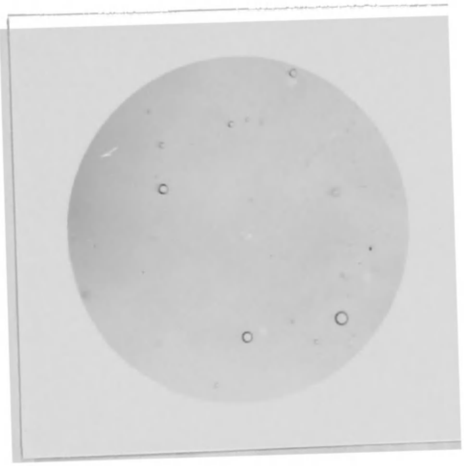

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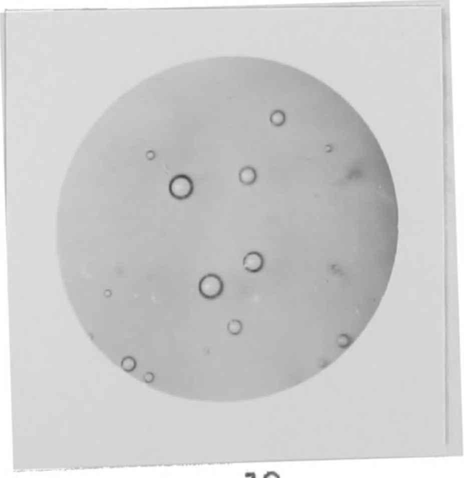

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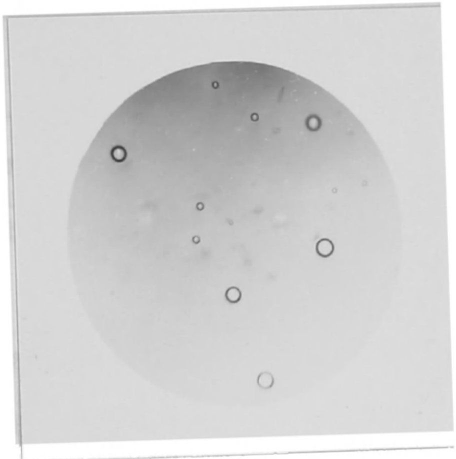
With Sulfur



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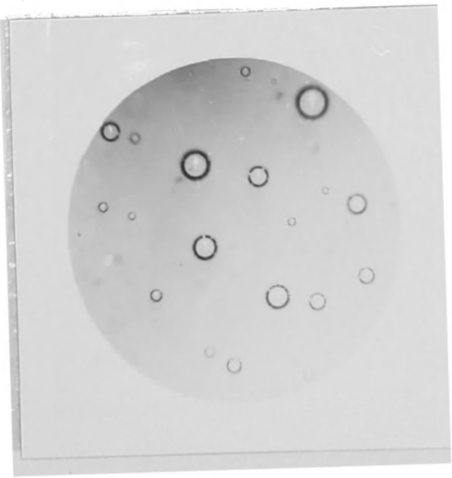

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TABLE 21

SUMMARY OF EXPERIMENTAL RESULTS

VII Glaze Ni - 1

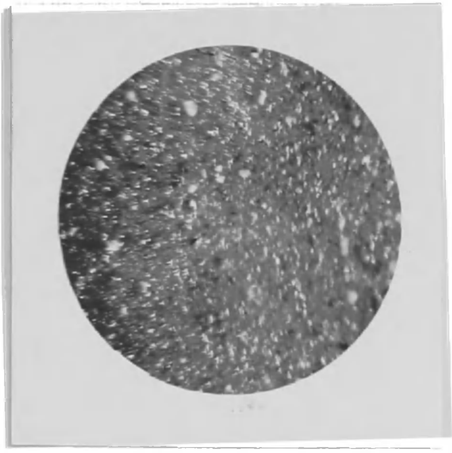
Reference	No.	Color	Texture	Var. (% Theor. Air)	Reflect-ivity	Specu-lar Gloss
A	1	Lt. Gray	dull,rougher	70.0	49.2	4.19
	2	dark gray	brighter,rougher	85.0	49.2	4.62
	3	greenish yellow	bright,rough	94.0	61.5	4.84
	4	greenish yellow	dull,smooth	107.0	68.9	5.21
	5	greenish yellow	dull,smoother	137.0	59.0	4.86
	6	greenish yellow	dull,smoother	air	64.0	5.05
				(grains S) (av./100 cu.ft.)		
B	6	greenish yellow	dull,smoother	air	64.0	5.05
	4	greenish yellow	dull,smoother	1	68.9	5.21
	7	greenish yellow	duller,smoother	5	66.5	4.94
	8	greenish yellow	duller,smoother	11	64.0	4.91
	9	greenish brown tinge	dullest, smoother	18	68.9	4.62
				(water vapor) (gm./cu.ft.)		
C	10	dark greenish yellow,lt. green spots	duller,pin-holed	dry	73.8	5.26
	6	greenish yellow	dull,smoother	1	64.0	5.05
	12	greenish yellow brown tinge	sl.bright,smooth	16	73.8	5.40
				(with sulfur)		
D	10	dark greenish yellow,lt.green spots	dull,fine pinholes	dry	73.8	5.26
	11	dark greenish yellow,brown tinge	dull,fine pinholes	dry + 5	73.8	4.99
	7	lt.greenish yellow	duller,smoother	gas + 5 (1.1)	66.5	4.94

Figure 25

Photomicrographs

VII Glaze Ni-1

Varying Theoretical Air



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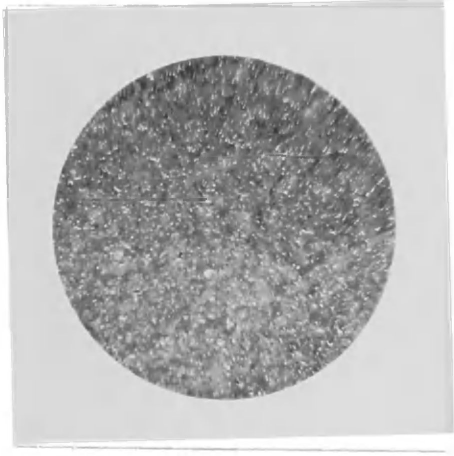

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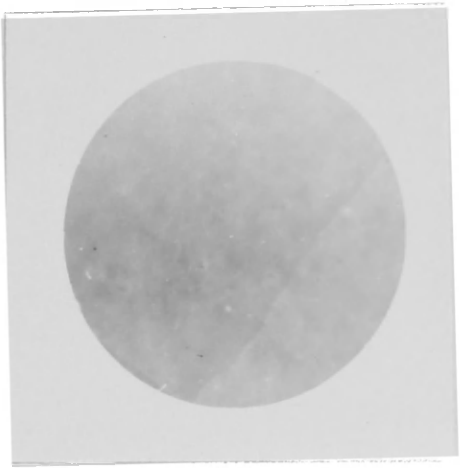

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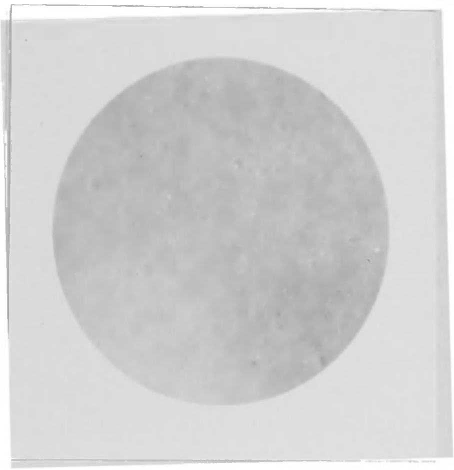

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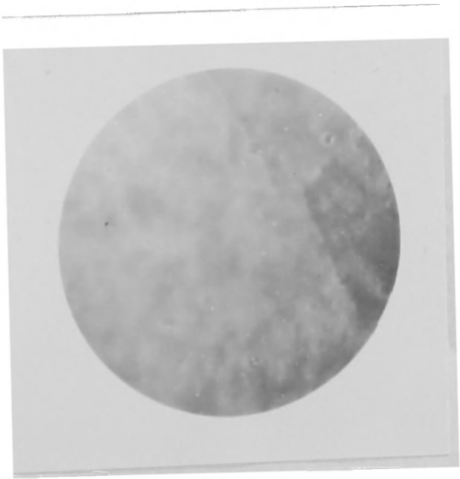

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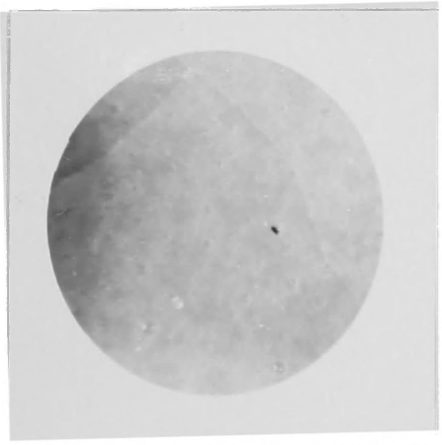

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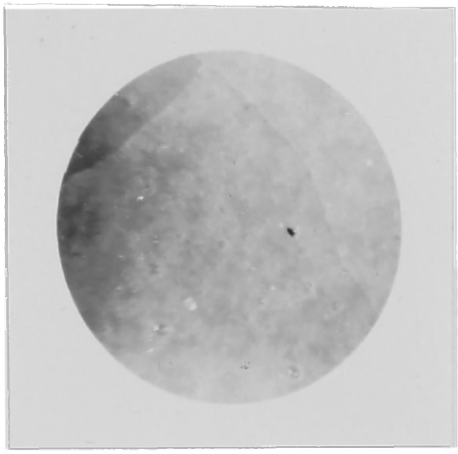
Figure 26

Photomicrographs

VII Glaze Ni-1

Varying Sulfur Content



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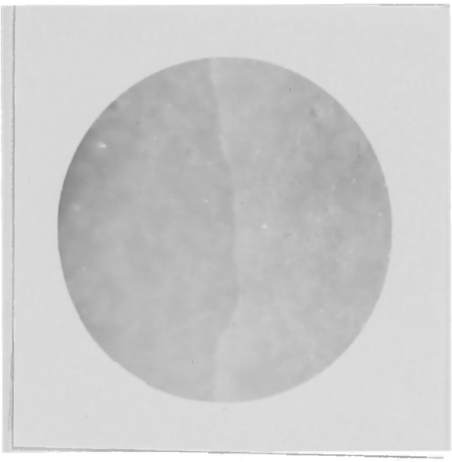

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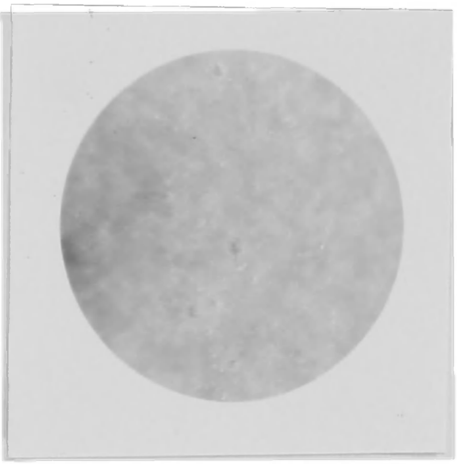

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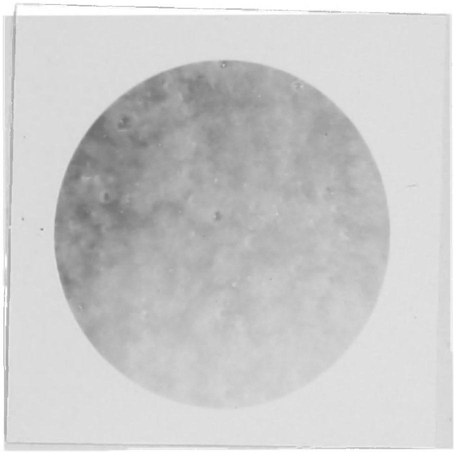

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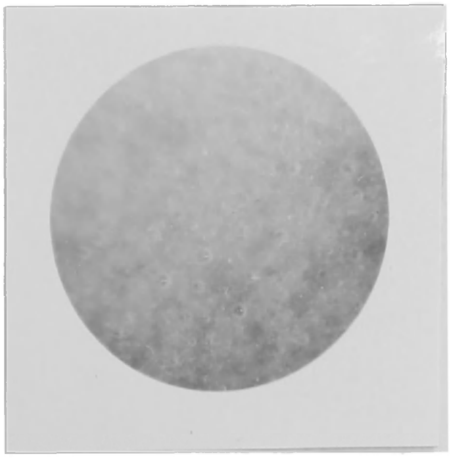

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Figure 27

Photomicrographs

VII Glaze Ni-1

Varying Moisture Content

Without Sulfur

With Sulfur

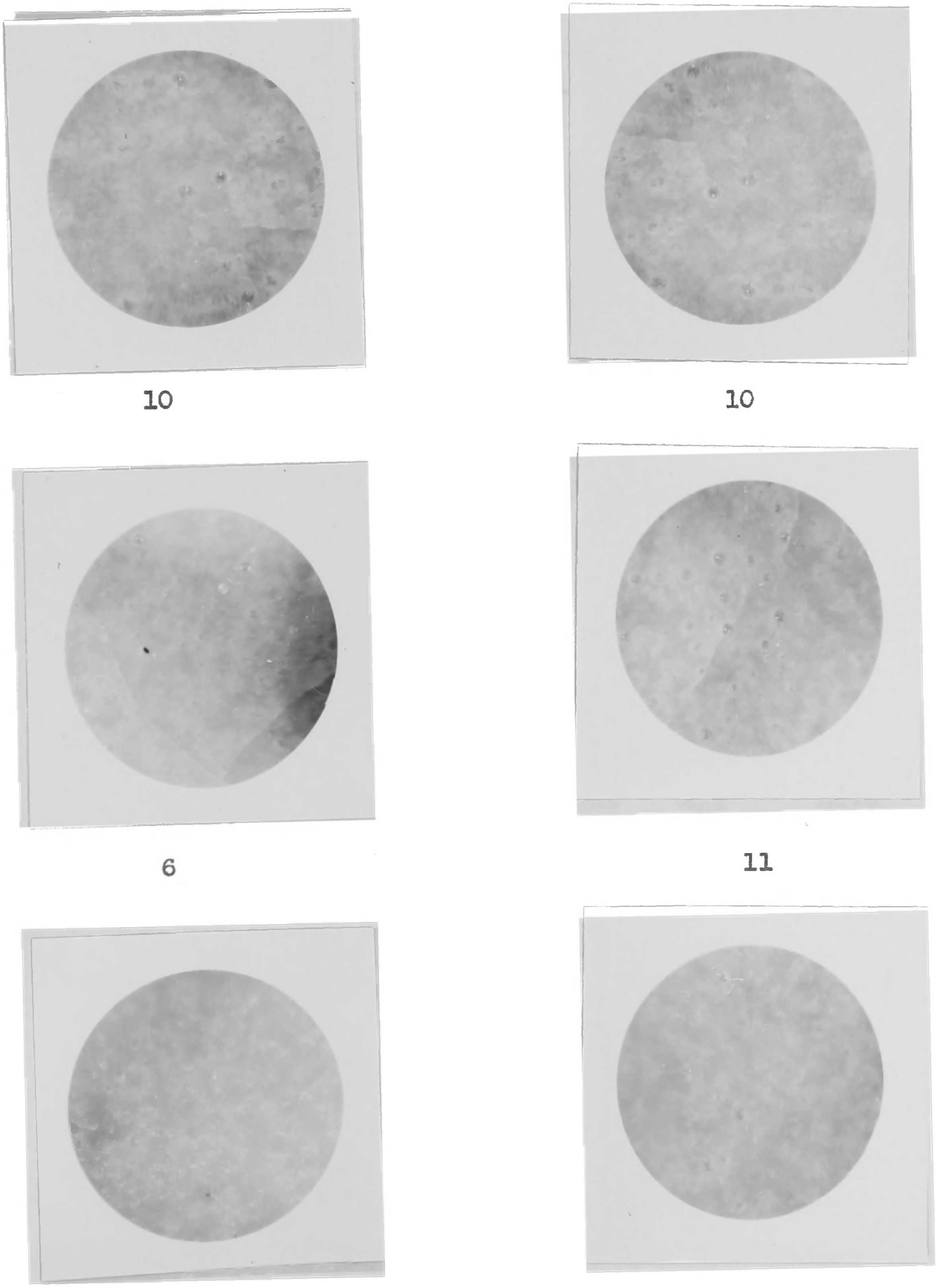

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TABLE 22

SUMMARY OF EXPERIMENTAL RESULTS

VIII Glaze Fe - 5

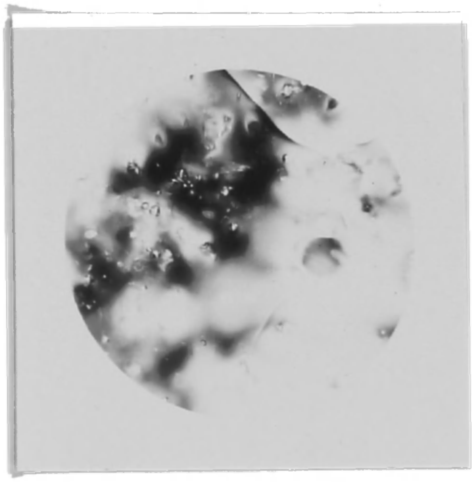
Reference No.	Color	Texture	Var. (% Theor. Air)	Reflectivity	Specular Gloss
A 1	blue	bright, large pinholes	70.0	36.9	5.37
2	blue	bright, large pinholes	85.0	39.4	5.53
3	blue-black	bright, small pinholes	94.0	36.9	5.83
4	dark brown	dull, small pinholes	107.0	39.4	5.75
5	brown	duller, small pinholes	137.0	41.8	5.53
6	brown	dullest, small pinholes	air	39.4	5.45
			(grains S) (av./100 cu.ft.)		
B 6	brown	dullest, small pinholes	air	39.4	5.45
4	dark brown	duller, small pinholes	1	39.4	5.75
7	darker brown	bright, small pinholes	5	41.8	5.94
8	darker brown	bright, badly pitted	11	36.9	5.37
9	blue-brown-black	bright, very badly pitted	18	39.4	4.84
			(water vapor) (gm./cu.ft.)		
C 10	brown, dark	bright, pinholes	dry	44.3	5.59
6	brown	dullest, small pinholes	1	39.4	5.45
12	light brown	most dull, pinholes	16	41.8	5.21
			(with sulfur)		
D 10	brown, dark	bright, pinholes	dry	44.3	5.59
11	brown, dark	dull, rough, brown scum	dry + 5	44.3	4.80
7	darker brown	bright, small pinholes	gas + 5 (1.1)	41.8	5.94

Figure 28

Photomicrographs

VIII Glaze Fe-5

Varying Theoretical Air



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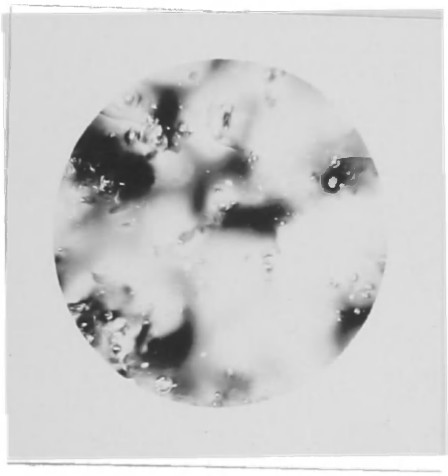

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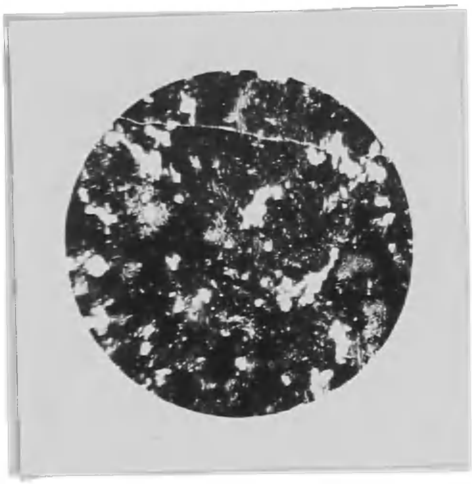

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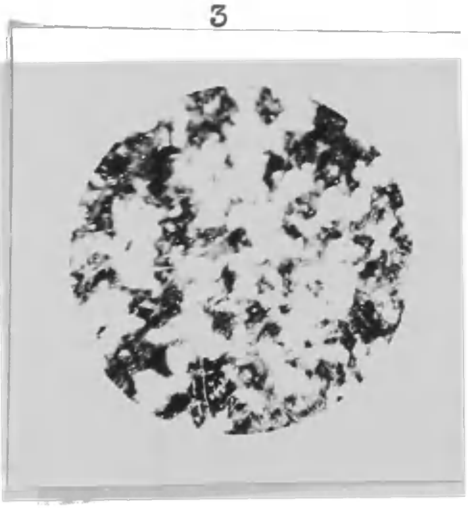

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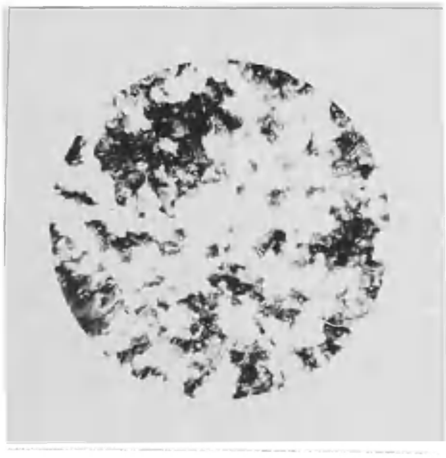

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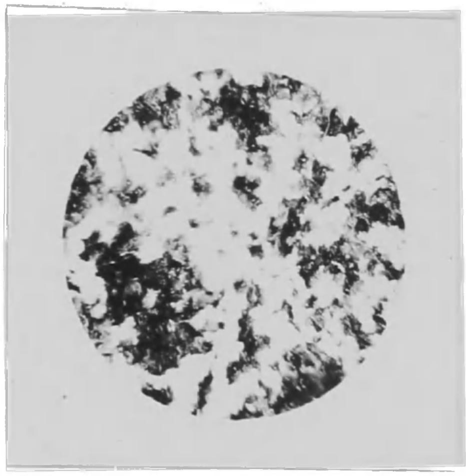
Figure 29

Photomicrographs

VIII Glaze Fe-5

Varying Sulfur Content



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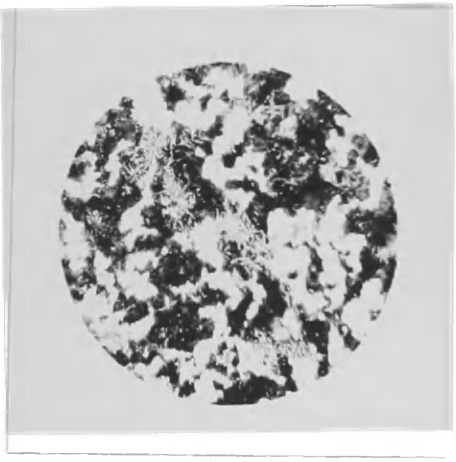

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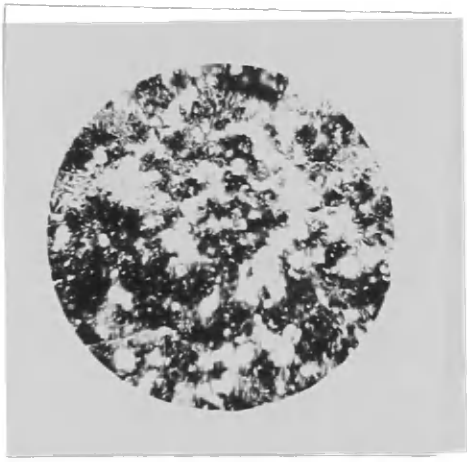

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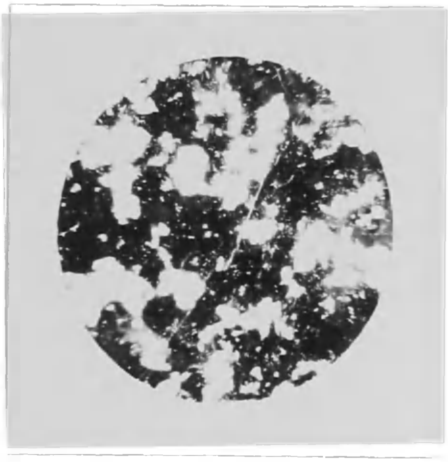

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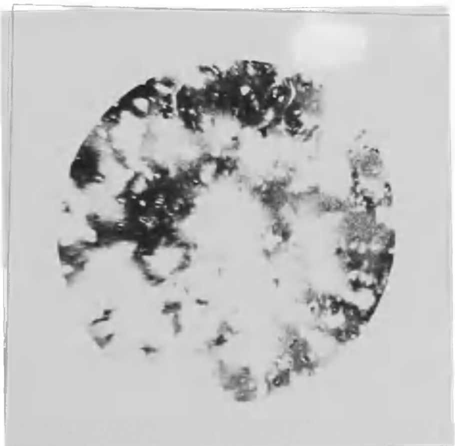

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Figure 30

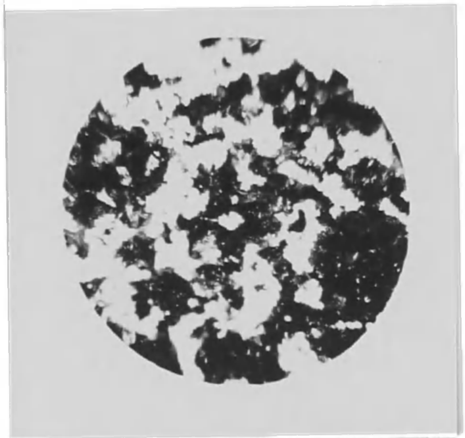
Photomicrographs

VIII Glaze Fe-5

Varying Moisture Content

Without Sulfur

With Sulfur



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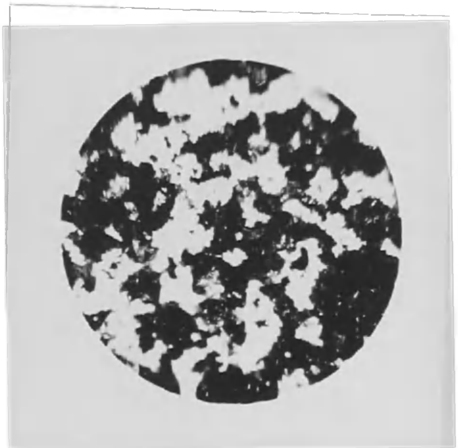

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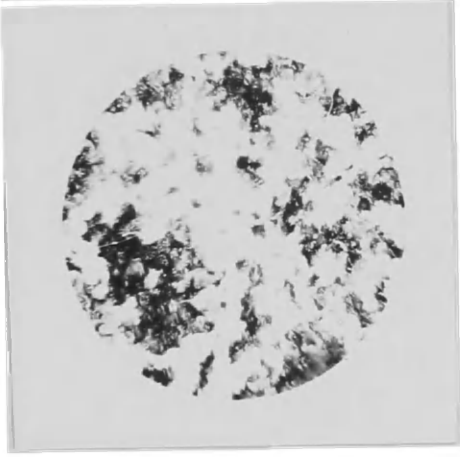

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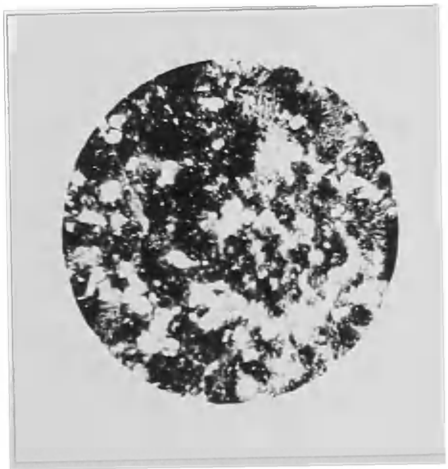

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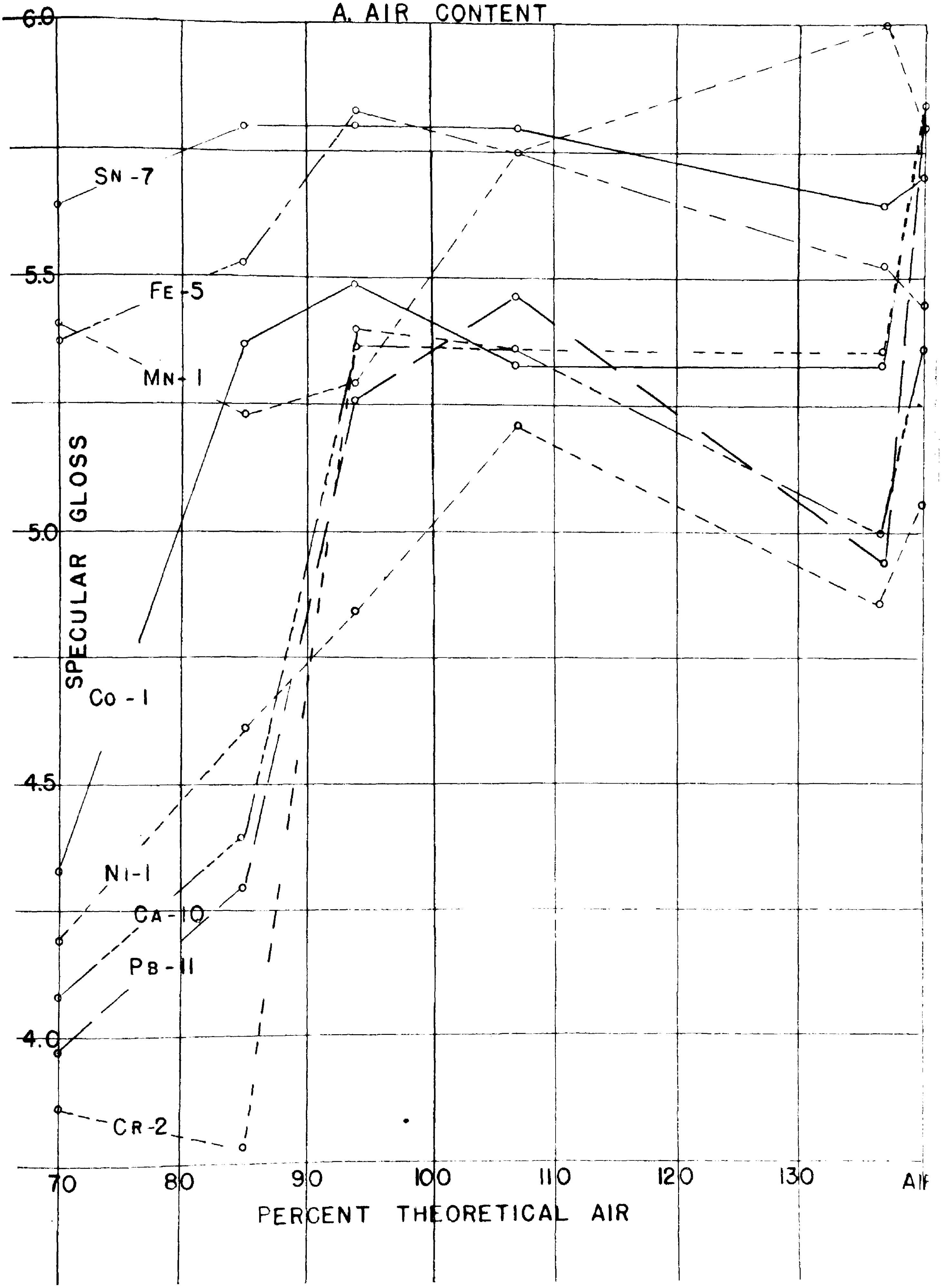
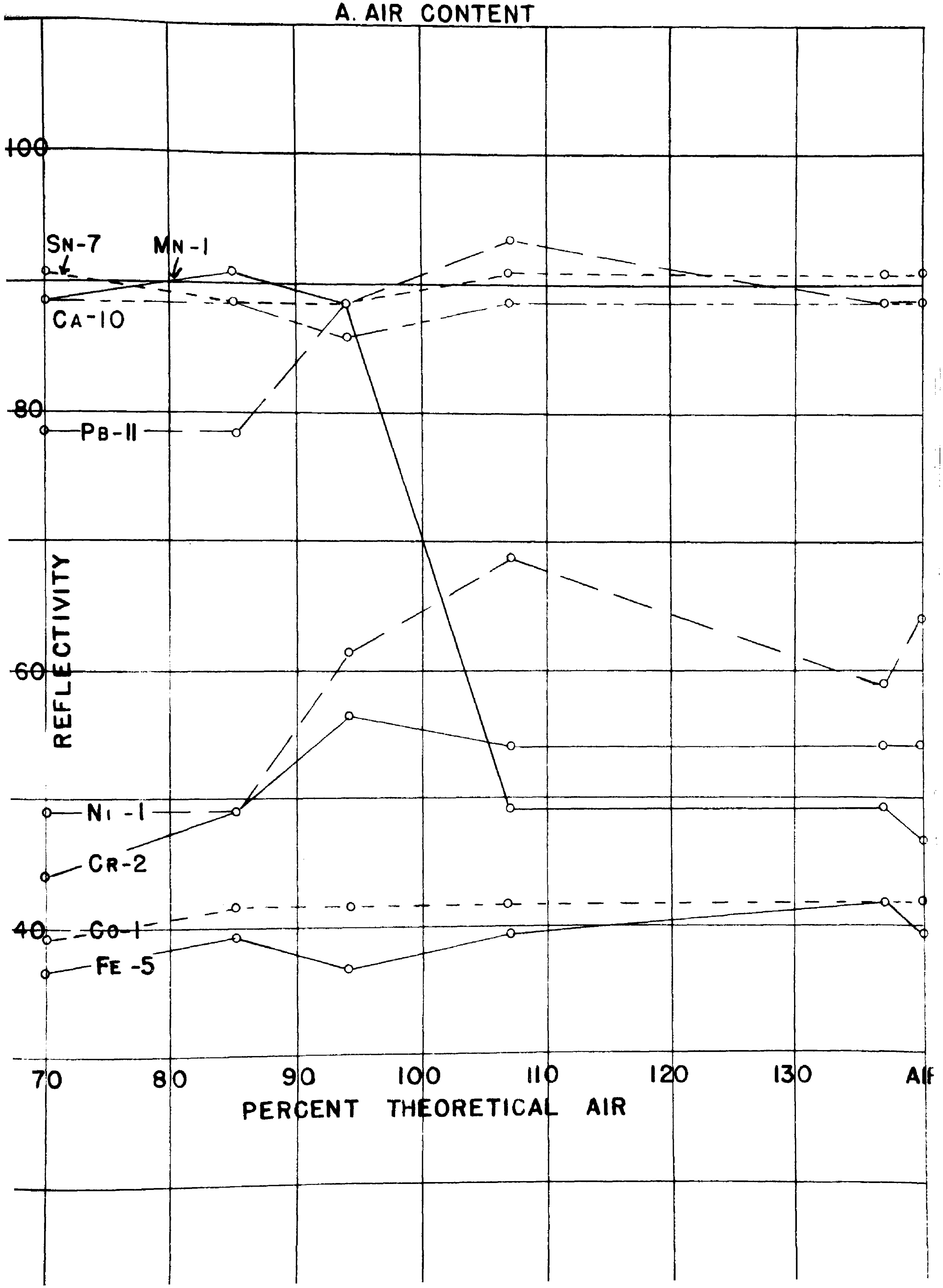
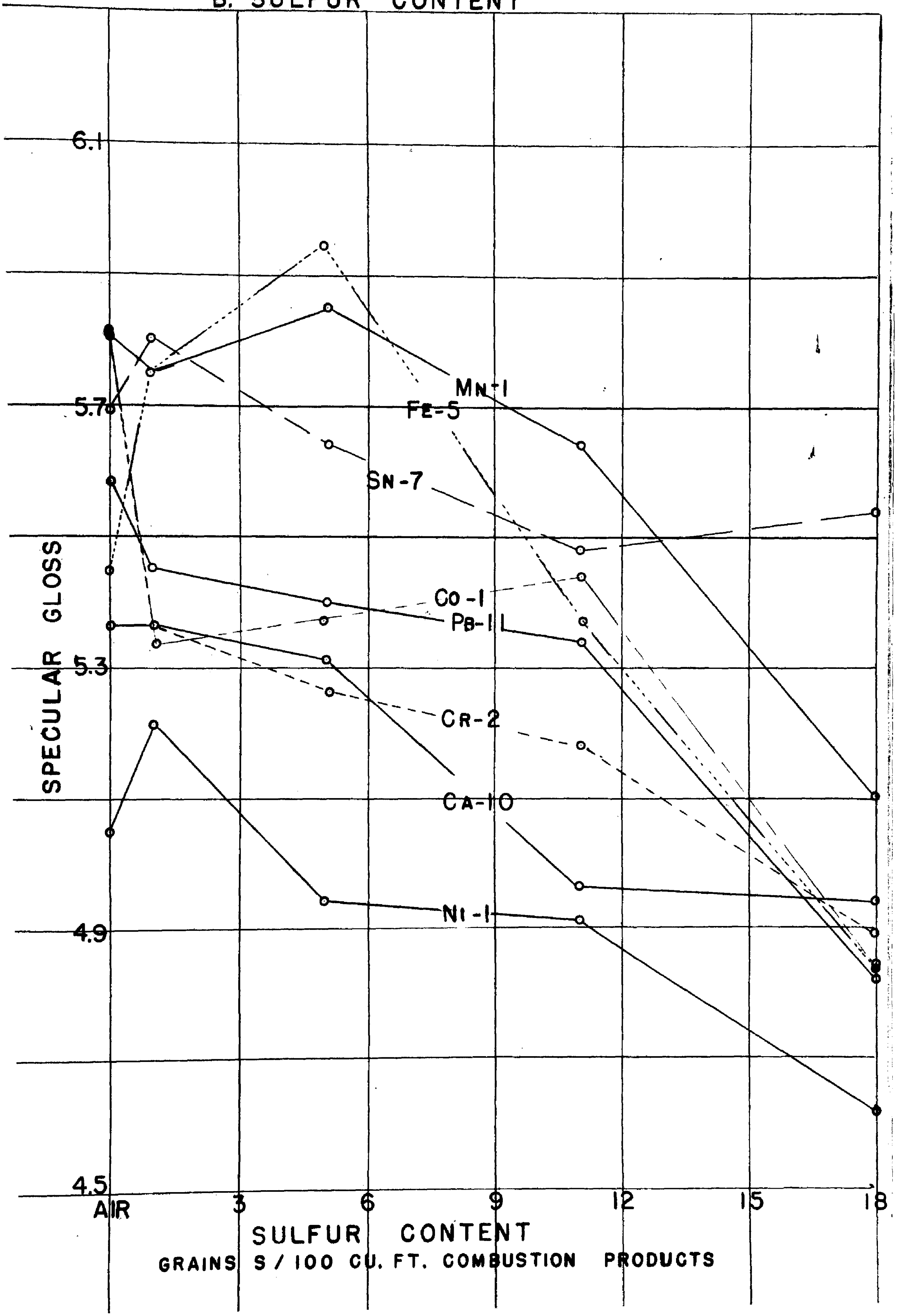
GRAPH 3.-
SPECULAR GLOSS
A. AIR CONTENT



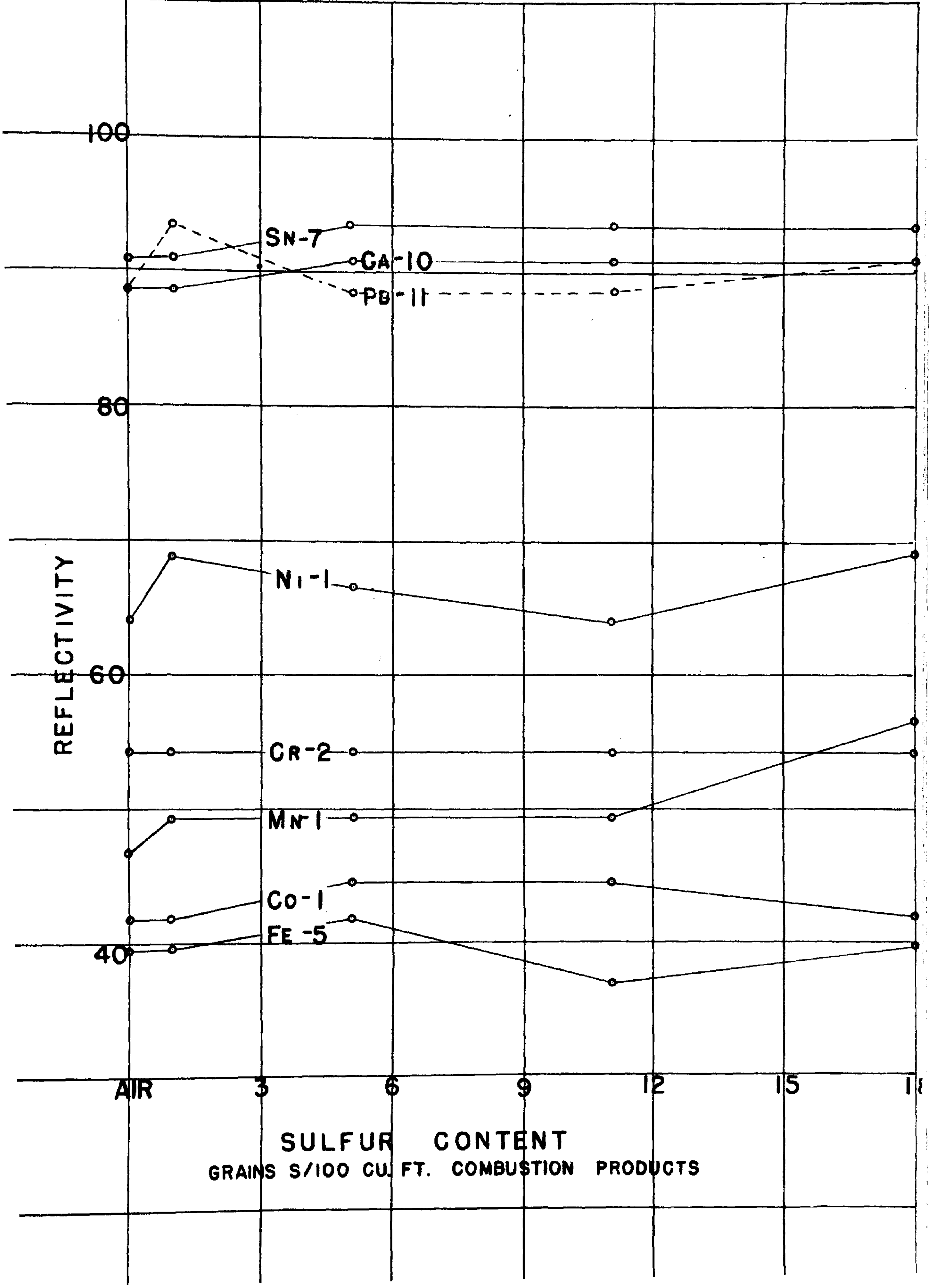
GRAPH 4.-
REFLECTIVITY
A. AIR CONTENT



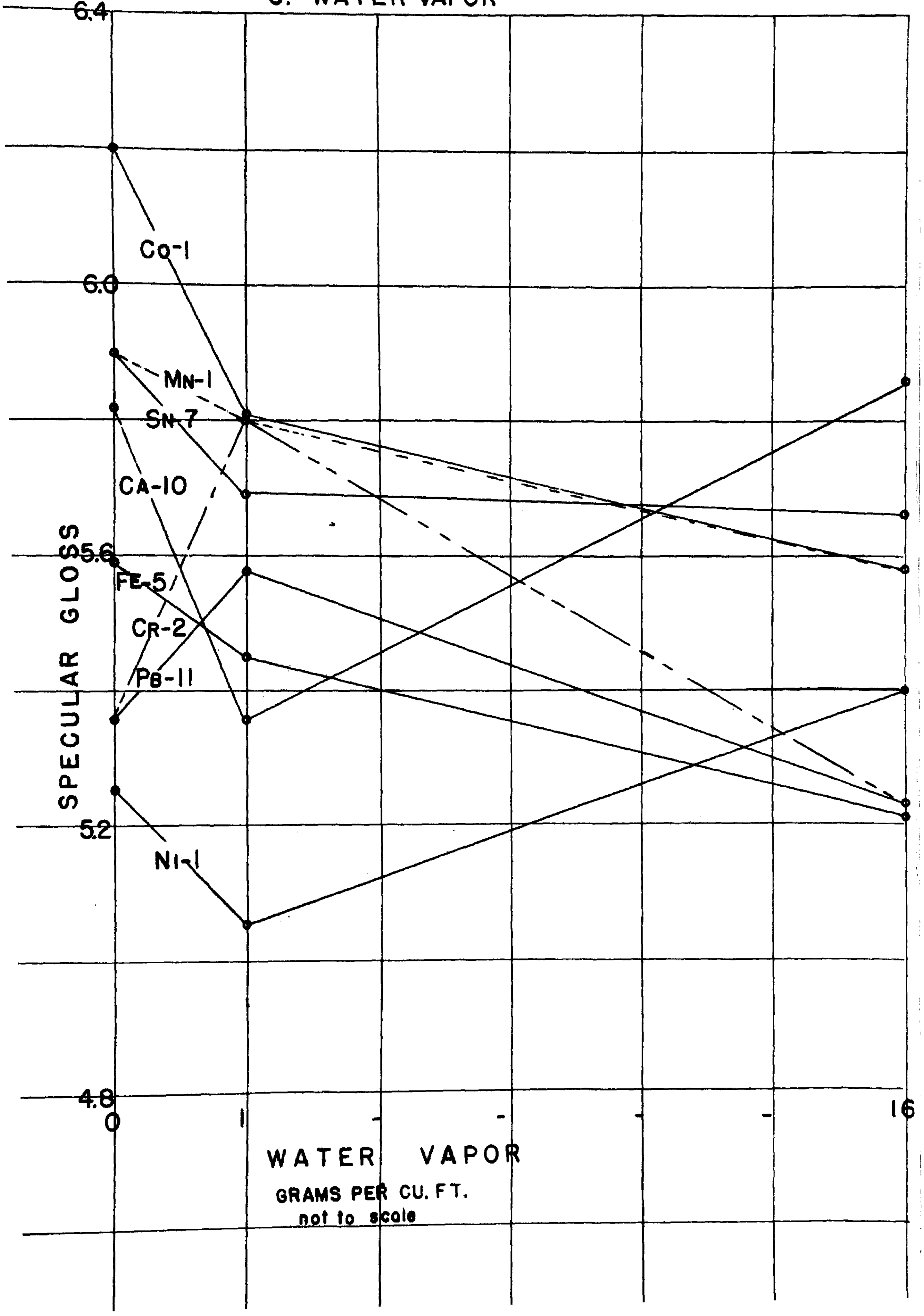
GRAPH 5.-
SPECULAR GLOSS
B. SULFUR CONTENT



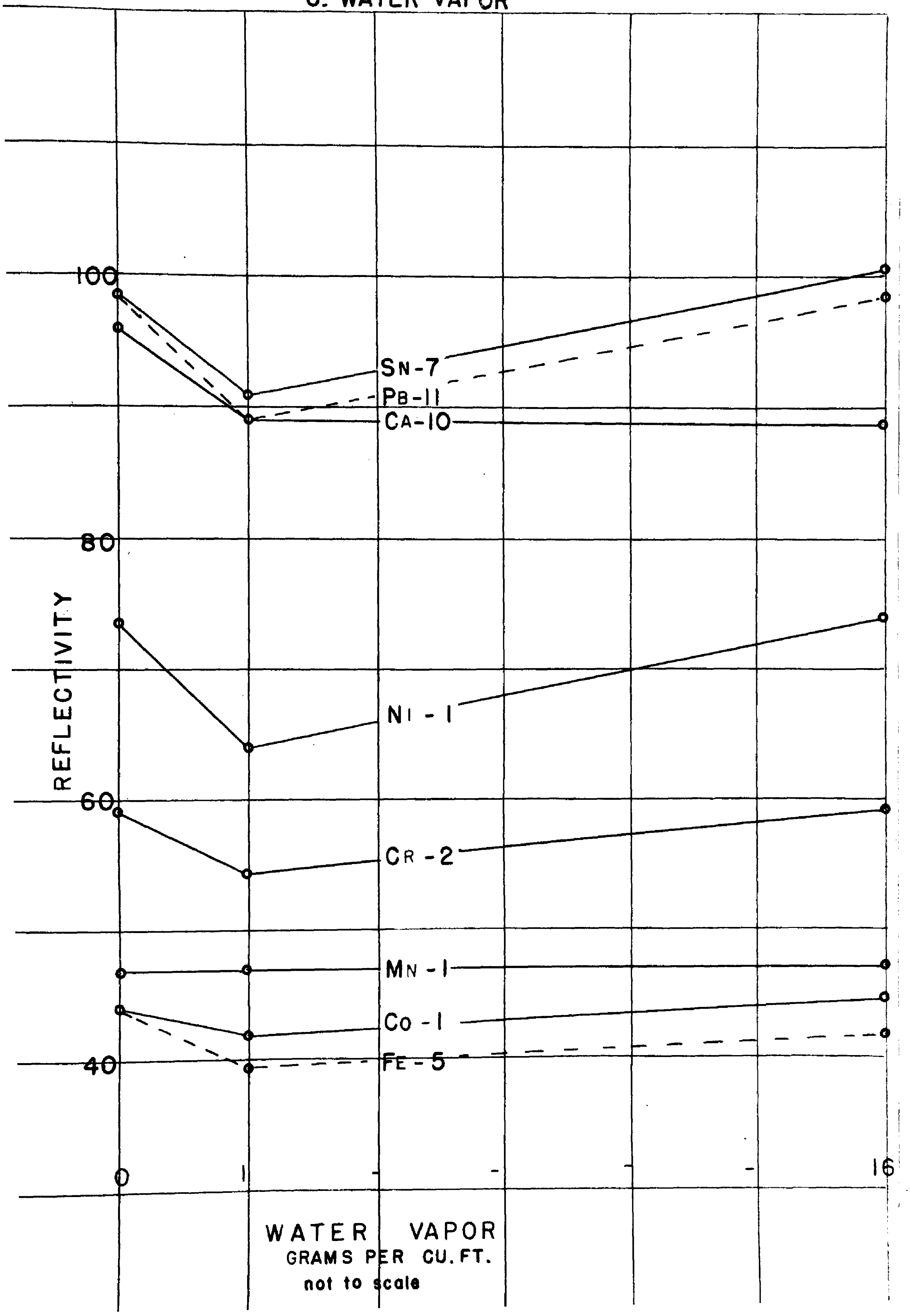
GRAPH 6.- REFLECTIVITY
B. SULFUR CONTENT



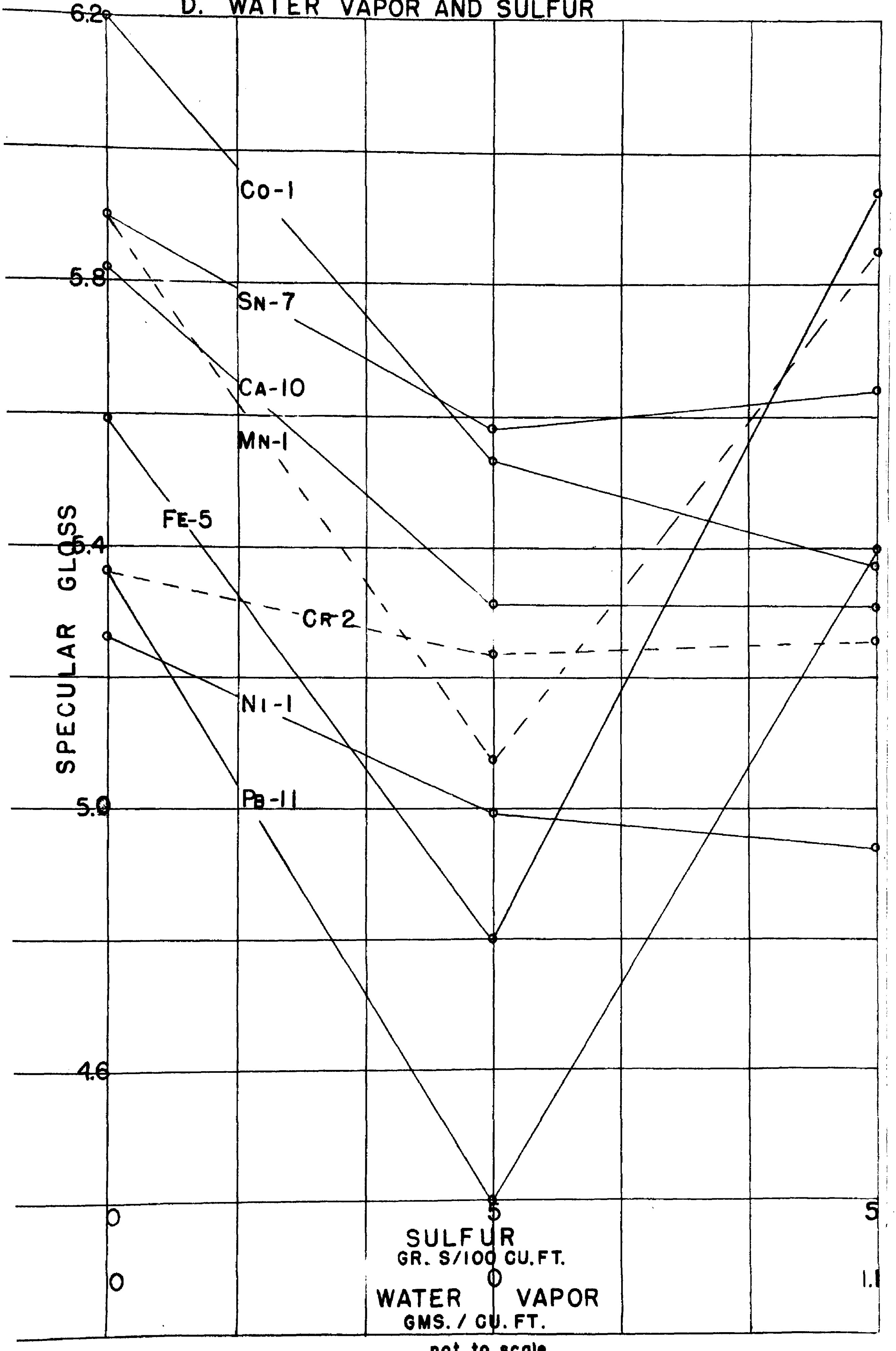
GRAPH 7.-
SPECULAR GLOSS
C. WATER VAPOR



GRAPH 8.-
REFLECTIVITY
C. WATER VAPOR

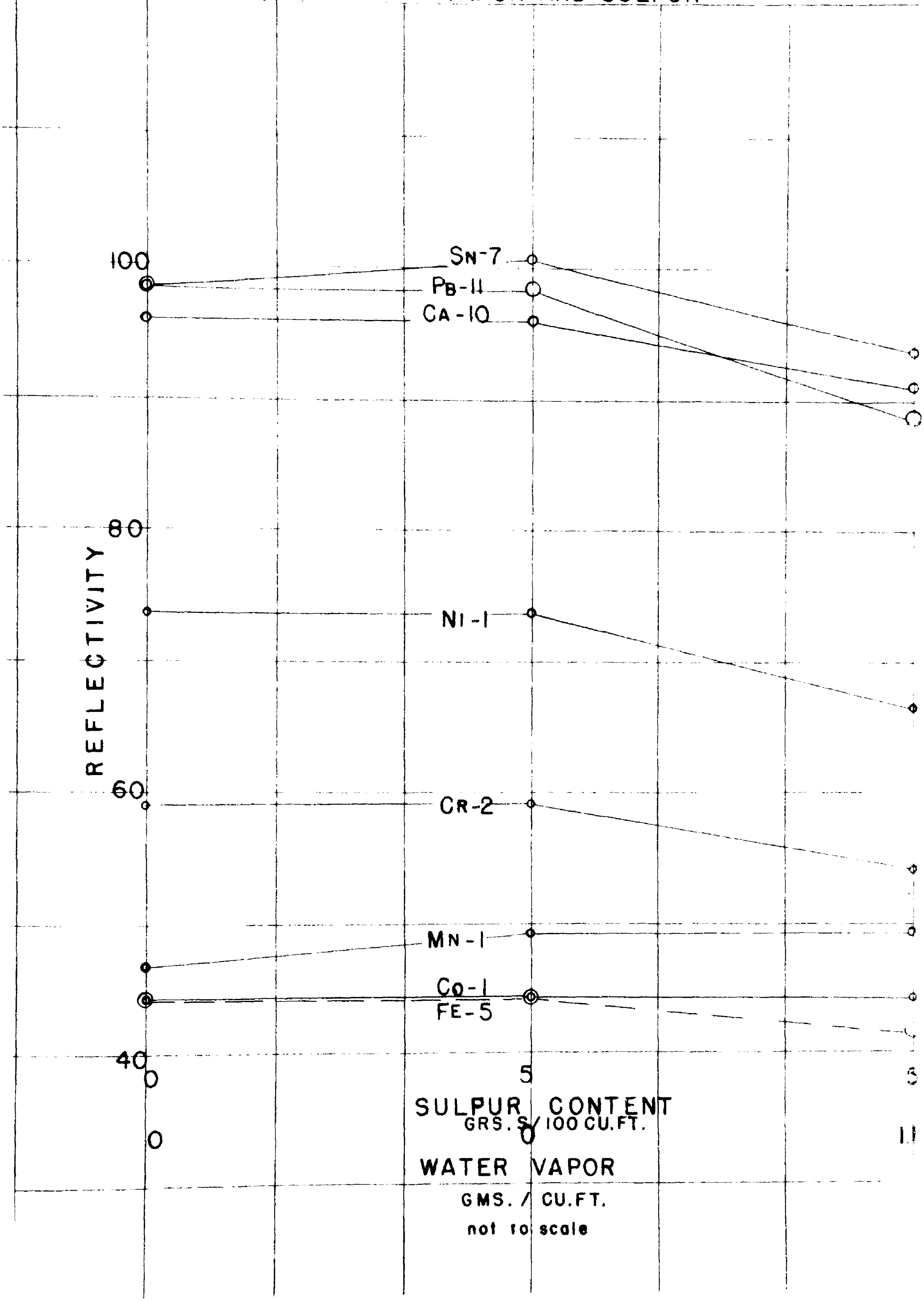


GRAPH 9.-
SPECULAR GLOSS
D. WATER VAPOR AND SULFUR



not to scale

GRAPH 10.-
REFLECTIVITY
D. WATER VAPOR AND SULFUR



H. DISCUSSION OF RESULTS

In the firing of glazes with manufactured gas of assumed relatively constant composition, two variables are apparent. These are the amount of excess air to be used and the amount of sulfur in the gas. The first variable is of considerable economic importance and lies within the control of the operator of the furnace. The second variable, sulfur, is dependent upon the efficiency of its removal in the gas manufacturing operations (and to some extent upon the type of fuel used in the gas making process). The effect of these variables is therefore investigated.

A. Variation of Excess Air[106]

Development of the glazes under an atmosphere obtained by the combustion of manufactured gas with about one hundred thirty-seven (137) percent theoretical air results in glazes essentially equivalent to air firing.[107] When the amount of air is decreased to give strongly reducing conditions,(seventy (70) percent theoretical air), it is noticed that the color and texture varies.

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[106] See Graphs and Data pages 118 and 66 in "Expression of Results".

[107] See "Summary of Experimental Results",pages 86 to 125.

These variations are dependent apparently upon the coloring agent added. Visually the changes of texture of the surface ranges from mere dulling to completely matte. Under the microscope, as shown by the photomicrographs, the loss of brightness is due to the occurrence of bubbles in the glaze. Comparison of the three methods for the expression of the results, i.e. visual, specular gloss, and photomicrographs, is given in Table 23, showing the relative results upon each glaze.[108]

---

[108] Color changes under reducing conditions are summarized in Table 24.

TABLE 23

TEXTURE CHANGES

A. VARYING THEORETICAL AIR

STRONG REDUCING CONDITIONS[109]

Glaze[110]	Visual Comparison		Specular Gloss		% Difference[111]	Photomicrographs	
	Gas	Air	Gas	Air		Gas	Air
Mn-1	dull wavy	bright wavy	5.41	5.80	6.7	very rough	random bubbles
Sn-7	dull rough	dull smooth	5.64	5.69	0.8	numerous small bubbles	smooth
Ni-1	dull rougher	dull smoother	4.19	5.05	17.1	very rough	random bubbles
Fe-5	bright large pinholes	dull small pinholes	5.37	5.45	1.5	glassy few large bubbles	smooth
Ca-10	dull matte	bright pinholing	4.08	5.36	23.5	glassy large bubbles	few bubbles small size
Co-1	very rough	smooth faint pinholes	4.33	5.81	25.5	very rough	smooth
Pb-11	shiny matte	shiny feels smooth	3.97	5.58	27.9	very rough	uniform bubbles
Cr-2	bright matte	dull rough	3.86	5.80	33.4	very rough	smooth

---

[109] About 70% theoretical air.

[110] In order of degree of change as based upon visual inspection.

[111] Based on air.

TABLE 24

COLOR DETERMINATION

Glaze	Reducing Conditions		Air Fired		Best or[112] Equiv. Gas Fired		% Theor. Air
	Visual	Reflectivity	Visual	Reflectivity	Visual	Reflectivity	
Sn-7	Yellow white	91.0	white	91.0	white	91.0	107
Ca-10	clear white	88.8	clear white	88.8	clear white	88.8	-
Pb-11	clear white(dark)	78.7	clear white	88.8	clear white	93.6	-
Ni-1	light gray	49.2	greenish yellow	64.0	greenish yellow	68.9	94
Cr-2	green	44.3	purplish gray	54.1	purplish gray	56.6	94
Mn-1	white	88.8	lt.brownish purple	46.8	brownish purple	49.2	107
Co-1	blue	39.4	blue (variable)	41.8	blue(indefinite)	41.8	107
Fe-5	blue	36.9	brown	39.4	brown	41.8	130

---

[112] The highest value or the value after which the reflectivity is constant is used provided the color is equivalent to air fired.

The amount of air for combustion is increased until all the glazes under visual inspection appears equivalent to air firing.[113] The percentage of air required varies between a ninety-four (94) percent and one hundred seven (107) percent. The lack of agreement among the various methods may be attributed to the fact that visual methods are influenced by color, texture, and amount of light reflected. The reflectometer measurements depend only upon the amount of light reflected in the direction of the measuring instrument while the panchromatic film used in photomicrographs[114] detects conditions which are beyond the scope of the eye and tends to avoid registration of mere color variations.[115,116]

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113. With the exception of the color of the iron (Fe-5) glaze which apparently was much higher than the other glazes.

114. It was difficult to make a photomicrograph of the glazes Co-1, and Fe-5 because there was no uniformity of color. The Fe-5 glaze was particularly difficult and the photograph did not record satisfactorily what was actually seen through the microscope.

115. Summation of the values obtained for the different glazes in regard to both texture and color, by the methods employed in Table 25.

116. Although the panchromatic film used is claimed to be equally sensitive to all colors, it is noted especially with the Fe-5 and Co-1 glazes that this is not strictly accurate.

TABLE 25

GAS EQUIVALENT TO AIR FIRING

A.TEXTURE

In Percent Theoretical Air

Glaze	Visual[117]	Specular Gloss[118]	Photomicrographs
Sn-7	107	b 85	107
Ca-10	94	94	107
Pb-11	107	107	107
Co-1	107	94	107
Cr-2	94	94	94 (107)
Mn-1	94	107	94 (107)
Ni-1	107	107	94
Fe-5	b 94	b 94	107

B. COLOR

		Reflectivity	
Sn-7	107	107	none made to show color
Ca-10	(no change)	107	
Pb-11	(no change)	107	
Co-1	107	85	
Cr-2	94	94	
Mn-1	107	b 107	
Ni-1	94	b 107	
Fe-5	130	130	

---

117. b indicates a value better than that of air firing.
118. Chosen at the highest point when values are rising.

B. Varying Sulfur Content

Sulfur in the combustion products may be increased sufficiently to affect the texture and color of the glazes tested. Under the higher concentrations (about eighteen (18) grains per hundred cubic feet) the texture might show complete roughness or a mere dulling of the surface.[119] The change in specular gloss readings do not in each case follow visual determinations but such readings are much better than the photomicrographs which do not allow much separation as to intensity of the effect. The photomicrographs do indicate that the effect is of a surface type as evidenced by the scumming, photographed in the case of the manganese (Mn-1) and cobalt (Co-1) glazes.

The color of the glazes is not basically changed; the scum formation only makes them lighter.

Data on the minimum concentration of sulfur affecting as shown in Table 27 indicate that a concentration of five (5) grains per hundred cubic feet will cause an effect that is visible. This is in agreement with the reflectometer data.

---

119. See Table 26 for summary and comparison of methods.

C. Varying Water Vapor Content

Of the components of the combustion products other than nitrogen, water vapor content is the largest, amounting to about fourteen (14) percent of the total volume. Water vapor is reported to have some affect upon the firing of ceramic products. Accordingly, a few tests were made with it as a variable to note whether it causes effects by its own action, or merely by decrease of the oxygen content in the combustion products.

The texture of the glazes is found to change with increasing water vapor concentration. The effect[120] varies with the coloring agent added. Some of the glazes show very small changes, in others very noticeable differences are observed. Some indication of the changes are recorded in the specular gloss readings. However, the photomicrographs indicate the causes of these differences more clearly. In a number of glazes studied, the differences may be attributed to the smaller number and size of bubbles formed by firing in atmospheres containing water than by firing in atmospheres dried by calcium chloride.

---

[120] The results and comparisons of the various methods are summarized in Table 28.

TABLE 26

SULFUR EFFECTS[121]

STRONG SULFUR CONCENTRATION[122]

	Visual		Specular Gloss			Photomicrographs[123]	
Glaze	Sulfur	Air	Sulfur	Air	% Diff.[124]	Sulfur	Air
Sn-7	bright sl.rough	bright smooth	5.54	5.69	2.6	changed density of prints	-
Ni-1	dullest smoother	dull smoother	4.94	5.05	12.0	changed density of prints	-
Cr-2	dull smoothest	dull rough	4.89	5.80	15.7	no change	-
Ca-10	dull smooth	bright wavy	4.94	5.36	7.8	changed density of prints	-
Mn-1	dull scum	bright wavy	5.10	5.80	8.5	scumming, decrease in bubbles	small bubbles
Fe-5	bright, very badly pitted	dull small pinholes	4.84	5.45	11.2	heavy pitted	pin-holes
Pb-11	roughest	sl.rough	4.83	5.58	13.4	no change	-
Co-1	dullest sl.rough	smooth faint pinholes	4.84	5.81	16.2	feathering or starring scum	glassy surface

---

121. In order of increasing effect determined visually.
122. About 18 grains sulfur per 100 cu.ft. of Combustion Product.
123. Based upon air.
124. The sulfur observation was made taking in consideration the effect of combustion products previously discussed.

TABLE 27

SULFUR LIMITATIONS

POINT OF FIRST NOTICEABLE EFFECT

grains sulfur per hundred cubic feet of Combustion Products

A. Texture

Glaze	Visual	Specular Gloss[125]	Photomicrographic
Sn-7	5	5	(no change)
Ca-10	5	5	(no change)
Pb-11	5	5	(no change)
Co-1	5	18	5
Cr-2	5	5	(no change)
Mn-1	5	11	5
Ni-1	5	5	(no change)
Fe-5	5	11	5

B. Color

		Reflectivity	
Sn-7	5	5	(no data available)
Ca-10	(no change)	5	
Pb-11	5	5	
Co-1	5	5	
Cr-2	(no change)	(no change)	
Mn-1	18	18	
Ni-1	18	5	
Fe-5	5	11	

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[125] Values are taken when the readings and comparisons are lower than the condition when firing in 107% theoretical air.

TABLE 28

VARYING WATER VAPOR CONTENT[126]

Texture

	Visual			Specular Gloss					Photomicrographs		
Glaze	Equiv. to Combustion	Normal Air	Dry[A] Air	Equiv.to Combustion Reading	Equiv.to Combustion % Diff.[127]	Normal Air Reading	Dry Air Reading	Dry Air % Diff.[127]	Equiv. to Combustion	Normal Air	Dry Air
Ca-10	brighter wavy	bright pinholes	brighter pinholes	5.85	-9.1	5.36	5.82	-8.6	feathering no bubbles	less bubbles	more bubbles
Sn-7	bright smoothest	dull smooth	brighter smoother	5.66	0.5	5.69	5.90	-3.7	sl.darker smooth	smooth	sl.darker smooth
Mn-1	bright smooth	bright wavy	bright smooth	5.58	3.8	5.80	5.90	-1.7	large bubbles darker	bubbles	large bubbles darker
Ni-1	Sl.bright smooth	dull smooth	duller pinholes	5.40	-6.9	5.05	5.26	-4.2	smaller and fewer bubbles	bubbles	darker larger bubbles
Co-1	Bright wavy	smooth faint pinholes	slightly rough	5.58	4.0	5.81	6.20	-6.7	small surface effect uniform color	non-uniform color	uniform color
Cr-2	duller sl.rough	dull rough	duller sl.rough	5.23	9.8	5.80	5.36	7.6	speckled darker	slightly speckled	speckled darker
Fe-5	most dull pinholes	dull small pinholes	bright pinholes	4.18	23.3	5.45	5.59	-2.6	much lighter colored particles	some lighter colored particles	some surface effect
Pb-11	very rough	sl.rough bright	deep pinholes bright	5.23	6.3	5.58	5.36	4.0	small bubbles large number	small bubbles large number	large bubbles

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[A] By dry air is meant air dried sufficiently by $CaCl_2$ to show no condensation at the temperature of ice.

[126] In the absence of combustion products, arranged in the order of increasing effect, visually determined.

[127] Based upon normal air, i.e. containing moisture.

The presence of water vapor, when effective, appears to lighten the color of the glazes.[128] The reflectivity drops in the case of each glaze[129] when fired in normal air but return to the original reading (in all cases except the glaze containing tin (Sn-7) when the water vapor content is equivalent to that found in combustion products.

D. Varying Water Content with Sulfur Present

Because the water vapor content has an effect upon the glazes studied, it was thought desirable to compare the effect of sulfur with and without water vapor present. The lowest concentration of sulfur required to cause noticeable results in combustion products (five (5) grains per hundred cubic feet) was added to dry air and the results of firing in this atmosphere compared with the results obtained in atmospheres of combustion products.

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[128] See Table 29.

[129] The glaze containing manganese (Mn-1) exhibits no change.

As indicated in Table 30, the dry sulfur content causes more serious effects than those obtained in combustion products. The texture changes with dry sulfur(when compared texture in dry air firing) varies from dulling to definite roughness of the surface. When other products of combustion are present at the same sulfur concentration, the effect is decreased in all cases.

TABLE 29

VARYING WATER CONTENT

Color

Glaze	Visual			Reflectivity		
	Dry Air	Normal Air	Equiv. to Combustion	Dry Air	Normal Air	Equiv. to Combustion
Sn-7	white (dark)	white	whitest	98.4	91.0	100.9
Ca-10	-	(no change)	-	96.0	88.8	88.8
Pb-11	-	(no change)	-	98.4	88.8	98.4
Co-1	blue (lt. copper tinge)	blue	blue	44.3	41.8	44.3
Cr-2	purplish gray spots	purplish gray	lt. purplish (spots)	59.0	54.1	59.0
Mn-1	brownish purple	lt.brownish purple	brownish purple	46.8	46.8	46.8
Ni-1	dark greenish yellow(lt. green spots)	greenish yellow	greenish yellow (brown tinge)	73.8	64.0	73.8
Fe-5	dark brown	brown	lt.brown	44.3	39.4	41.8

TABLE 30

VARYING WATER CONTENT WITH SULFUR PRESENT[130]

Texture

Glaze[131]	Visual		Combustion	Specular Gloss			Combustion		Microphotographs		
	Dry Air	Dry Air with Sulfur	products with Sulfur	Dry Air	Dry Air with Sulfur	% Difference[132]	products and Sulfur	% Difference[132]	Dry Air	Dry Air and Sulfur	Combustion Products and Sulfur
Sn-7	brighter smoother	bright smooth	brighter smoother	5.90	5.58	5.4	5.64	4.4	(change only in density of print)		
Cr-2	dull smooth	duller smooth	dull sl. rough	5.76	5.23	2.4	5.26	1.9	(no change)		
Ca-10	dull smoother	duller smoother	dull smoother	5.82	5.31	8.8	5.31	8.8	(no change)		
Ni-1	dull faint pinholes	dull faint pinholes	duller smoother	5.26	4.99	5.1	4.94	6.1	bubbles	bubbles	fewer and smaller bubbles
Co-1	dull some pinholes	dullest pinholes	duller some pinholes	5.20	5.53	-6.4	5.37	-3.3	uniform surface	definite feathering	less uniform surface
Mn-1	brighter smooth	dull feathering smooth	bright light scum	5.90	5.07	14.0	5.85	0.9	medium bubbles	dull smooth	large bubbles
Fe-5	bright pinholes	dull, rough scum	bright small pinholes	5.59	4.80	14.1	5.94	-6.3	surface effect	rougher more light areas	more dark areas
Pb-11	deep pinholes	very rough	rougher	5.36	4.40	17.9	5.40	-0.5	large bubbles	numerous smaller bubbles	numerous smaller bubbles

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[130] Sulfur content of 5 grains per 100 cubic feet of Combustion Products.

[131] In order of increasing sulfur effect in dry air evaluated visually.

[132] Based upon dry air.

The color changes with dry sulfur are not very apparent, being similar to those obtained with dry air in firing in most cases. With combustion products present, however, the color is made darker for the majority of the glazes.

The effects produced by the sulfur in dry air result from a surface film formation as in the variation of sulfur in combustion products and shown in the photomicrographs[133].

E. Examination of Results

1. Hypothetical explanations for the Causes of Texture and Color Changes.

From the photomicrographs, the presence of bubbles in the glaze texture changes with the variation of the excess air in combustion products. This is particularly true in the case of the calcium glaze. From thermodynamic calculations[134], it can be shown that calcium carbonate added to the glaze may decompose, liberating carbon dioxide and forming calcium oxide. Calcium oxide does not decompose at this temperature, as indicated by free energy considerations, and has a relatively high

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[133] Comparison of the results of the various methods is given in Table 30.

[134] See Appendix VI for tabulation of thermodynamic data and calculations. Data upon the silicates are scarce and few thermodynamic relations have been calculated.

melting point. It appears, therefore, that the carbon dioxide formed may be the cause of the bubbles and the fusion process may be so slow, because of the presence of calcium oxide, that the time allotted does not suffice for the release and smoothing of the surface.

The glazes containing tin (Sn-7), iron (Fe-5) chromium (Cr-7), and cobalt (Co-1)are smooth under air firing. These have lower melting oxides than does calcium and in addition are added in forms which do not decompose at the temperatures involved and therefore may be expected to form better surfaces. Under reducing conditions, however, these compounds may decompose.

The tin glaze develops a few bubbles, its lower melting point may be sufficient to allow escape of most of the gases formed. The chromium and cobalt glazes are very rough indicating that the reducing atmosphere may have caused subsequent change in the condition of oxidation to disturb the surface by the evolution of the gases. The change in the condition of oxidation may also vary the fusion point. The chromium glaze definitely was green under reducing conditions.

The iron glaze becomes glassy and contains a few large bubbles. It shows a blue color. From thermodynamic considerations, ferrous oxide and ferrous silicate may be present. The blue coloration in iron containing glazes has been attributed in the literature to ferrous silicate, (H-10).

The melting point of this silicate is not known to the writer but it is probably low enough to depress the fusion point of the glaze sufficiently to allow escape of the gases.

Nickel (Ni-1) and manganese (Mn-1) glazes show random bubbles under air firing. In firing both glazes, decomposition takes place under oxidizing conditions, the manganese carbonate going to manganous oxide with the loss of carbon dioxide and the nickelic oxide losing oxygen to give compounds having approximately the same melting point. It appears from thermodynamic considerations that the manganous oxide, however, may form the silicate, which is red in color and has a much lower melting point, thus accounting for both the smoother surface and the brownish tinge found in the glaze. Under reducing atmospheres these reactions may proceed even further, giving metallic nickel. However, no explanation is offered for the bleaching of the manganese glaze under these conditions.

The action on the lead glaze (Pb-11) may be explained on the assumption that the lead oxide, or free lead under reducing conditions, is readily vaporized at relatively low temperatures and that possibly a small fraction is converted to silicates. Such changes would cause considerable variation in the composition and explain the bubbles observed.

Under conditions in which sulfur concentrations caused noticeable changes, scumming, roughness, and similar defects commonly ascribed to the reaction of sulfur were found upon all the glazes. Ferrous sulfates and calcium sulfate may be formed under the operating conditions and are stable at the highest temperature attained. Other sulfates that may be formed but are unstable at lower temperatures are those of chromium, ferric iron, lead, and tin. Sodium and potassium are common to each glaze. The components calcium, sodium, and potassium are approximately equal in each of the glazes and the observed action of the sulfur should bear some relation to the reaction with the coloring or addition agent. However, certain of the agents may act as catalysts. For example, the cobalt and manganese glazes show more reaction than the base calcium glaze although the sulfates of cobalt and manganese are not likely to occur. The glazes of tin and chromium show action to a smaller degree than the base glaze.

The effect of water vapor upon the surface texture, as indicated in tests with water vapor in air, is variable. In each glaze, a small amount of water vapor improves the texture, while an amount equivalent to the water vapor in combustion of manufactured gas causes destruction in the cases of lead, iron, and chromium glazes but slightly improves the others. Some silicates will hole water in combination at high temperatures and some such change in water content of the glaze may take place under the experimental conditions. There may also be some formation of hydroxides. Either condition would cause a change in the properties of the glaze and explain the effects observed.

When sulfur dioxide is added to atmospheres containing water vapor, it is noted that the effect is less severe than dry sulfur dioxide alone.

Comparing the findings with water vapor in air and with the combustion products when one hundred seven (107) percent theoretical air is present[135], it will be noted that there are small differences in the case of calcium and tin glazes. In glazes containing manganese, nickel,

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[135] See Table 31.

cobalt, and chromium, the texture is better when fired with water vapor, and in the iron and lead glazes it is worse. From such observations, it is suggested that three components found in combustion products, namely, water vapor, sulfur, and oxygen, influence the texture of the glaze surface; the action of each varying with concentration and with the added coloring agents in the glaze.

Comparison of the changes in texture of the visual, reflectometeric, and photomicrographic methods for expressing the experimental results are found in Table 32. It is evident from this that the reflectometeric method follows the visual more closely than does the photographic. The values obtained from the reflectometer readings may be expressed graphically and give an easy means for evaluating the relative changes in the surface. However, certain shortcomings must be realized, first, that the reflectometer readings are dependent slightly upon color changes, and secondly, that the values obtained are dependent upon the brightness as well as the texture.

TABLE 31

COMPARISON OF WATER VAPOR ACTION TO THE EFFECTS OF COMBUSTION PRODUCTS

Glaze	Water Vapor Content Equiv. to Gas Firing	Gas Firing 107% Theoretical Air	Normal Air
Ca-10	bright, wavy	brighter, wavy	bright, pinholes
Sn-7	bright,smoothest	brighter, smoothest	dull,smooth
Mn-1	bright,smooth	bright, wavy	dull,wavy
Ni-1	slightly,bright smooth	dull,smooth	dull,smooth
Co-1	bright, wavy	smooth,faint pinholes	smooth,faint pinholes
Cr-2	duller,slightly rough	duller,rougher	duller,slightly rough
Fe-5	most dull pinholes	dull, small pinholes	bright pinholes
Pb-11	very rough	slightly rough feels smooth	deep pinholes bright

TABLE 32

RELATIVE EFFECT OF COLORING AGENTS[136]

A. Visual Rating

Strongly Reducing Condition	Strong Sulfur Conditions	Water Vapor Conditions	Dry Sulfur Condition	Dry Air	Normal Air
Mn-1	Sn-7	Ca-10	Sn-7	Ca-10	Mn-1
Sn-7	Ni-1	Sn-7	Cr-2	Mn-1	Sn-7
Ni-1	Cr-2	Mn-1	Ca-10	Co-1	Ni-1
Fe-5	Ca-10	Ni-1	Ni-1	Sn-7	Fe-5
Ca-10	Mn-1	Co-1	Co-1	Ni-1	Co-1
Co-1	Fe-5	Cr-2	Mn-1	Cr-2	Ca-10
Pb-11	Pb-11	Fe-5	Fe-5	Fe-5	Pb-11
Cr-2	Co-1	Pb-11	Pb-11	Pb-11	Cr-2
B. Specular Gloss[137]					
Sn-7	Sn-7	Ca-10	Co-1	Ca-10	Co-1
Fe-5	Ca-10	Ni-1	Cr-2	Co-1	Mn-1
Mn-1	Mn-1	Sn-7	Ni-1	Ni-1	Cr-2
Ni-1	Fe-5	Mn-1	Sn-7	Sn-7	Sn-7
Ca-10	Ni-1	Co-1	Ca-10	Fe-5	Pb-11
Co-1	Pb-11	Pb-11	Mn-1	Mn-1	Fe-5
Pb-11	Cr-2	Cr-2	Fe-5	Pb-11	Ca-10
Cr-2	Co-1	Fe-5	Pb-11	Cr-2	Ni-1
C. Microphotographs					
Sn-7	Cr-2	Pb-11	Cr-2	Sn-7	Sn-7
Fe-5	Pb-11	Sn-7	Ca-10	Co-1	Co-1
Ca-10	Sn-7	Cr-2	Sn-7	Cr-2	Fe-5
Co-1	Ni-1	Co-1	Ni-1	Fe-5	Cr-2
Cr-2	Ca-10	Fe-5	Co-1	Ca-10	Mn-1
Mn-1	Mn-1	Ca-10	Mn-1	Mn-1	Ni-1
Ni-1	Co-1	Mn-1	Fe-5	Ni-1	Ca-10
Pb-11	Fe-5	Ni-1	Pb-11	Pb-11	Pb-11

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[136] Condensed from Tables 23, 24, 25, 26, 28.

[137] Arrangement by direct Specular Gloss readings.

The visual method will allow the observer to note fine differences such as tinges on colored glazes that the reflectometer may not detect but upon white glazes the visual evaluation of color texture changes is difficult.

The photomicrographs, however, show the structure of the surface and changes upon it but give no definite evaluation of color or of the visual effect of these changes.

Color determination by the use of the reflectometer is sufficiently accurate to express large changes but will not indicate faint surface changes that are very noticeable.

In summation, the use of the reflectometer to read specular gloss, or reflectivity, is a rapid and dependable method for determining surface and color changes. The photomicrographs permit inspection of the surface but do not correlate well with visual effects.

IV. CONCLUSIONS

Raw glazes similar to those developed in the experimental study herein reported may be fired in the presence of the combustion products of manufactured gas. The experiments indicate that in order to produce such glazes equivalent in color and texture to air firing a minimum of one hundred seven (107) percent theoretical air must be present in the atmosphere. In order to prevent surface coatings commonly attributed to sulfate formation, the sulfur concentration in the furnace atmosphere should be lower than five (5) grains per hundred cubic feet of combustion products.

The presence of coloring or other addition agents may influence the action of the combustion products upon the glaze tested. Those glazes containing tin, manganese, and nickel were found to be less reactive in the presence of combustion products with or without excess air, or atmospheres of water vapor, sulfur dioxide, or mixtures of these atmospheres, than the base glaze (Ca-10) or glazes of the other coloring agents tested.

In atmospheres of combustion products, the texture changes found to occur were due to (a) the roughening of the surface by increase in the number of the bubbles present with variations of the theoretical air and (b) by the formation of a surface scum with variations in the sulfur concentration. With a high percentage of oxygen (free air) present in the firing atmosphere high water vapor content or with high dry sulfur dioxide content gave scumming and other texture changes. Water vapor apparently decreases the effect of sulfur under the conditions studied.

The colors of the glazes depended upon the amount of excess air and upon the sulfur concentration. The reduction in the ratio of the air to the fuel to values below 94% theoretical air caused the reduction of the coloring agents and, where the reduced agent gave a color different from the oxidized form, the change was very apparent. The effect of the sulfur concentration, and, to a lesser degree, the water vapor content was to lessen the color by causing a surface scum.

Of the various methods used for expressing the results, it was observed that the reflectometer values followed by the visual observations and allowed the assignment of numerical values to such observations. With such numerical values, graphs may be made and the effects of various conditions indicated by the change in these values. Although the photomicrographs did not give results that agreed with visual recording, they did allow the observation and recording of changes made by the various conditions of the surfaces. The photographs did not permit evaluation of the color changes.

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APPENDIX I

Reference Number	Method			Atmosphere					Composition of Ceramic Materials				
	Industrial Firing Direct	Industrial Firing Muffle	Lab.	Mfg. Gas	Coal Oil Nat. Gas	Mixtures SO_2	Mixtures Misc.	Analysis S/S	Name Glaze	Name Glass	Name Enamel	Name Misc. & Clay	Analysis
I. Direct Firing													
a. Mfg.Gas													
1. G7;W3;													
W8;(M4)	x			x				(x)	x				
W4	x			x					x				x
R5	x	x		x			x		x				
2.R1;Z2 (M14)	x		(x)	x			(x)			x			
3.A1;A14;G8; (P9)	x			x				(x)			x		
4. H6	x			x			x					x	
b.Coal,etc.													
1.B2;S2;(M17)	x				x			(x)	x				
A13;(H17)	x				x			(x)	x				x
M16	x				x		x		x				
2.A7;(W1)	x				x					x			(x)
W5;(P3)	x		(x)		x	x	x			x			
3.G9	x				x	x	x				x		
4.A16;H5;H8; P1;P2;H10; R2;R4;(C1; P7)	x				x	(x)	(x)					x	
B9;H7;B11; (J6)	x		(x)		x	x		(x)				x	
L4;(L5)	x				x		x	(x)				x	
II. Muffle Firing													
1.F2;(W7;A6; A8)		x			(x)		x		x				x
E5;(C7)		x				(x)	x		x				
O1		x		x	x			x	x				
3.A9;(E2)		x					(x)				x		
R3		x			x						x		
S7		x	x				x	x			x		
4.B1		x	x				x	x				x	x

Reference Number	Method		Atmosphere					Composition of Ceramic Materials Name				
	Industrial Firing Direct	Lab. Muffle	Mfg. Gas	Coal Oil Nat. Gas	Mixtures SO$_2$	Misc.	Analysis	Glaze	Glass	Enamel	Misc. & Clay	Analysis
III. Lab. Testing												
1. M10;(B8; G5)		x			x		(x)	x				
D2;(W2)		x	x		x	(x)	(x)	x				
B4;N1		x			x	x	x	x				
2. B15;H12;L1		x				x			x			
T1;C8		x			x				x			x
C3;L3;T2; T5;(D4)		x	x		(x)				x			
3. A5;(A4)		x	x		x	(x)	x			x		x
C5;E1;(E3; R8;R9)		x				x				x		(x)
K3;(G3)		x			x	(x)	(x)			x		(x)
4. B13;M12 R7		x	x								x	
K1;K2;V3		x			x	x					x	x
H11;P5;(P6; H9;S5)		x			(x)	x					x	

APPENDIX II

Reference Number	Atmospheres Reported	Effects Noted	Limits Expressed
1. Glazes B2;G6;H14;M17	Combustion Products (Oxidizing) (a) Coal; wood, etc., fuels	1.(1) Ruined ware (2) No effect (3) Small spit-out	
2. Enamels A6;G7;P9;R3		2.(1) Glossy ware (2) Disagreeable colors (3) Sulfate formation	2.(1) O_2 7.3%; CO_2 7%
3. Glass A7;R1;T5;Z2		3.(1) Blue-gray deposit (2) Scumming (3) Good appear.	
4. Clays and Misc. A16;B9;B11;B13 C1;H7;H8;H10; L3;M12;P1;P2; R4;S5;V4		4.(1) Variation in colors (2) Red colors from iron (3) Colors depend upon lime (4) Scumming	4.(1) 0.46 gm S per cu. ft. CO_2 causes scumming
		5. Surface defects as (a) Blistering, etc.	
1. Glazes D2;G6;M4; R4;W2;W3	(b) Gas fuels	1.(1) No effects (2) Crazing, pinholing	1.(1) 10% excess O_2 (2) 4-5% excess O_2
2. Enamels A2;A3;A14		2.(1) No effects	2.(1) 7% free O_2
3. Glazes C3;D4;H12; M14;T2		3.(1) Rings and halo formation (2) Scumming (bloom)	3.(1) Reduce organic below 2.5 gr

APPENDIX II CONT'D.

Reference Number	Atmospheres Reported	Effects Noted	Limits Expressed
4. Clay and Misc. H5;H6;J6; L5;V3		4.(1)Scumming (2)Discoloration (3)Soluble Sulfates (4)Reduction of SiO_2	4.(1) 12.3 to 28.0% oxygen content
1. Glazes (a) Coal C7;E5; F2;H14;M16; M17;O1;W8 (b) Gas D2;O1;R5	Reducing Atmospheres (a) Combustion products,etc.	1.(1) Coloration (2) Carbon deposition (3) Sulfate formation (4) Surface defects as (1)Blistering (2)Spit-out,etc. (5) Scumming (6) Decrease above effects	
2. Enamels A1;A2;A3;A5; P9		2.(1) Coloration (2) Scumming (3) Blistering, and other surface defects (4) Irridescence (5) No effect on tin glaze	2.(1) 10% excess O_2 (2) Less (a) 0.6% CO (b) 0.002% SO_2
3. Glass		3. Decrease bloom	
4. Clays and Misc. (a) Coal H10;L3;L4;M12; P7;S5 (b) Gas H5;H6;L5;R4		4.(1) Coloration (2) Carbon Deposition	

APPENDIX II CONT'D.

Reference Number	Atmospheres Reported	Effects Noted	Limits Expressed
1. Glazes A8;A13;B8;C7;D2;G4;M10;N1;W2;W7	Sulfur Compounds (a) SO_2 organic sulfur, hydrogen sulfide, etc.	1.(1)Sulfate increases (2)Blistering, pinholing spit-out and other surface texture changes (3)Discoloration (4)Scumming (5)Metal Marking	1.(1)0.25% SO_2 (311 grains) (2)1.2-3% SO_2 (2500-3000 gr.) (3) less than 1% (1250 gr.)
2. Enamels A2;A3;A4;A5;A9;G3;R3;S7		2.(1)Scumming (2)Pock marks and other surface defects (3)Coloration	2.(1)23 to 88 ppm (3-12 gr.) (2)3.0% SO_2 (3000 gr.) (2) 0.002% SO_2 (2 gr.)
3. Glass B5;C3;C8;D4;M14;P3;T1;T5;W5		3.(1)Clouding, scumming and bloom (2)Roughening	3.(1)less than 2.5 grains attack in 70 mon. (2)1% SO_2 (1250 gr.)
4. Clays and Misc. B9;B10;B11;C1;H7;H9;J6;K1;K2;P6;R2;V3;V4		4.(1)Discoloration (2)Scumming (3)Effects melting Pt.; does not change vitrification	4.(1)0.5% S will affect
1. Glazes M16;R5;W2	Water Vapor	1.(1) Spit-out (2) Bubbles	
2. Enamels E1;E2;G3;S7		2.(1) Bubbling and blistering (2) Scumming	2.(1) 1% H_2O vapor or less

APPENDIX II CONT'D.

Reference Number	Atmospheres Reported	Effects Noted	Limits Expressed
3. Glass B 15		3.(1)Attacks gloss, roughens it	
4. Clays and Misc. B1;C1;K1;K2; P6;P7;R7;V3		4.(1)Blistering and other defects (2)Discoloration (3)Retards vitrification (4)Decreases melting point	
1. Glazes W2	Oxygen,Nitrogen and Carbon dioxide	1. O_2-nothing;N_2-gray tinge CO_2-small pinholes	
2. Enamels A2;A3;A4; C5;G3	(100% gases)	2. Good enamels (a)CO_2-blistered (b) Some believe N_2 and CO_2 roughens (c) Decrease impact resistance	
3. Glass W5		3. Coloring depending upon impurities	
4. Clays and Misc. B1;H11;P5;P6;V3		4. Small changes not much difference	
B1;G3;G4;G8;L1 L4;N1;P5;P6;P7 V3;W2	Misc.Atmospheres (100% gases) as HCl;CO_2,H_2,etc.	The reducing gases reduce the constituents,causing surface defects, and other gases react with the constituents with the power usually attributed to them as well as replacing oxygen from the atmosphere.	

APPENDIX III

COMPOSITION OF MATERIALS

I. Clay Body (2-1/8" x 1-1/16" x $\frac{1}{4}$") - fired

- 45% Feldspar
- 5% Flint
- 40% Kaolin

II. Clay Raw Materials

a. Feldspar (Elbrook Feldspar #47)

Loss	0.1%	CaO	0.3%
SiO_2	65.5%	MgO	trace
Al_2O_3	18.5%	Na_2O	1.9%
Fe_2O_3	0.07%	K_2O	13.7%

b. Kaolin

Loss	14.0%
SiO_2	46.5%
Al_2O_3	39.4%
Fe_2O_3	0.1%

c. Flint

Fe_2O_3 - trace

III. Chemicals

a. $CaCO_3$ - C. P. Chemical

b. ZnO - C. P. Chemical - analyzed

SO_4	0.005%	Pb	0.006%	Cl	0.0006%
Fe	0.0003%	Mn	0.001%	NO_2	0.003%

c. Fe_2O_3 - C. P. Chemical - analyzed

NO_3	0.00%	PO_4	0.015%
SO_4	0.10%	Zn	0.005%
SiO_2	0.055%	Mn	0.04%
PO_4	0.015%	Cu	0.005%

Not ppt. NH_4OH 0.04% As 0.0000%

d. SnO_2 - C. P. Chemical - analyzed

Soluble	0.50%	Alkali (as NaOH)	0.10%
Cl	0.001%	As	0.01%
SO_4	0.02%	Fe	0.0003%

e. Basic Lead Carbonate[$2(PbCO_3)Pb(OH)_2$] -C. P. Chemical - Analyzed

Cl	0.000%	Cu	0.003%
N	0.000%	Fe	0.001%
SO_4	0.001%	Earth and Alkalis (as sulfates)	0.24%

APPENDIX III CONT'D.

f. CoO - C. P. Chemical - analyzed

Cl	0.002 %	Zn	0.00%
SO_4	0.03%	Cu	0.012%
PO_4	0.002%	Fe	0.013%
N	0.40%	N	0.013%

(Alkalis (as sulfates) 0.23%

g. Cr_2O_3 - C. P. Chemical - analyzed

Cl	0.001%	Fe	0.025%
NH_3	0.04%	Not ppt.	0.20%
SO_4	0.09%		

h. NiO_2 - C. P. Chemical - analyzed

Cl	0.012%	N	0.001%
PO_4	0.002%	Cu	0.02%
SO_4	0.08%	Fe	0.025%
Co	0.02%	Zn	0.00%

(Alkalis (as sulfates) 0.15%

i. $MnCO_3$ - C. P. Chemical - analyzed

Cl	0.03%	Fe	0.0015%
SO_4	0.002%	Zn	0.02%

Heavy Metals (Pb) 0.02% Not ppt. $(NH_4)_2S$ 0.3%

APPENDIX IV

DETERMINATION OF SULFATES

Wilson, C. W. and W. A. Kemper, Determination of Organic Sulfur in Gas, Industrial and Engineering Chemistry, Analytical Edition, 10, No. 8, 418 (1938)

"For the determination of organic sulfur gas, the following procedure is now proposed.

The metered gas is burned at a rate from 14 to 28 liters (0.5 to 1 cubic foot) per hour and the products of combustion are absorbed in sodium carbonate in the A. S. T. M. sulfur lamp (1,3). At the conclusion of the test, the lamp is washed down with the smallest possible quantity of distilled water, and 3 drops of methyl orange indicator are added. The solution is neutralized with dilute hydrochloric acid which, if standardized, will give an estimate of the sulfur present. At this point the determination was concluded according to the earlier procedure.

The tan color of the acid methyl orange is discharged with a few drops of the sodium carbonate solution, and 30 ml. of ethyl or isopropyl alcohol

APPENDIX IV CONT'D.

are added (2). About 0.22 gram of tetrahydroxyquinone indicator is added, and the solution is mixed well and titrated with standard barium chloride solution. The end point is reached when the color of the solution changes from yellow to red, which is permanent with good mixing."

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(1) Am. Soc. Testing Materials, Tentative Standards, p. 391, D 903oT (1930)

(2) Sheen, Rt. and Kahler, H. L., Ind. Eng. Chem., Anal. Ed., 8, 127 (1936); 10, 206 (1938)

(3) Wilson, C. W., Ibid., 5, 20 (1933)

APPENDIX V

Glaze	Reference Number	Test Number	
Sn-7	1	wh-7	1A4
	2		3A26
	3		3A31
	4		3A34
	5		1A7
	6		1A1
	7		4A46
	8		3A45
	9		3A38
	10		4A50
	11		4A54
	12		4A58
Ca-10	1	wh-10	1A12
	2		3B26
	3		3B31
	4		3B34
	5		1A13
	6		1A11
	7		4B46
	8		3A42
	9		3B38
	10		4B50
	11		4B54
	12		4B58
Pb-11	1	wh-11	1A12
	2		3B27
	3		3B32
	4		3B35
	5		1A13
	6		1A11
	7		4A47
	8		3B42
	9		3A39
	10		4A51
	11		4A55
	12		4A59
Co-1	1	Bl-1	1A6
	2		3B30
	3		3A33

APPENDIX V CONT'D.

Glaze	Reference Number	Test Number	
Co-1	4	Bl-1	3B37
	5		1A9
	6		1A3
	7		4B49
	8		3B44
	9		3B41
	10		4B53
	11		4B57
	12		4B61
Cr-2	1	Cr-2	2B23
	2		3B28
	3		3B29
	4		3A36
	5		2B24
	6		2B22
	7		4B48
	8		3A43
	9		3A40
	10		4A52
	11		4A56
	12		4A60
Mn-1	1	Mn-1	2A19
	2		3B27
	3		3B32
	4		3B35
	5		2A20
	6		2A18
	7		4B47
	8		3B45
	9		3B39
	10		4B51
	11		4B55
	12		4B59
Ni-1	1	Ni-1	2B19
	2		3A30
	3		3A33
	4		3A37
	5		2B20
	6		2B18

APPENDIX V CONT'D.

Glaze	Reference Number	Test Number	
Ni-1	7	Ni-1	4A49
	8		3A44
	9		3A41
	10		4A53
	11		4A57
	12		4A61
Fe-5	1	Fe-5	1B5
	2		3A28
	3		3A29
	4		3A36
	5		1B8
	6		1B2
	7		4A48
	8		3B43
	9		3B40
	10		4B52
	11		4B56
	12		4B60

APPENDIX VI[138]

Reaction	F1473.1
$CaCO_3 \rightarrow CaO + CO_2$	-10,070
$CaO \rightarrow Ca + \frac{1}{2}O_2$	132,373
$2CaO + 2SO_2 + O_2 \rightarrow 2CaSO_4$	-52,727
$CO_2O_3 \rightarrow 2CoO + \frac{1}{2}O_2$	21,000
$2CrO_3 \rightarrow Cr_2O_3 + 1\frac{1}{2}O_2$	-112,601
Cr_2SO_4	unstable low temperatures
$2Fe_2O_3 \rightarrow 4FeO + O_2$	37,596
$2Fe_2O_3 + 4SiO_2 \rightarrow 4FeSiO_3 + O_2$	44,066
$Fe_2(SO_4)_3$	unstable low temperatures
$2FeO + 2SO_2 + O_2 \rightarrow 2FeSO_4$	-286,740
$MnCO_3 \rightarrow MnO + CO_2$	-23,300
$MnO \rightarrow Mn + \frac{1}{2}O_2$	61,369
$MnO + SiO_2 \rightarrow MnSiO_3$	-306,770
$2MnO + 2SO_2 + O_2 \rightarrow 2MnSO_4$	56,380
$Ni_2O_3 \rightarrow 2NiO + \frac{1}{2}O_2$	20,383
$2NiO + 2SO_2 + O_2 \rightarrow 2NiSO_4$	46,150
Pb, PbO, $PbSO_4$ are liquids with appreciable vapor pressures.	
$SnO_2 \rightarrow SnO + \frac{1}{2}O_2$	31,571

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[138] Data compiled from "Contributions to the Data on Theoretical Metallurgy" by K. K. Kelley. Bulletins 350,371,383,384,393,394,406, U. S. Department of the Interior, Bureau of Mines.

APPENDIX VI CONT'D.

$SnSO_4$ decomposes at low temperatures[139]

Alkaline Sulfate (Na, K, etc.) all melt below 1400°K and have appreciable vapor pressures.

$2SO_2 + O_2 \rightarrow 2SO_3$ -178,576

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[139] A spectroscopic analysis of condensed fumes from the firing chamber showed Sn, K, Ni, Pb, Si to be present.