A STUDY OF SOME OF THE FACTORS RELATED TO THE MECHANISM OF SCALE PREVENTION BY ORGANIC ADDITIVES AT HIGHER BOILER PRESSURE

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY

Kalyanji Kanjibhai Vithani

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By

KALYANJI KANJIBHAI VITHANI

AN ABSTRACT

Submitted to the College of Engineering of Michigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemical Engineering

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Approved 

Kalyanji Kanjibhai Vithani

ABSTRACT

The problem of scale formation on the heating surface of the boiler has been analyzed considering the crystallization process: the formation of crystalline nuclei and their subsequent growth. The effect of solution properties such as temperature, and properties of the system such as degree of turbulence, heat flux etc., on the rate of nucleation and the rate of crystal growth are discussed.

An equation has been derived considering the heat transfer and mass transfer to and from the heating surface to predict whether or not a given salt will form scale on a heating surface. Theoretical calculations made are in agreement with the experimental data available. However, more extensive tests for validity of the equation are desirable.

In the experimental work of this thesis it was established that molecular weight of an organic additive is an important factor in prevention of calcium phosphate scale. Organic polymers were found superior to their monomers in prevention of scale. Methacrylic acid polymers were found much more effective than the industrially used organic additives in scale prevention.

In this thesis it has been postulated that the organic additives may function by acting as more efficient nucleation sites for calcium phosphate crystal formation than the nucleation sites on the heating surface. By this mechanism scale formation may be prevented and the calcium phosphate may exist as a large number of small crystals suspended in solution.

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Dedicated

to

My Mother, Father,

and Sister

ACKNOWLEDGEMENTS

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INTRODUCTION

One of the most troublesome problems encountered in steam generation is the formation of scale and deposits of sludge on boiler heating surfaces due to the presence of impurities in the boiler feed water. Impurities form precipitates because of increased concentration caused by evaporation and by reaction with chemical additives. It is known that the addition of certain natural organic products such as lignins, tannins, etc. reduces the rate at which boiler precipitates form scale on heating surfaces. These addititives were found primarily by trial and error methods, with little attention paid to the many variables which may affect scale formation. In this investigation some of the variables related to the role played by the organic additives in preventing scale were explored.

One possible mechanism by which organic additives prevent scale is the formation of a protective coating on the inorganic precipitates by colloidal action. Since the molecular weight of the additive would affect its colloidal properties, the effect of molecular weight of additive on scale formation was studied. The determination of the changes that occur in the additive during its stay in a boiler was also explored by utilizing infrared spectra analysis.

Other methods of approaching the problem, such as studies of the crystallization process and the effect of additive on it, the effect of functional groups in the additive on rate of scale formation, and the adsorption of additive on metal surfaces and crystal surfaces were considered.

THEORY OF CRYSTALLIZATION IN ANALYSIS OF SCALE FORMATION

A review of the literature on the mechanism of scale formation revealed that each author considered only a few of the variables involved in the scale formation process. Therefore before discussing the literature it is desirable to consider the manner by which each of the variables in a scale forming system affects the rate of scale formation. The variables may be divided into two groups: properties of the solution such as temperature and concentration which determine the rate of nucleation and the rate of crystal growth at any point in the system; and properties of the system including such variables as heat flux, degree of turbulence, and mass transfer coefficient, which determine the solution properties at each point in the system. The solution properties which determine the rate of crystal growth and the rate of formation of new nuclei will be considered first.

Scale formation consists of the formation of crystal nuclei on a scaling surface, and their subsequent growth. Crystals which first form in solution and then adhere to the scaling surface due to impact against the surface also take part in the scale formation process. However, it is believed (1) that only a minor portion of the scale develops by the latter process. Therefore only the formation of scale in situ will be considered here. The theory of crystallization will be reviewed to analyze the effect of solution properties on the scale formation process.

Crystallization occurs in two steps; the formation of crystalline nuclei and their subsequent growth. The formation of crystalline nuclei from a saturated solution is similar to the formation of liquid nuclei from saturated vapor. The latter process has been treated theoretically by LaMer (16) by assuming that molecules formed clusters or nuclei which were spherical and which existed in a homogeneous phase by virtue of fluctuations of local density and energy with time. Thus there is a constant removal and addition of molecules or atoms on the nucleus. The extent of addition or removal of atoms on the nucleus depends upon the free energy difference between the nucleus and the saturated vapor and is given by the following equation:

$$\Delta G = 4\pi r^2 \sigma + (\frac{4}{3}\pi r^3)\Delta G_v \qquad [1]$$

where

r = radius of the nucleus

σ = interfacial energy per area between liquid and vapor

ΔG_v = the free energy difference per volume between vapor and liquid phase.

In the above equation ΔG_v is negative and is independent of r.

Figure 1 is a plot of ΔG versus r in which r_c is the critical radius of nucleus i. e. minimum radius of the nucleus necessary for further growth.

ΔG_c = free energy difference of critical size nucleus

$$\Delta G_c = \frac{1}{3}\sigma s = \frac{4}{3}\pi r_c^2 \sigma \qquad [2]$$

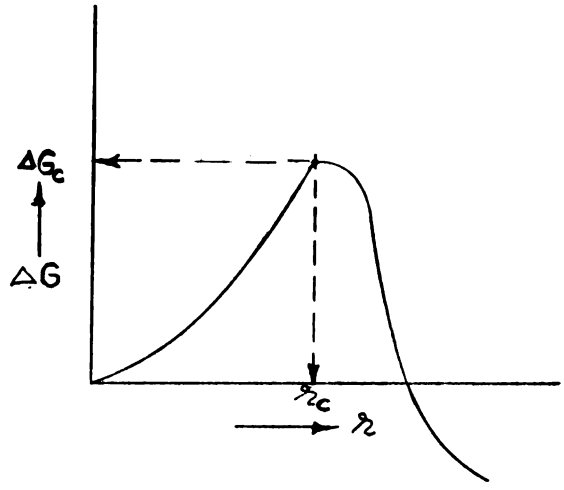


Figure 1. A plot of free energy difference (ΔG) versus critical radius (r)

This plot shows that further growth of a nucleus of radius $r > r_c$ will be accompanied by a decrease in free energy and therefore the nucleus will grow spontaneously. In the case where $r < r_c$ the nucleus will disintegrate spontaneously.

The rate at which nuclei form may be estimated by Equation [3], which was derived from the kinetic theory of gases by assuming that the nuclei develop by a bimolecular collision process.

$$I = B\, e^{-(\Delta G_c/kT)} \qquad [3]$$

where

I = the rate of formation of nuclei, $\frac{\text{number}}{\text{vol-time}}$

k = Boltzman constant

T = absolute temperature

$B = [P/(2\pi mkT)^{1/2}]\, S_c N$

P = total pressure

m = mass of a molecule

S_c = area of the nucleus

N = number of single molecules in the system.

For the case of the formation of crystalline nuclei from solution, Preckshot and Brown (23) have modified the equation for ΔG_c. They have used wr^2 where w is the ratio of nucleus surface to the square of the radius, in place of s in Equation [2], and Thompson equation

$$\mu_r - \mu_\infty = \frac{(0.239 \times 10^{-7})\, 2\sigma M_2}{r\rho_2}$$

for the equilibrium relationship between a solid and its solution. Thus A, the energy of activation for the formation of nuclei, which is equivalent to ΔG_c has been given as:

$$A = (0.239 \times 10^{-7})^3 \frac{4w\sigma^3 M_2^2}{3\rho_2^2(\mu_r - \mu_\infty)^2} \qquad [4]$$

and the rate of formation of nuclei from solution has been given as:

$$J = C e^{-U_1/RT} e^{-A/RT} \qquad [5]$$

In equations [4] and [5]:

A = energy of activation for the formation of nucleus

C = constant (approximately)

M_2 = molecular weight of solid phase

J = rate of formation of nuclei

R = gas constant

T = absolute temperature

μ_r = thermodynamic potential of nucleus of radius r

μ_∞ = thermodynamic potential of nucleus of radius infinity

ρ_2 = density of the solid phase

σ = interfacial energy

w = dimensionless factor nucleus surface/r^2

r = radius of solid crystal

U_1 = energy of activation for the molar transition from solution to solid phase.

The term, $e^{-U_1/kT}$ in Equation [5] takes into account the effect of diffusion of molecules from solution to the crystal on the rate of formation of the nuclei. Both A and U_1 depend upon the degree of supersaturation of the crystallizing solution. The percent supersaturation in terms of concentration can be expressed as $\frac{C-C_s}{C_s} \times 100$, where C and C_s are the actual concentration and the saturation concentration respectively at T_s, the solution temperature. As much as 50 percent supersaturation may be necessary for the formation of nuclei from a pure solution. On the other hand, if impurities or foreign substances (17) are present, only 1 to 5 percent may be sufficient to cause nucleation. The former is called homogeneous nucleation and the latter heterogeneous nucleation. Heterogeneous nucleation arises from the catalytic effect of the surfaces of foreign substances as well as from walls of

the containing vessel, pores, etc. The foreign substances or containing vessel may act as nuclei or they may act as a suitable site on which atoms or molecules can condense or adsorb preferentially, causing crystal formation. Heterogeneous nucleation takes place readily when the nucleation catalysts, i. e. foreign substances etc., have structures (7) with a symmetry and lattice pattern similar to the crystal for which the solution is supersaturated. LaMer (16) has reported that foreign nuclei decrease the critical free energy ΔG_c, and therefore the degree of supersaturation required for nuclei formation. Thus the properties of a solution which may affect the rate of the formation of nuclei and hence the rate of scale formation are the degree of supersaturation and the concentration of foreign materials which may act as nuclei. Other variables such as the heat of formation of nuclei ΔG_c and the rate of formation I or J of nuclei depend upon the properties of solute to be crystallized as well as the solution properties.

Once the nucleus is formed it begins to grow. Solute molecules from the liquid solution collide with the nucleus and diffuse over the surface until they either find a suitable site or leave the nucleus surface. Two different theories, namely, two dimensional surface nucleation and one dimensional nucleation in the case of a screw dislocation growth have been proposed (17) for the mechanism of crystal growth. According to Lawson and Nielson (17) colliding atoms crystallizing on a surface prefer sites with a maximum number of nearest neighbors, as site A in Figure 2 (a). This process corresponds to one dimensional

nucleation in the X direction which can occur at a few percent supersaturation. Occupation of sites in this manner would produce a close packed surface over the crystal, Figure 2 (b). At this stage further growth requires the formation of a two dimensional nucleus which forms an "island" nucleus on the surface, Figure 2 (c). This process requires 25 to 50 percent supersaturation; therefore crystal growth by this mechanism will be controlled by the surface nucleation step. However Volmer observed the growth of iodine and naphthalene crystals at only 1 percent supersaturation. Frank (9) has explained this phenomenon by postulating that growth takes place at screw dislocations in the crystal. As shown in Figure 3, the crystal structure is assumed to be twisted so that an edge is always available for further growth, thus making formation of a two dimensional nucleus unnecessary.

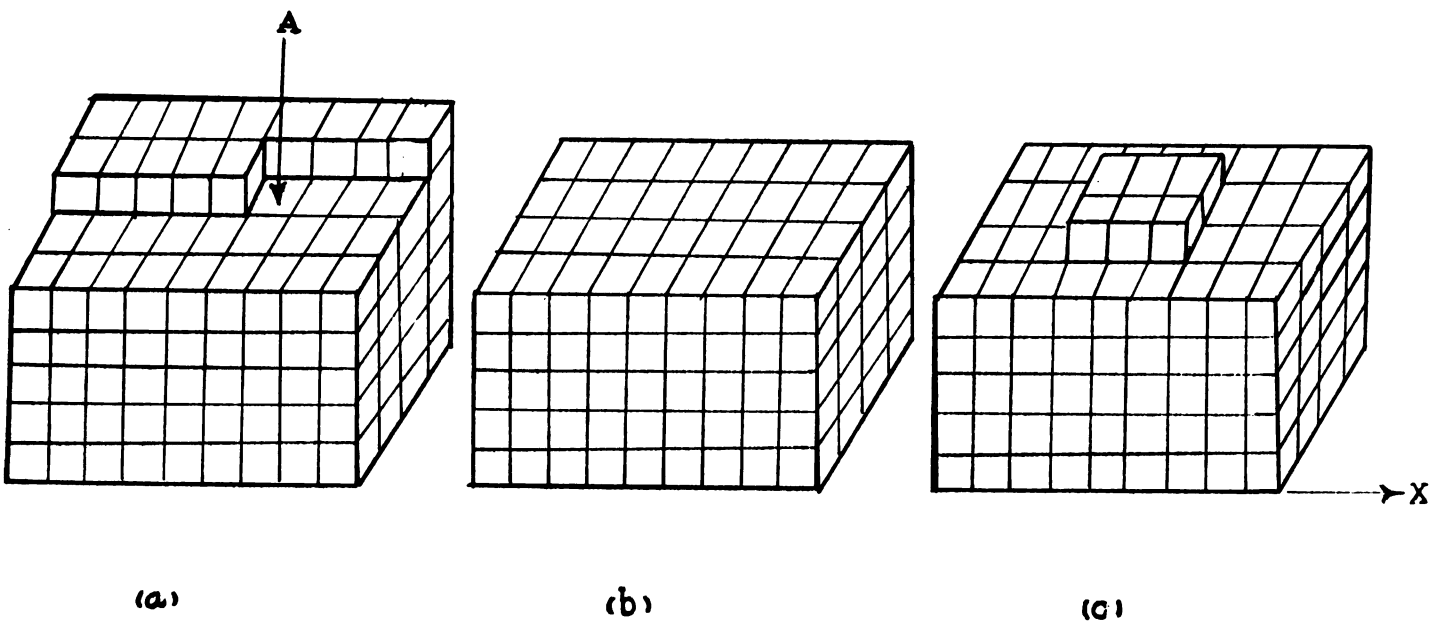


Figure 2. Various stages of crystal growth.

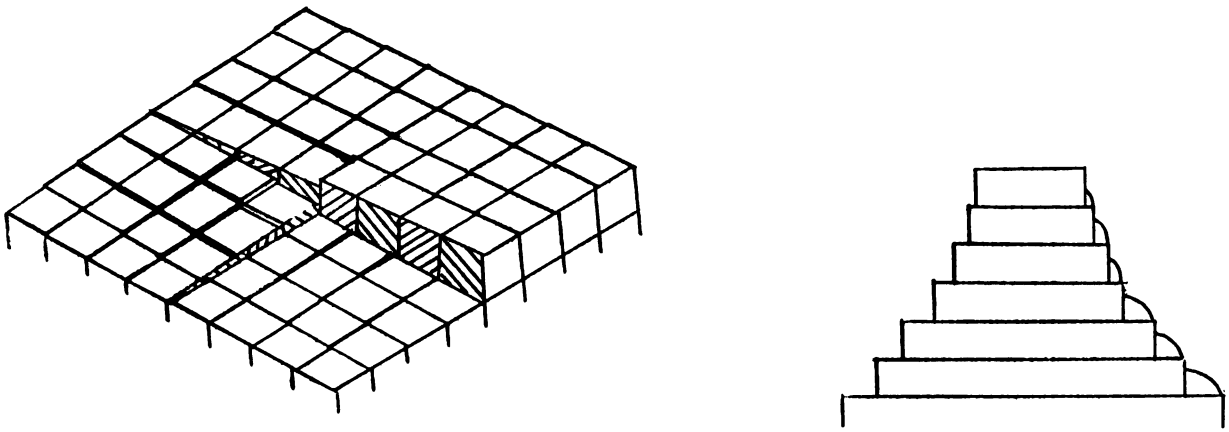


Figure 3. Frank's concept of screw dislocation in a crystal lattice.

The effect of supersaturation on the rate of growth of a perfect crystal and of a crystal with screw dislocations is shown (7) in Figure 4.

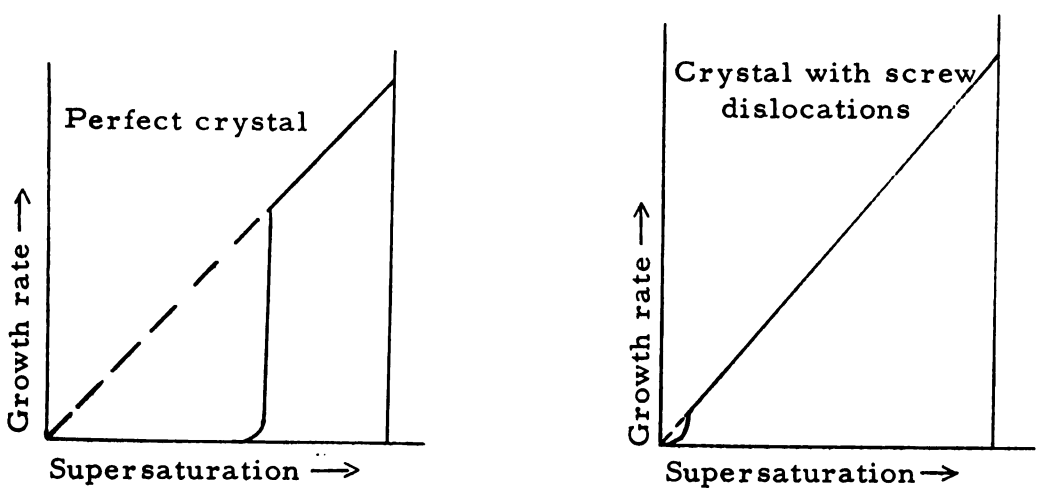


Figure 4. Theoretical curves for crystal growth.

In order to obtain crystal growth, molecules from the bulk solution must diffuse to the nucleus, and then orient themselves properly with respect to the crystal lattice. Thus a process of crystal growth has two resistances. One is the diffusional resistance through a stagnant liquid film surrounding the crystal. Then the orientation of each molecule requires a finite time, and this effect may be considered as the second resistance. According to Berthoud-Valeton (22) the rate of deposit of the molecules on the crystal surface for a first order interfacial reaction is:

$$\frac{dw}{d\theta} = US\Delta C = \frac{S[C-C_o]}{\frac{1}{k}+\frac{1}{k'}} \qquad [6]$$

where $\frac{dw}{d\theta}$ = growth rate weight/time

S = crystal surface area

C = concentration of bulk solution

U = kk'/k+k'

k = mass transfer coefficient

k' = coefficient of orientation.

From Equation [6] it can be seen that if k is large in comparison with k' the orientation process controls the growth rate. And, if k' is large in comparison with k, diffusion is the controlling factor. k is the function of the properties of solution such as viscosity and the relative velocity between the crystal and the bulk solution. On the other hand k' is independent of velocity and dependent on impurities in solution.

The manner in which impurities affect the growth rate is not completely known, but in general it has been explained by a preferential adsorption of the impurity on one or more surfaces of the crystal. This hinders growth and changes the normal surface energy relationship. On the other hand, if a sufficient amount of impurity is present in the solution and the lattice or atomic spacing is reasonably similar, the original material may be seeded (10) by the impurity; or the impurity may crystallize out as a pseudomorph of the original material. The concentration of impurity and the supersaturation of the solution also influence the rate of growth of crystals. Cabrera and Vermilyea (4) have shown that at a given concentration of a certain impurity there is a critical supersaturation below which the crystal will not grow. Above this critical supersaturation the crystal growth rate is less than that of a crystal growing in a pure solution. Buckley (3) has stated that the effectiveness of an impurity in reducing the growth rate decreases as the temperature and supersaturation increase.

Thus, the properties of a solution which may affect the rate of crystal growth and hence the rate of scale formation are: the degree of supersaturation and the amount and type of foreign material present. Other variables such as mass transfer coefficient, orientation coefficient, and rate of nucleation depend upon the properties of solute and foreign material as well as solution properties.

The second group of variables to be considered is that which determines the solution properties at each point in a boiling system;

i. e. the heat flux, degree of turbulence or mixing, the rate of material transfer, and the temperature. If the heat flux is fixed then the temperature at any point in the bulk phase will depend upon the heat transfer coefficient at the heating surface and the degree of bulk mixing. The degree of supersaturation depends upon the degree of mixing, the rate of crystallization or material transfer, and the rate at which material is added and withdrawn from the system.

In the case of "perfect" mixing, the temperature of the bulk phase at any point will be constant and can be determined by a heat balance. The concentration in the bulk phase at any point will be constant and hence the rate of material transfer to boiler surfaces will depend upon the mass transfer coefficient and the concentration gradient between bulk phase and surface.

When mixing is imperfect the temperature and concentration will vary from point to point in the boiler due to the addition of cold, concentrated feed at some point in the system. It would be possible to determine temperatures and concentrations only if the degree of mixing throughout the boiler were known. Thus the rate of crystal and scale formation will vary throughout the boiler.

MECHANISM OF SCALE FORMATION

Hall (11) investigated the mechanism of scale formation by operating an experimental boiler at atmospheric pressure with calcium sulphate as the scaling salt. He found that most of the calcium sulphate was deposited on the heating surface and only a small amount was present as suspended solids in the boiler. Therefore it was concluded that a very high percentage of the material deposited by the boiler water crystallized as adherent scale in situ on the evaporating surface and never existed as independent crystals subject to movement with the flow of boiler water. Although this theory is generally accepted, experimental results do not prove that most of the scale formed in situ. The scale could have formed rapidly from suspended solids, thus giving a low concentration of suspended solids in the boiler. In addition, salts such as calcium iodate and potassium sulphate with a solubility curve of positive slope were also tested. It was found that salts with a negative change in solubility with temperature formed a hard adherent scale on the heating surface much more readily than the salts with a positive solubility change with temperature. This result was explained by considering that under operating conditions the hottest portion of water was next to the heating surface. Thus salts with a negative solubility-temperature coefficient have the lowest solubility at the heating surface and hence are precipitated thereon; on the other hand, salts of increasing solubility with increasing temperature are more soluble at the heating surface and do not precipitate as readily.

A portion of this thesis was devoted to the prediction of whether or not a given salt would form a scale on a heating surface. This was accomplished by considering heat transfer and mass transfer to and from the heating surface. During evaporation there is a net movement of material to the evaporating surface since the evaporation of water vapor leaves the impurities behind. Thus the concentration of salt or impurity will be greater at the evaporating surface, and even salts with a positive solubility-temperature coefficient may form scale. It was assumed that the concentration and the temperature of the bulk phase were constant and that there was no crystallization of the salt.

Consider the following picture of the heating surface.

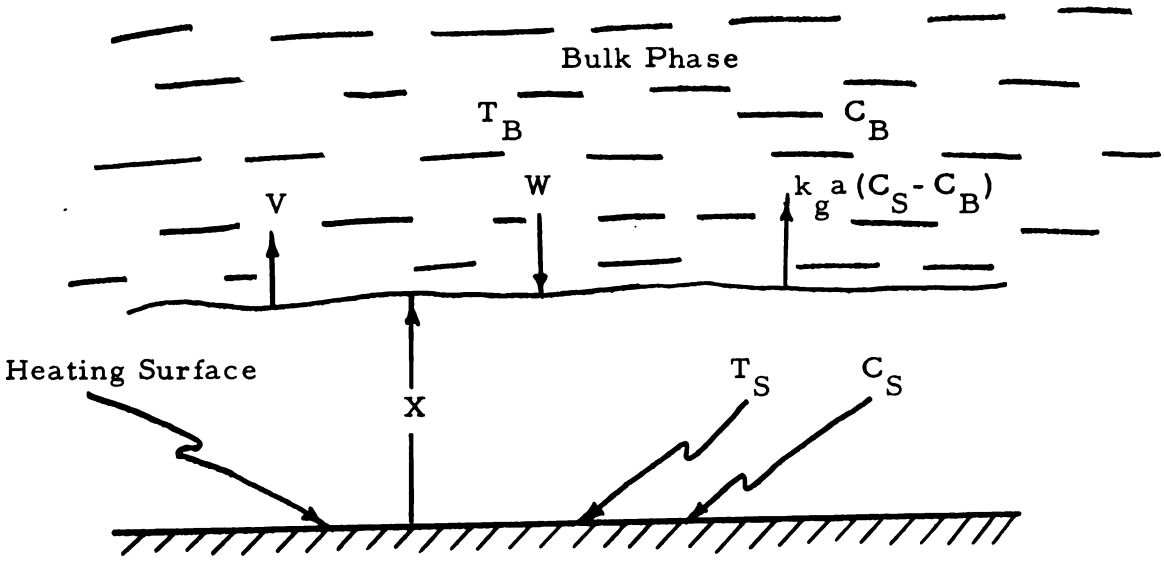


Figure 5. Schematic diagram of the heating surface.

In Figure 5:

V = moles of vapor/hr-ft^2

W = moles of hard water/hr-ft^2

k_g = mass transfer coefficient ft/hr

C_B = moles of salt/mole of water

C_S = moles of salt/mole of water

C_{sat} = saturation concentration at temperature T

T_B = bulk phase temperature

T_S = heating surface temperature

a = conversion factor moles/ft^3

The material balance of salt will be:

input - output = accumulation

$$WC_B - k_g a(C_S - C_B) - V(0) = \text{rate of crystallization} \qquad [7]$$

Since V = W, if there is no crystallization of salt, Equation [7] reduces to

$$VC_B = k_g a(C_S - C_B) \qquad [8]$$

rearranging [8] for C_S

$$C_S = C_B \left(\frac{V}{k_g a} + 1\right) \qquad [9]$$

In order to obtain scale on heating surface, $C_S > C_{sat}$ at T_S or $C_S - C_B > C_{sat}$ at $T_S - C_B$ in the case where the bulk phase is saturated $C_B = C_{sat}$ at T_B. Substituting this expression into the above inequality, and dividing by $(T_S - T_B)$, the following equation was obtained in which dC_{sat}/dT is the slope of the solubility-temperature curve.

$$\frac{C_S - C_B}{T_S - T_B} > \frac{C_{sat} \text{ at } T_S - C_{B\,sat} \text{ at } T_B}{T_S - T_B} \cong \frac{dC_{sat}}{dT} \qquad [10]$$

Substituting C_S from [9] into [10],

$$\frac{C_B}{T_S - T_B} \frac{V}{k_g a} > \frac{dC_{sat}}{dT} \qquad [11]$$

Thus a given salt will form scale on heating surface if it satisfies Equation [11].

The mass transfer coefficient, k_g, was estimated by the analogy (20) of mass transfer and heat transfer, and Equation [11] was calculated for salts of different solubility at various pressures for a constant heat flux. A sample of calculations is in Appendix 1 and a summary of results is shown in Figure 6.

Salt	dC/dT	Heat flux BTU/ hr-ft^2	Pressure lb/in^2	Equation [11] L. H. S.	Equation [11] R. H. S.	Possibility of scale formation
$CaSO_4$	negative	50, 000	200	0. 084	-0. 333	yes
NaCl	positive	50, 000	200	82. 800	+33. 300	yes

Figure 6. Summary of calculations using equation to predict scale formation.

From the above figure it is seen that a given salt with dC/dT positive may also form scale if it satisfies Equation [11].

Hanlon (12), in a discussion of scale composition and thickness, has stated that as heat transfer rate increases the crystals formed as a result of phosphate treatment tend to precipitate out of the boiler water and deposit as a sludge upon the heated surfaces of the boiler. He found that neither scales nor sludges are normally deposited within a boiler in pure form, i. e. they are usually mixtures of the various chemical compounds in the boiler water from which their components are precipitated.

Thurston and Furnival (27), working with an experimental boiler operated with carbonate treatment, found deposits of a similar form and of the same thickness on heated and unheated surfaces of the boiler. They concluded that scaling on the hot surface was neither due to reduced solubility of the scaling phase at the elevated temperature nor due to evaporation. The scaling was attributed to a permanent state of supersaturation in the boiler, generally, which was being relieved at all metal surfaces and presumably on suspended solids also.

Holmes and Jacklin studied boiler scale formation at 800 psi (14) and 1500 psi (15) with phosphate treatment and concluded that (1) more scale forms from the same amount of hardness at 1500 psi than at 800 psi; (2) more organic matter is needed at 1500 psi than 800 psi to prevent deposits.

Man'kina (19) and his co-workers explained the deposition of iron oxide on boiler heating surfaces by considering the electrostatic charges on the dispersed iron oxide particles and heating surface.

The dispersed particles are positively charged in a medium of 5 to 12 pH, and the heating surface is negatively charged due to rise in electron concentration caused by heat input. Thus the positively charged particles of the oxides of iron precipitate on the negatively charged heating surface and stick to it. In addition, these authors have reported that the rate of formation of iron oxide deposit depends on both the iron content in the boiler and on the magnitude of the heat input to the heating surface.

ROLE OF ORGANIC ADDITIVES

Organic matter has been used in the treatment of boiler water for various purposes such as: conditioning of boiler sludge to prevent it from adhering to the boiler metal, elimination of scale and corrosion in the pipe lines, prevention of embrittlement of boiler metal, and antifoam. Among the organic additives which reduce the scale formation on evaporating surfaces are: tannins, lignins, starch, and seaweed derivatives. These additives were found primarily by trial and error methods with little attention paid to their function in preventing scale formation.

There are several different proposed (13) mechanisms by which organic additives function to reduce boiler scale formation. Various workers disagree as to the exact function of organics. Some believe that the organic coats the crystal as it is formed, thus preventing its growth and decreasing its tendency to cohere and adhere to the boiler surface. Others believe that it is entirely a colloidal reaction resulting in either dispersion or coagulation of boiler precipitates depending upon the quantities of organic used, the pH, and the structure of the additive. For example, with sodium mannuronate polymers a coagulant effect is secured by absorption of inorganic precipitates in the organic floc. Tannins and lignins (6) cause dispersion of precipitates by acting as a protective colloid, thus preventing sticking together or to heating surfaces. Others believe that the organic additives actually delay or

hold back chemical reactions, thereby preventing precipitation especially where there is high heat transfer rate.

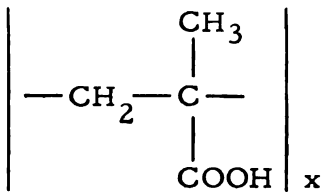
The lack of knowledge about the manner by which the additives function in reducing scale formation has impeded the development of superior synthetic additives. Thus one purpose of this investigation was to explore some of the variables related to the mechanism by which organic additives prevent scale formation. Calcium phosphate was chosen as the scaling salt since it is important in the medium pressure boiler range. Initially the additive pyrogallol (1, 2, 3-trihydroxy benzene) was selected in this study because it prevents (26) calcium carbonate and calcium sulphate scale and it appears to be of value in preventing calcium phosphate scale also. In addition pyrogallol is chemically similar to the organic additives in industrial use, i. e. hydroxy groups attached to a benzene ring, and its physical and chemical properties are known. Since adsorption of additives on scaling precipitates or boiler surfaces may be important in scale prevention, the adsorption phenomenon of pyrogallol was explored. Experiments were planned in which the effect of temperature and concentration on the amount of organic adsorbed on metal surfaces and calcium phosphate precipitates could be evaluated. During the development of a suitable method of analysis of pyrogallol, it was found by another study that pyrogallol did not aid in the prevention of calcium phosphate scale. Instead this additive actually increased the rate of scale formation. Consequently the adsorption studies were discontinued.

Scaling rate data of lignin, palconate, polyfon, marecell "E" etc. were available. All these additives were equally effective in reducing scale formation. Thus the correlation of the physical and chemical properties of these additives with the rate of scale formation might yield important information on the mechanism of scale formation. Two important properties might be the functional groups and the molecular weight of the additive. It is believed that (13) the position and type of functional group plays an important role in scale prevention. Therefore to determine functional groups and any change of the additive during its stay in the boiler, infrared spectra of additives and their corresponding sludge and scale were obtained. These spectra were obtained employing the KBr pellet technique. A mixture of KBr and the substance to be analyzed were hydraulically pressed into a pellet and analyzed in an infrared spectrometer using a NaCl pellet as the reference. Infrared spectra of the sludge showed the presence of calcium phosphate and an organic compound which could not be identified. Spectra of the scale showed the presence of calcium phosphate and iron. Spectra of additives did not yield sufficient information concerning their functional groups or changes in their structure, so an attempt was made to extract a certain fraction of organic additive with ethyl alcohol and ethyl ether. These were chosen as extraction media because their spectra have certain ranges in which other fractions, if extracted, can be clearly distinguished. Ten grams of additive were mixed with 300 ml of ethyl alcohol, refluxed for fifteen hours, and filtered.

After cooling, infrared spectra of the filtrate were obtained. The resulting spectra of pure ethyl alcohol and ethyl ether showed no trace of the additive. All these spectra are shown in Appendix 3.

The determination of the other important property of the additive, molecular weight, was attempted by the light scattering technique which is useful over a wide range of molecular weights; however, solutions of the additives were found to be too dense for light scattering measurements. Other methods such as viscosity measurements and osmotic pressure determinations were not applicable as the former does not give the absolute molecular weight and the latter is only useful over a narrow molecular weight range and is also inapplicable (8) to colloidal substances.

Lignite showed excellent scale preventive properties (see Appendix 2) hence it was decided to test a polymer of known and similar structure. Russell (24) has reported that Gymosperm (Larch) lignin can be synthesized from vanillin monoacetate by a Claisen condensation with anhydrous aluminum chloride. Since the experimental conditions were not cited in the reference and because of technical difficulties encountered, the above mentioned polymer could not be prepared. However, vanillin, which is believed to be a monomer of lignin, was tested in the boiler. As in the case of pyrogallol, vanillin also did not reduce the rate of scale formation. These results indicated that the molecular weight of an additive may be an important factor. Thus, two straight chain polymers of structure $(-CH_2-CH_2-O-)_x$ and

molecular weights 4000 and 1, 000, 000 were tested in the boiler and scaling rates were measured. Both polymers gave scaling rates of about 20 gm/hr-cm^2 compared to 30 gm/hr-cm^2 in a blank run, even though these polymers were not chemically similar to industrially used additives. Consequently more polymers of known structure were studied. A polymer of methacrylic acid of molecular weight 127, 000 and of structure  was prepared.

Scaling rates were measured with the polymer and its monomer (i. e. methacrylic acid, mol. wt. 86). The polymer reduced the rate of scale formation to a negligible amount and the monomer decreased the rate of scale formation by 50 percent. This result confirmed the theory that the molecular weight of an additive is an important factor in scale prevention. In order to further study the effect of molecular weight, a series of polymers of methacrylic acid of different molecular weights were prepared. The polymers of molecular weights 6500; 12,400 43, 000; and 127, 000 were tested in the boiler. Molecular weights of all the polymers were obtained by the viscosity measurement technique which is described in Appendix 5.

EQUIPMENT AND PROCEDURE

Description of the Boiler

Drawings of the boiler are shown in Figures 7a and 7b; Figure 8 is a photograph of the unit. Essentially, the boiler consists of a cylindrical body surrounded by three side arms spaced 120° apart. The arms are connected to the upper and lower portion of the cylindrical body, causing water to flow through the arms and into the cylindrical body. Each side arm contains a separate heating tube, so three different heat flux levels can be attained in one run. The liquid capacity of the boiler is controlled by means of three liquid level control cells attached to the side of the boiler. This also provides an on-off control to the feed and blow-down pumps. A drain is located at the bottom of the boiler. The boiler is surrounded by an insulation jacket for the purpose of reducing heat losses. Auxilliary equipment consists of a dead weight valve, duplex feed pump and blow-down pump, feed tanks, heating system and a central panel board.

The dead weight valve consists of an inverted cone, mounted vertically, to provide an adjustable boiler pressure. It is located above the jet orifice through which steam from the boiler is released. The weight on the cone can be varied to control the pressure within the boiler to within 10 psi variation. A rupture disc (Figure 7a) is also included to insure pressure release in the event of clogging in the jet orifice.

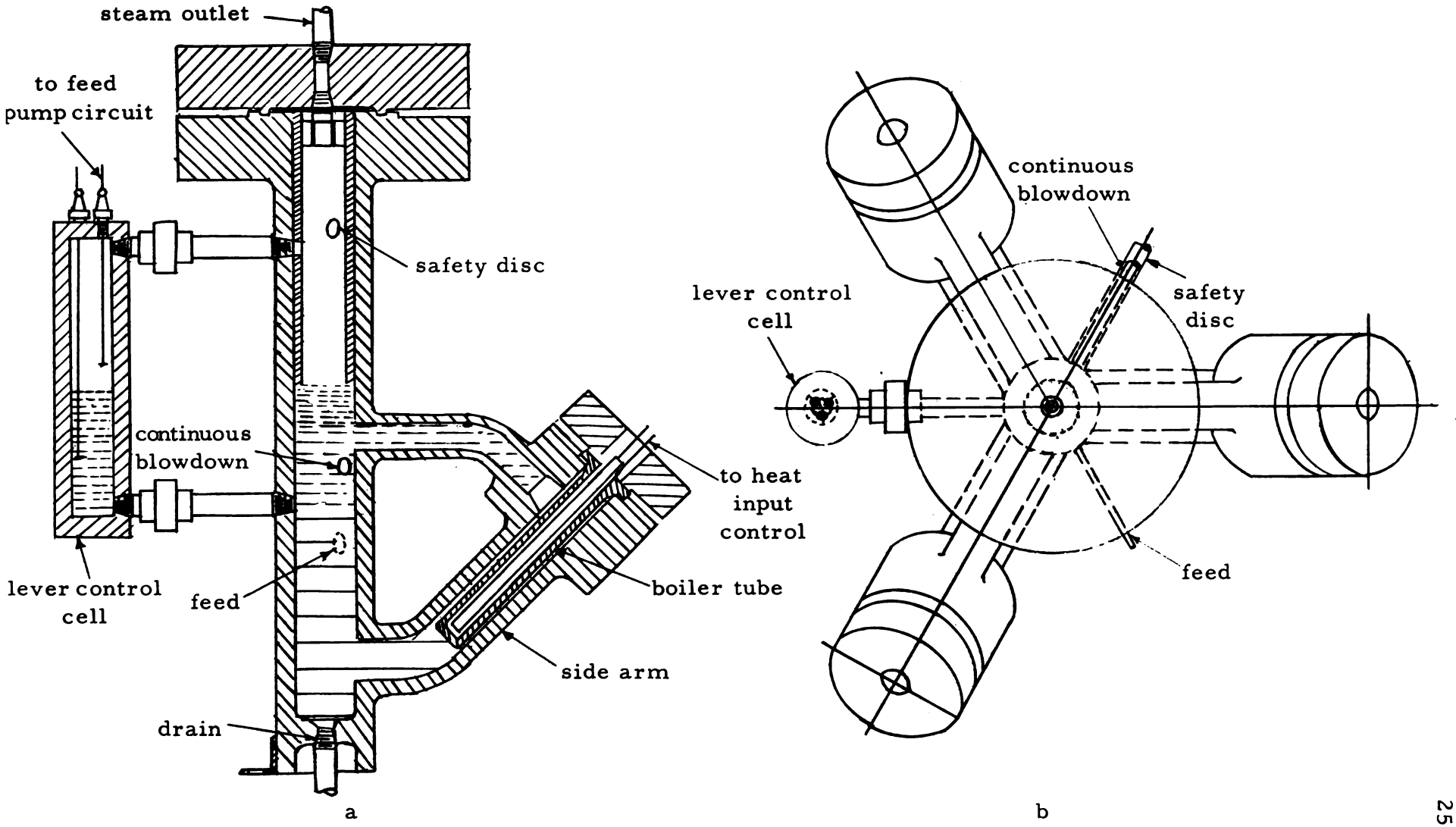


Figure 7. Drawings of experimental boiler

Legend for Figure 8

A - Feed tank

B - Chemical tank

C - Blow-down tank

D - Boiler with insulation on

E - Duplex feed pump

F - Liquid level control

G - Side arm with heating tube in

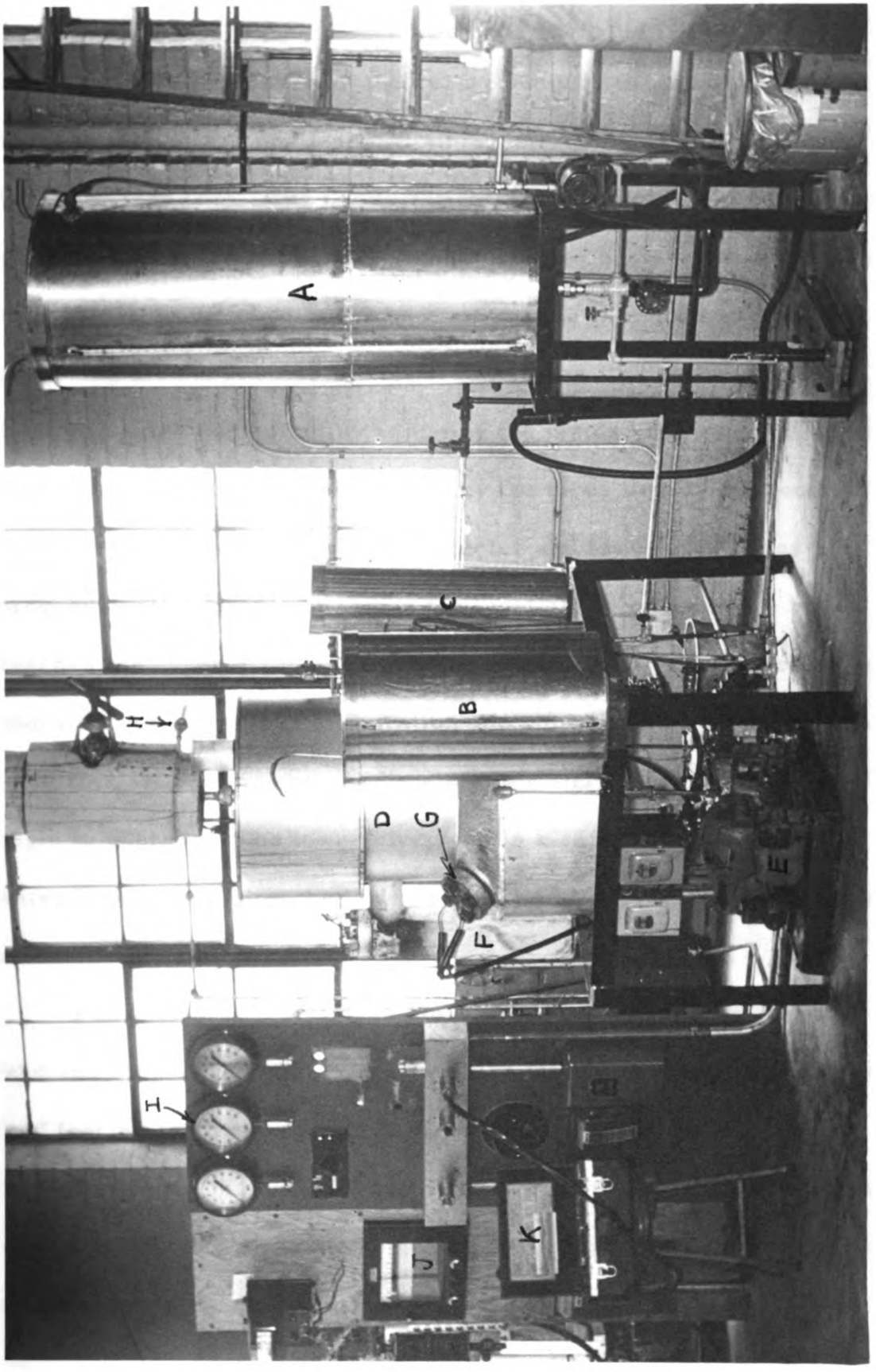
H - Safety rupture disc

I - Pressure gages

J - Temperature recorder

K - Power analyzer

Figure 8. Experimental boiler unit.


A
B
C
D
E
F
G
H
H
J
K

Duplex feed and blow-down pumps are located in the base of the boiler unit. The function of the duplex pump is to pump two separate feeds to the boiler, one feed containing only the calcium hardness, the other feed containing the conditioning chemicals. The blow-down pump is used to remove water from the boiler against a high-pressure relief valve to the blow-down tank. A double-pipe heat exchanger preceding the pump cools the blow-down steam to prevent flushing. Feed rates are controlled by adjusting the piston strokes of the pumps. These pumps operate automatically by the three liquid-level control cells or electrodes. The upper, middle, and lower electrodes are progressively shorter, and when the level of the water in the boiler reaches the upper electrode, the feed and blow-down pumps cease to operate. As a result of evaporation and blow-down removal, the water level then falls below the middle electrode and at that position the pumps begin to operate. The lower electrode is a safety device; when the water level falls below the lower electrode all power to the boiler is automatically turned off.

Four calibrated stainless steel tanks are used to measure the feed and blow-down rates. A 100-gallon tank is used for the raw water feed (containing only calcium hardness) and a 30-gallon tank is used for the conditioning chemicals feed. A third tank of 2-gallon capacity is used to fill the boiler at the beginning of each run, with a solution of approximately the same composition as the steady-state boiler water

composition. The fourth tank is used to collect blow-down. The chemical and blow-down tanks are blanketed with oxygen-free nitrogen during tests to prevent conversion of sodium sulphite to sodium sulphate. The three feed tanks are connected to the duplex pump with suitable valves so that any one, two, or three of the tanks can be connected at the same time.

Steel tubes closed at one end serve as heating tubes. The open end of each tube has a flange which sealed the tube into a side arm on the boiler. Electric "fire rod" heating units manufactured by the Watlow Electric Company of St. Louis, Missouri, fit snugly into the heater tube. The fire rod unit is 10 inches long and 5/8-inches in diameter; the heater tubes are 11.5 inches long and 1.127 to 1.242 inches in diameter. Although the heaters were rated at 4700 watts, they did not burn out until 12.5 kilowatts was applied. The power input was fixed at 4 kw in one arm, variable from 0 to 4 kw in the second arm, and variable from 0 to 12.5 kw, in the third arm. A line voltage of 220 was used in the first two heaters while voltage of 440 was used for the third heater. Power input to the heaters was measured using the Westinghouse Type TA Industrial Analyzer.

The control panel board contains on-off switches for the heaters and pumps, plugs for power input measurement, variacs to control the power input in the heating tubes, and three pressure gages.

Operating Procedure

Before each run all the tanks were washed with water which was obtained by condensing steam. The feed, chemical, and synthetic chemical tanks were filled with condensate to their capacity and the required amounts of chemicals were added. The tanks were then blanketed with nitrogen which had first passed through a series of absorbers containing an alkaline solution of pyrogallol to absorb any oxygen present. The heating tubes were cleaned with a fine grade of emery cloth and replaced in the boiler side arms. The synthetic feed solution was then added to the boiler, and the electric heaters were turned on. A pressure of 500 psig was attained after 35 to 40 minutes. In most of the runs the dead weight valve was adjusted to give 500 psig boiler pressure. Although the boiler operated automatically, the heat inputs, feed rates, and blow-down rate were periodically checked. Samples of the feed entering and leaving the boiler were analyzed periodically to assure steady-state boiler operation. Calcium, phosphate, OH alkalinity, p-alkalinity, sulphite and dissolved solids analyses were determined by the standard methods of the Dearborn Chemical Company.

At the end of each run the power was turned off, steam pressure was released through a side valve, and sludge was removed through a drain located at the bottom of the boiler. After the heating tubes were removed and photographed, the scaling rates were determined

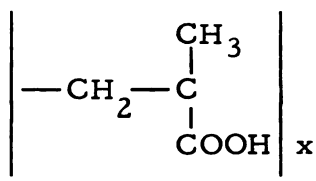
from the weight of scale scraped from a known surface area of the heating tube. Finally, the boiler was cleaned with a Versene solution (supplied by Dearborn Chemical Company) and rinsed with water. Cleaning with Versene solution was accomplished by heating until the pressure reached 150 psig and immediately flushing the hot solution through the bottom drain.

DISCUSSION OF RESULTS

Table 1 of Appendix 2 summarizes the scaling rate data obtained with calcium phosphate as the scaling salt and pyrogallol as the organic additive, at various pressures. The data show that pyrogallol did not prevent calcium phosphate scale formation. The scaling rate increased with increasing heat flux and increasing boiler pressure. Straub (26) reported that pyrogallol prevented calcium sulphate and calcium carbonate scale at atmospheric pressure, but did not prevent scale formation at higher pressures. He attributed this result to decomposition of pyrogallol at higher temperatures and pressures. However, the results of the present investigation cannot be explained by decomposition of the pyrogallol at higher pressures as an appreciable amount of scale also formed at lower pressures.

Infrared spectra of lignite, Polyfon, Maracell "E" etc., and their corresponding scales and sludges are given in Appendix 3. The spectra of additives do not give definite information about their structure or their functional groups. The spectra of scales show the presence of calcium phosphate and iron. Spectra of sludges show the presence of calcium phosphate and some type of organic compound which could not be identified. Thus by infrared spectrum analysis it was not possible to detect the presence of functional groups in the additives, scales, or sludges; and any changes in the structure of the additives due to their action in the boiler could not be detected. Hence, the correlation of functional groups with the rate of scale formation was not possible.

Scaling rate data of industrially used additives such as lignite, Maracell "E," Polyfon, Palconate, etc., and vanillin are given in Table 2. Table 3 summarizes the scaling rate data obtained using methacrylic acid polymers of various molecular weights, and monomers. The data of Table 2 and 3 of Appendix 2 show that high molecular weight additives (lignin, Maracell "E," etc.) reduced the rate of scale formation about 90 percent compared to the scaling rate without any additive present. On the other hand monomers such as vanillin and pyrogallol did not reduce the scaling rates. Also straight chain polymers of structures $(-CH_2-CH_2-O-)_x$ (known as Polyox) reduced the scaling rate by about 30 percent (see Table 4) even though these polymers were not chemically similar to the industrially used additives. Thus it is concluded that molecular weight or size of an additive is an important factor in prevention of calcium phosphate scale. Tables 3 and 4 show that the scaling rates with the polymers of methacrylic acid,



are much lower than the scaling rates with two straight chain polymers $(-CH_2-CH_2-O-)_x$, which indicates the functional group of an additive is also an important factor in prevention of scale.

All the polymers of methacrylic acid (see Table 3) decreased scale formation to a negligible amount. The monomer decreased

the scaling rate by 33 percent compared with the scaling rate without any additive present. With the polymers of molecular weight 43, 000 and 127, 000, scale formed at the end of the heating tube where the heat flux was very small, even though scale formation on the inner boiler surfaces was negligible. This unusual phenomenon could not be adequately explained. Examination of heating tubes (see Appendix 4) showed that the 6, 500 and 12, 400 molecular weight polymers were superior to all other polymers tested.

Among the several theories of the mechanism by which organic additives prevent scale formation, perhaps the most acceptable one is that the additive prevents crystal growth by physical adsorption on the crystal surface thus giving a large number of small crystals not capable of adhering to the boiler surfaces.

The data on the methacrylic acid polymers show that a chemical reaction between the calcium and the polymer would only account for one-third of the calcium hardness. The calculation was based on equating each -COOH group in the polymer to one calcium ion. Although a complete chemical reaction does not account for all the calcium hardness, it may still be an important factor in scale prevention. For example, the polymer molecules may act as nucleation sites for calcium phosphate crystals by a chemical reaction. These polymer sites would compete with nucleation sites on the metal surfaces. Thus large numbers of small crystals may form in the solution rather

than on the metal surfaces so that the scale prevention might also occur by this mechanism.

McCartney and Alexander (18) have studied the adsorption of acrylic and methacrylic acid polymers on the crystallization of calcium sulphate at room temperature. They reported that acrylic acid polymer was most effective in retarding crystallization of calcium sulphate while methacrylic acid polymer was found to have less retarding power. The less retarding power of methacrylic acid polymer was attributed to steric hinderence by the methyl group interfering with the adsorption of the molecule on the crystal surface. At the higher temperature of 70°C, they observed that calcium sulphate crystals grew extremely rapidly to a size whose general shape could be distinguished with naked eyes. It appears that the work of McCartney and Alexander, and the fact that the adsorption decreases with increase of temperature, support the postulated mechanism that the methacrylic acid polymer provides sites for calcium phosphate crystals at higher temperatures and pressures.

Figure 6 (page 16) summarizes the results obtained by the theoretical calculation from the equation derived to predict whether or not a given salt will form scale on a heating surface. The results of Figure 6 show that both calcium sulphate and sodium chloride will form scale on the heating surface. Hall (11) has found experimentally that the calcium sulphate forms scale on the heating surface. Coffey (5), while boiling sodium chloride solution in the experimental boiler

at atmospheric pressure, also observed the scale formation on the heating surface. Therefore it may be concluded that the derived equation is in agreement with the experimental data available.

CONCLUSIONS

Polymers of methacrylic acid of molecular weight 6, 500 and 12, 400 were superior to either higher molecular weight polymers or to the monomer in the prevention of calcium phosphate scale in a 500 psig boiler.

The methacrylic acid polymers were at least 5 times as effective as the industrially used organic additives in scale prevention. Organic polymers were always superior to their monomers in the prevention of scale.

It was postulated that the organic additives may function by acting as more efficient nucleation sites for calcium phosphate crystal formation than the nucleation sites on the heating surface. By this mechanism scale formation may be prevented and the calcium phosphate may exist as a large number of small crystals suspended in solution.

An equation was derived to predict whether or not a given salt will form scale on a heating surface. The equation is in agreement with the experimental data available, however, more extensive tests of the validity of the equation are desirable.

BIBLIOGRAPHY

1. Betz, W. H. and L. D. Betz, "Betz Handbook of Industrial Water Conditioning," Chapter 23, pp. 91-93, 1953.

2. Blanning, H. K. and A. D. Rich, "Boiler Feed and Boiler Water Softening," Chapter 18, pp. 114, Nickerson and Collins Co., Chicago, 1942.

3. Buckley, H. E., "Crystal Growth," pp. 378-466, John Wiley & Sons, Inc., New York, 1951.

4. Cabrera and Vermilyea, "The Growth of Crystals from Solution," pp. 393 of "Growth and Perfection of Crystals" edited by Doremus, R. H., et al., John Wiley & Sons, Inc., New York, 1958.

5. Coffey, J. F., ."B. S. Thesis in Chemical Engineering" M. I. T., 1939.

6. Feller, E. W. ed., "Fundamentals of Feed-Water Treatment," Power, December, 1947.

7. Findlay, R. A. and D. L. McKay, "Separation by Crystallization," pp. 163 in Reaction Kinetics and Unit Operations, No. 25, Vol. 55, 1959. A. I. Ch. E. Publication.

8. Flory, P. J., "Principles of Polymer Chemistry," p. 269, Cornell University Press, Ithaca, New York, 1953.

9. Frank, F. C., "The Influence of Dislocations on Crystal Growth," Discussion of Faraday Society, No. 5, 48, 1949.

10. Garrett, D. E. and G. P. Rosenbaum, "Crystallization," Chem. Eng., pp. 125-140, August, 1958.

11. Hall, R. E., "A System of Boiler Water Treatment Based on Chemical Equilibrium," Ind. & Eng. Chem. 283, 17, 1925.

12. Hanlon, R. T. "Deposit Composition and Thickness," Modern Power and Engineering, January, 1957.

13. Holmes, J. A. "The Development of Organics for Water Treatment," Proc. Midwest Power Conference (1951).

14. Holmes, J. A. and C. Jacklin, "Experimental Studies of Boiler Scale at 800 psi," Proc. Engineers Society, Western Pa. November, 1942.

15. Holmes, J. A. and C. Jacklin, "Experimental Studies of Boiler Scale at 1500 psi," Proc. Engineers Society, Western Pa. October, 1945.

16. LaMer, V. K., "Nucleation in Phase Transition," Ind. & Eng. Chem. 44, 1270 (1952).

17. Lawson, W. D. and S. Nielson," Preparation of Single Crystal Growth," Butterworth's Scientific Publication, London, 1958.

18. McCartney, E. R., and A. E. Alexander, "The Effect of Additives upon the Process of Crystallization of $CaSO_4$," Journal of Colloidal Science, 13, 383-396 (1958).

19. Man'Kina, N. N., Przhiyalkovskiy, M. M. Bulavitskiy, Yu. M., and Petrova, I. N., "Formation of Iron Oxide Scales in Steam Boilers with Multiple Circulation," Teploenergetika, 1959, No. 2, pp. 79-83 (U. S. S. R.).

20. McAdams, W. H., "Heat Transmission," Chapter 9, pp. 213, McGraw-Hill Book Company, Inc., New York, 1954.

21. McAdams, W. H., "Heat Transmission, Chapter 14, p. 382, McGraw-Hill Book Company, Inc., New York, 1954.

22. McCabe, W. L., "Crystallization," in J. H. Perry, ed., "Chemical Engineers' Handbook," McGraw-Hill Book Company, Inc., New York, 1950.

23. Preckshot, G. W. and G. G. Brown," Nucleation of Quiet Supersaturated Potassium Chloride Solutions," Ind. & Eng. Chem. 44, p. 1314 (1952).

24. Russell, A., Chem. and Eng. News, 25, 2849 (1947).

25. Sherwood, T. K. and R. L. Pigford, "Absorption and Extraction," p. 22, McGraw-Hill Book Company, Inc., New York, 1952.

26. Straub, F. B., "A Study of the Reactions of Various Inorganic and Organic Salts in Preventing Scale in Steam Boilers," Bulletin 283, Eng. Experiment Station, University of Illinois, 1936.

27. Thurston, E. F. and L. Furnival, "Boiler Water Treatment: A Formula for the Control of Sludge and Scale in Internal Carbonate Treatment," J. Inst. Fuel, 30, 585, 1957.

APPENDIX

APPENDIX 1

SAMPLE CALCULATION OF THE EQUATION DERIVED TO PREDICT SCALE FORMATION ON THE HEATING SURFACE

The following Equation [11] was derived in Section 2 (pages 13-18) by considering heat transfer and mass transfer to and from the heating surface. A given salt will form scale on heating surfaces if it satisfies Equation [11]:

$$\frac{C_B}{T_S - T_B} \frac{V}{k_g a} > \frac{dC_{sat}}{dT} \qquad [11]$$

where

C = concentration of salt moles of salt/mole of water

T = temperature ^{o}F

V = moles of vapor/hr-ft^2

k_g = mass transfer coefficient ft/hr

a = conversion factor mole/ft^3

Subscripts B indicate the bulk phase and S indicate the heating surface.

In order to estimate the moles of vapor forming per hour per square foot the following estimations were made:

Heat flux = 50,000 BTU/hr-ft^2

Boiler pressure = 200 lb/in^2

Then, from steam tables, the properties at 200 lb/in^2 are as follows:

$T_B = 381.8^{o}F$

λ (latent heat of vaporization) = 843 BTU/lb

Hence $V = \frac{50,000}{843 \times 18} = 3.3$ moles/hr-ft^2.

The mass transfer coefficient k_g was estimated by the analogy of mass transfer and heat transfer, i.e., Nusselt number, $\frac{hD}{k}$, being equivalent to Sherwood number, $\frac{k_g D}{D_L}$, and Prandtl number $\frac{Cp\mu}{k}$, being equivalent to Schmidt number, $\frac{\mu}{\rho D_L}$.

where

C_p = heat capacity of water

D = diameter of heating tube

D_L = diffusivity in liquid (water)

h = coefficient of heat transfer

k = thermal conductivity of liquid (water)

k_g = mass transfer coefficient

μ = viscosity of water

ρ = density of water

The following assumptions made:

diameter of heating tube = 1.242 inches

length of heating tube = 10.0 inches

diffusivity (25) of salt in liquid (after applying the temperature correction)

$= 1.15 \times 10^{-3}$ ft^2/hr.

Then at heat flux of 50,000 and pressure of 200 lb/in^2, ΔT, i.e. $T_S - T_B$, was found from McAdam's heat transfer (21) to be 15°F. The properties of the solution such as μ, ρ, k, etc. were obtained from the Perry's handbook.

Now $q = hA\Delta T$

$$\therefore h = \frac{q}{A\ T} = \frac{50,000}{15} = 3,330 \text{ BTU/hr-ft}^2\text{-}^{\circ}\text{F}$$

also

$$N_{Nu} = \frac{hD}{k} = \frac{3,330 \times 1.242}{0.383 \times 12} = 900$$

$$N_{Pr} = \frac{C_p \mu}{k} = \frac{1.2 \times 0.07 \times 2.42}{0.383} = 0.53$$

$$N_{SC} = \frac{\mu}{\rho D_L} = \frac{0.01 \times 2.42}{54.4 \quad 1.15 \times 10^{-3}} = 2.7$$

Then from the plot (19) of Reynold number vs. Nusselt number with the Prandlt number as parameter, the Reynold number corresponding to N_{Nu} of 900 and N_{Pr} of 0.53 was found to be 9×10^5. From the same plot but by the analogy of mass transfer and heat transfer, Sherwood's number, $\frac{k_g D}{D_L}$ was estimated at a Reynold number of 9×10^5 and a Schmidt number of 2.7 to be 2100. Thus

$$N_{Sr} = \frac{k_g D}{D_L} = 2100$$

$$\therefore k_g \quad \frac{2100 \times D_L}{D} = \frac{2100 \times 1.15 \times 10^{-3} \times 12}{1.242} = 23.3 \text{ ft/hr}$$

The remaining unestimated quantities C_B and $\frac{dC_{sat}}{dT}$ of Equation [11] can be estimated by choosing a salt for which scale formation on heating surfaces is to be predicted. First consider the salt whose solubility decreases with increase in temperature, for example, calcium sulphate. From Betz Handbook (1) at T_B of $381.8^{\circ}F$, C_B was found to be 27 parts per million and $\frac{dC_{sat}}{dT}$ was estimated to be -0.333.

Thus

$$\frac{C_B}{T_S - T_B} \frac{V}{k_g a} > \frac{dC_{sat}}{dT} \qquad [11]$$

$$\frac{27}{15} \frac{3.3 \times 18}{23.3 \times 54.4} > -0.333$$

or

$$0.084 > -0.333$$

Next consider the salt whose solubility increases with increase in temperature, for example, sodium chloride. From the literature (12) C_B and $\frac{dC_{sat}}{dT}$ were estimated to be 26, 500 grains per U. S. gallon and +33. 3 grains per U. S. gallon per ^{o}F respectively. Substituting these values in Equation [11] we have

$$\frac{26,500}{15} \frac{3.3 \times 18}{23.3 \times 54.4} > +33.3$$

or

$$82.8 > +33.3$$

APPENDIX 2

HEAT FLUX AND SCALE DATA FOR VARIOUS ORGANIC ADDITIVES

TABLE 1. Heat flux and scale data for pyrogallol at various pressures

Run	Additive	Concentration in boiler mg/L	Boiler pressure psig	Heat flux BTU/hr-ft^2	Total run time hours	Scale gm/hr-cm^2
1-83	pyrogallol	70	490 ± 10	82,000	48	39.9×10^{-6}
				51,500		31.4×10^{-6}
				51,500		26.1×10^{-6}
1-77	pyrogallol	70	355 ± 10	82,000	44.5	55×10^{-6}
				57,000		36×10^{-6}
				45,000		34×10^{-6}
1-79	pyrogallol	70	150 ± 10	81,000	41.84	31×10^{-6}
				58,000		23×10^{-6}
				44,000		21×10^{-6}
1-81	pyrogallol	70	0 ± 0	44,000	46.5	17.6×10^{-6}
				40,000		7.9×10^{-6}
1-73	oxidized pyrogallol	70	504 ± 15	82,000	138	32×10^{-6}
				59,000		35×10^{-6}
				56,000		32×10^{-6}

TABLE 2. Heat flux and scale data for various additives

Run	Additive	Concentration in boiler mg/L	Boiler pressure psig	Heat flux BTU/hr-ft^2	Total run time hours	Scale gm/hr-cm^2 x 10^{+6}
1-71	Marecell "E"	70	500 ± 15	80,000	160.3	3.8
				59,000		5.3
				57,000		5.4
1-85	Polyfon	70	502 ± 12	82,000	119.75	3.1
				57,000		4.88
				50,400		3.51
1-89	Palconate	70	540 ± 20	82,000	120	5.65
				57,000		5.62
				50,400		6.66
1-95	Standard Lignite	70	560 ± 15	55,300	120	0.941
				52,000		0.497
				57,000		0.596
1-87	Solubilized Lignite	70	506 ± 15	82,000	120	5.33
				50,400		5.26
1-93	Vanillin	70	530 ± 15	93,500	50	48.8
				50,400		34.9
				57,000		32.3

TABLE 3. Heat flux and scale data for methacrylic acid polymers

Run	Mol. wt.	Concentration in boiler mg/L	Boiler pressure psig	Heat flux BTU/hr-ft^2	Total run time hours	Scale on hot surface gms/hr-cm^2	Scale on the end of boiler tube*
1-103	127,000	70	550 ± 20	89,000	46	negligible	43×10^{-6}
				49,000		negligible	26.5×10^{-6}
				52,000		negligible	40×10^{-6}
1-105	86	70	550 ± 10	88,000	46	19.6×10^{-6}	negligible
				49,000		7.05×10^{-6}	negligible
				52,000		17.8×10^{-6}	negligible
1-107	127,000	70	515 ± 20	89,000	47	negligible	48×10^{-6}
				50,000		negligible	34.6×10^{-6}
				54,000		negligible	45.7×10^{-6}
1-109	43,000	70	490	93,000	48.3	negligible	32×10^{-6}
				50,000		negligible	12.3×10^{-6}
				54,000		negligible	31.0×10^{-6}
1-111	12,400	70	435 ± 15	93,000	48.5	negligible	negligible
				52,000		negligible	negligible
				54,000		negligible	negligible
1-113	6,500	70	350	90,000	48	negligible	very, very slight
				50,000		negligible	"
				48,000		negligible	"

*gms/hr-cm^2

TABLE 4. Heat flux and scale data for Polyox (polymer) and blank

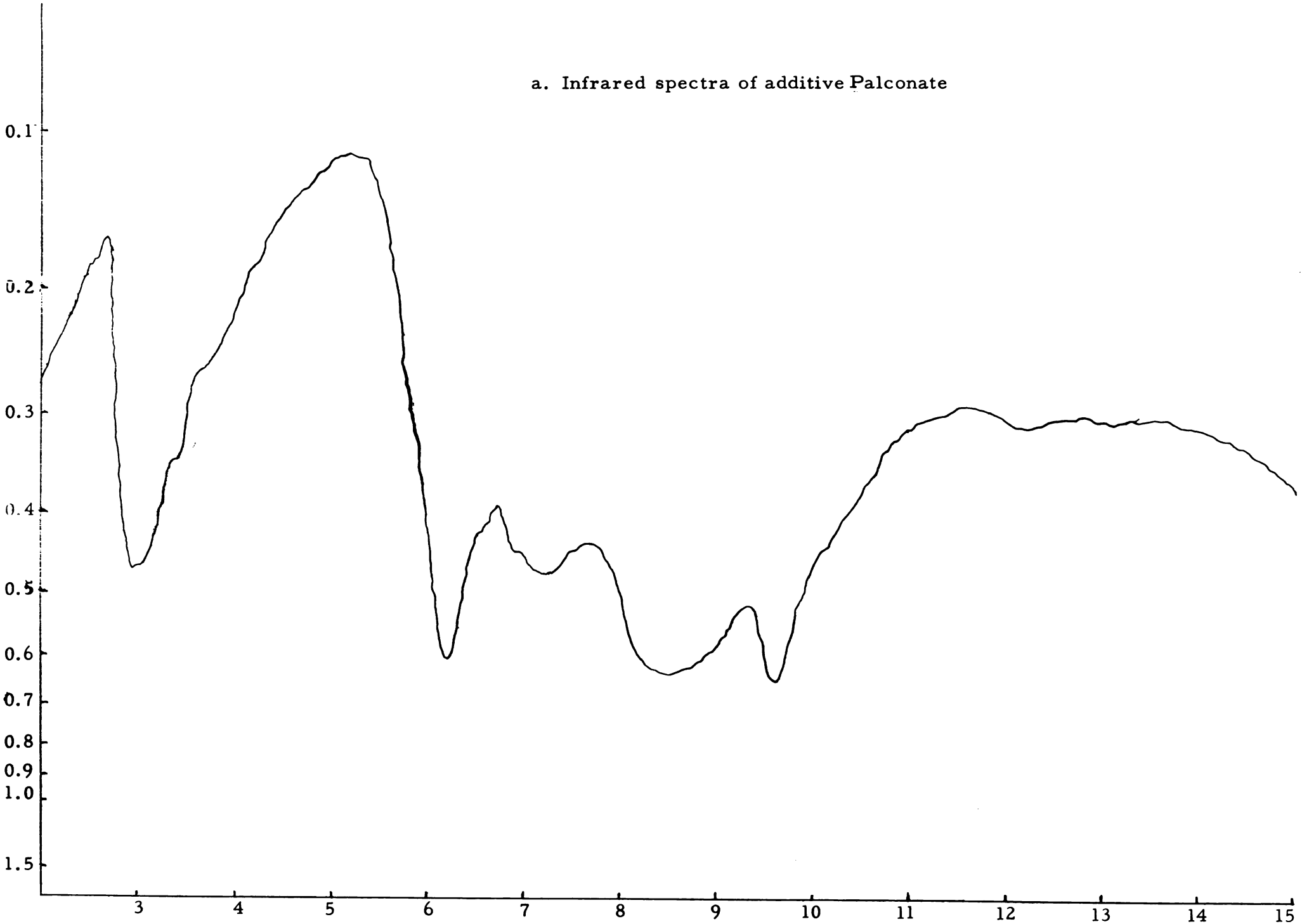
Run	Additive	Concentration in boiler mg/L	Boiler pressure psig	Heat flux $BTU/hr\text{-}ft^2$	Total run time hours	Scale $gm/hr\text{-}cm^2$
1-99	Polyox mol. wt. 1,000,000	70	500 ± 15	94,600	58	13.9×10^{-6}
				50,200		19.6×10^{-6}
				53,800		20.2×10^{-6}
1-101	Polyox mol. wt. 4,000	70	530 ± 20	94,600	47.5	26.6×10^{-6}
				50,200		19.7×10^{-6}
				53,800		16.2×10^{-6}
1-75	None	--	300 - 400	79,000	47.25	30.0
				53,900		29.0
				52,600		39.0

APPENDIX 3

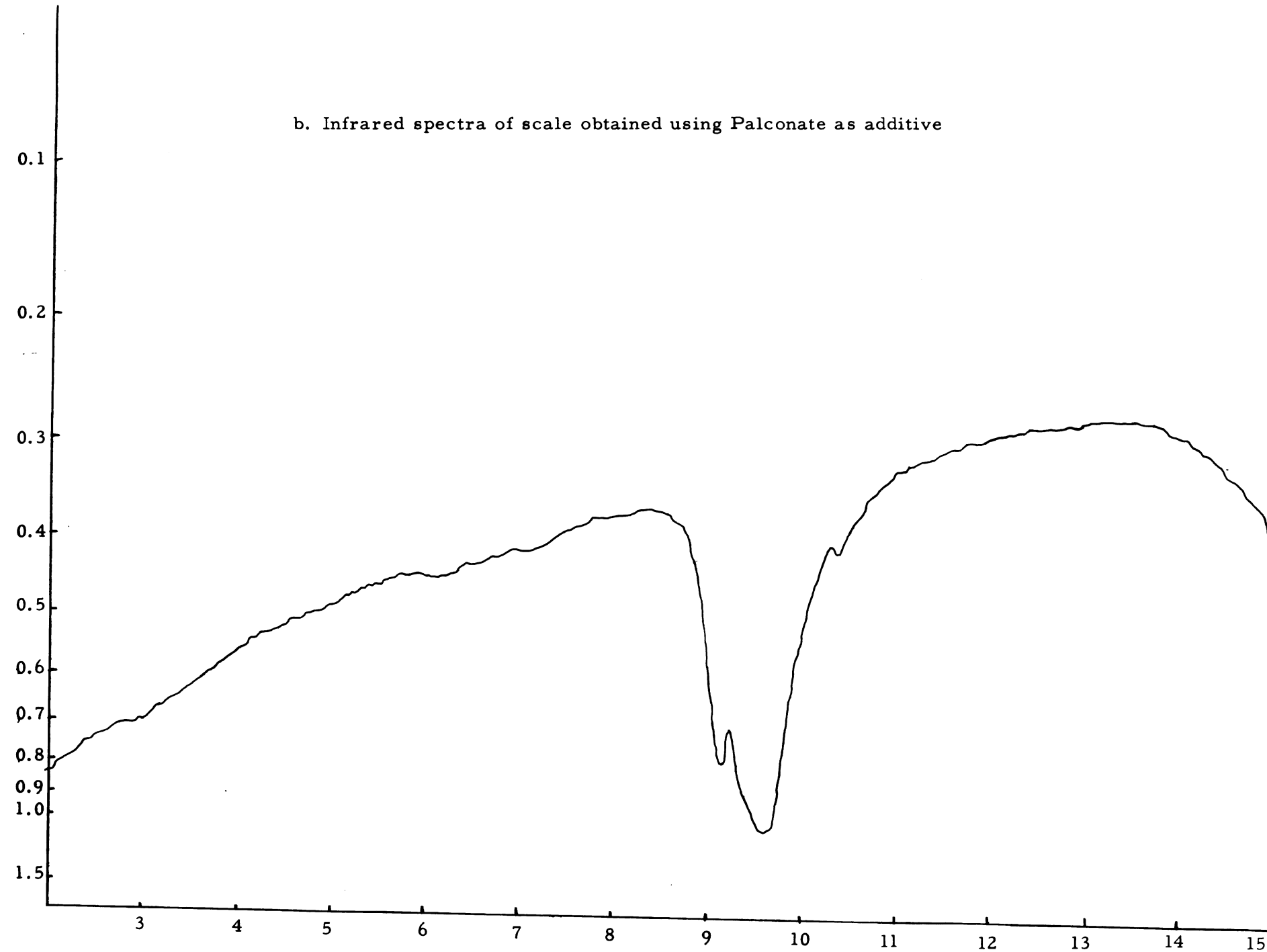
INFRARED SPECTRA OF ADDITIVES, SLUDGES AND SCALES

(Wavelength versus Absorbance)

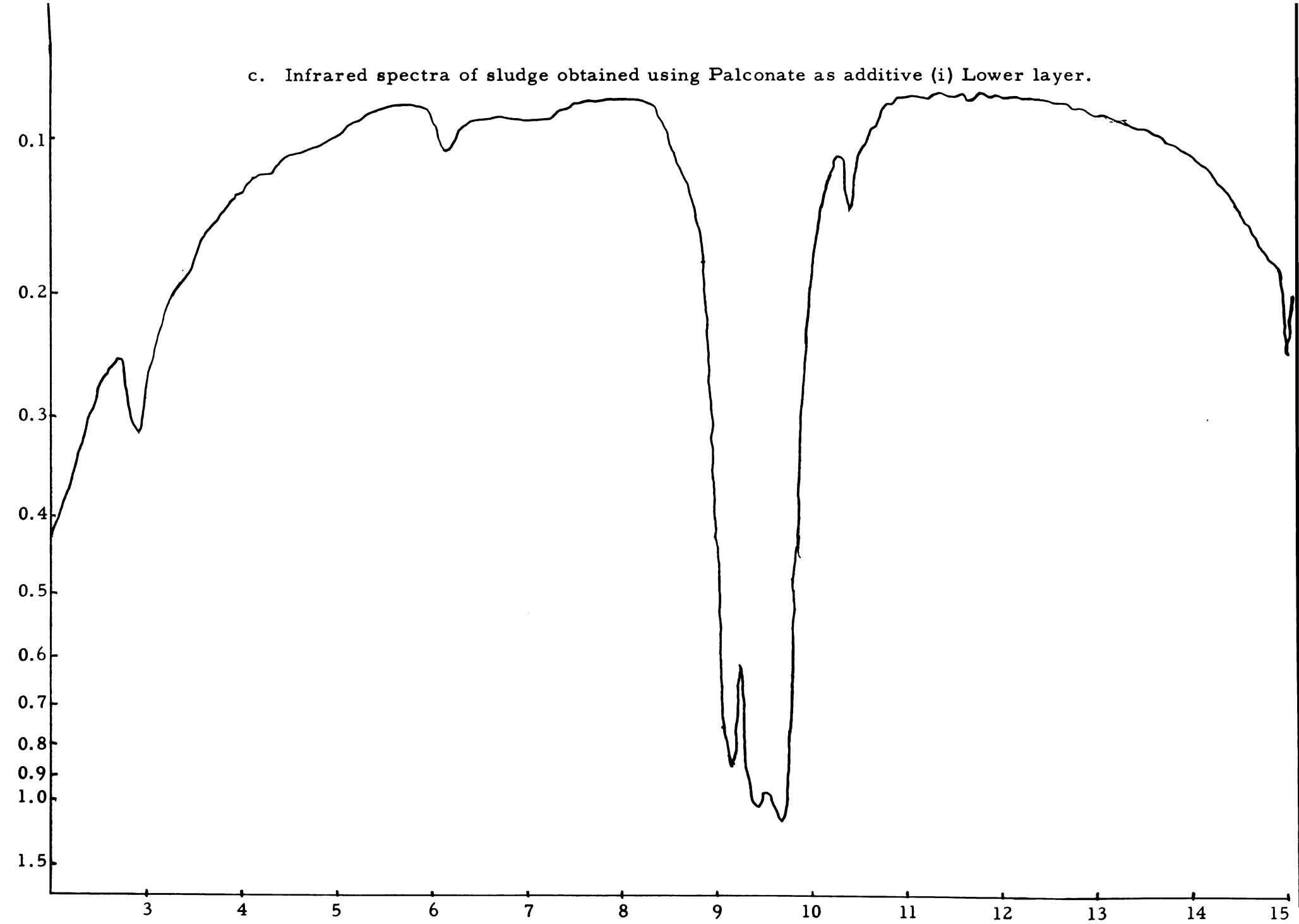
a. Infrared spectra of additive Palconate



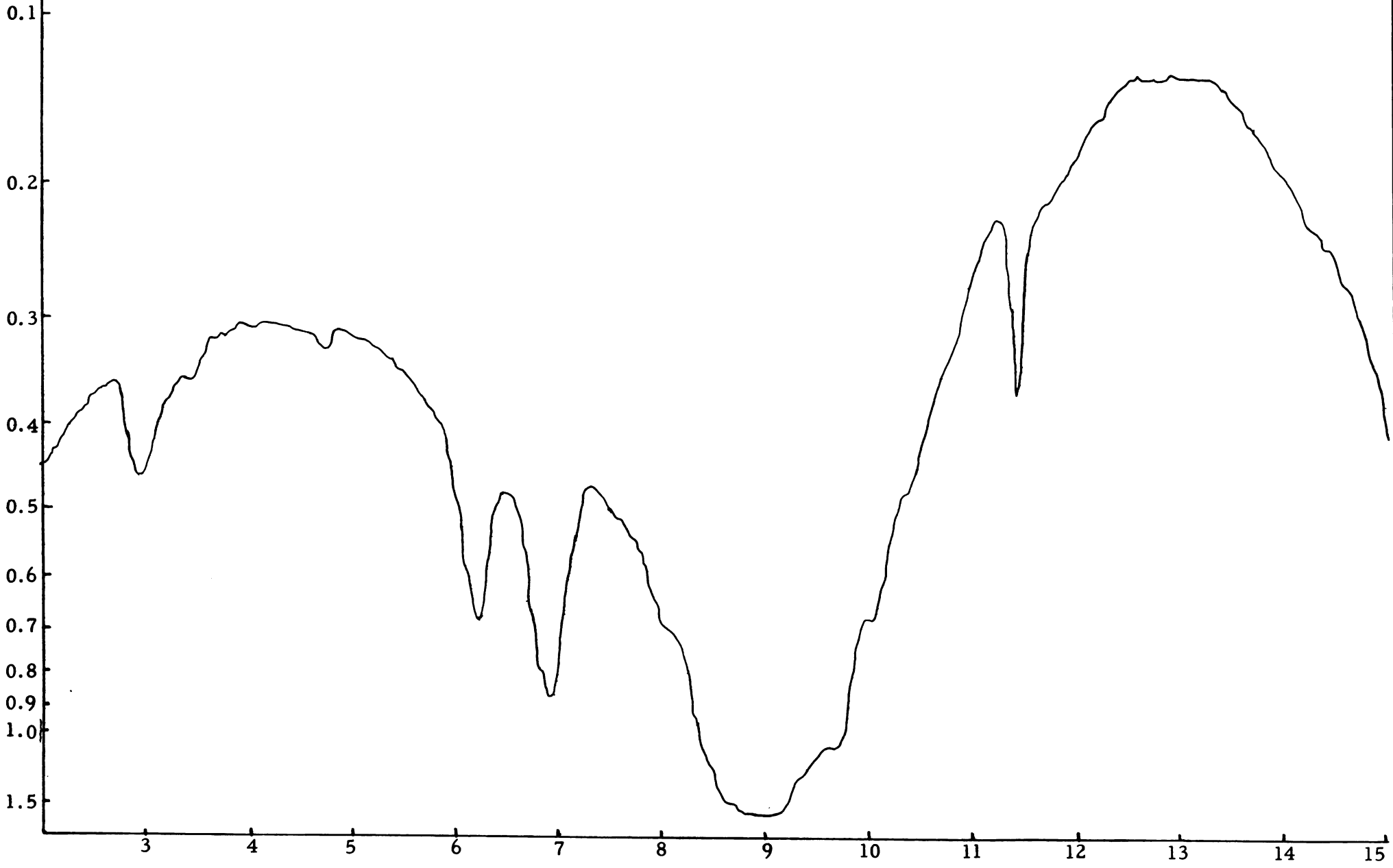
b. Infrared spectra of scale obtained using Palconate as additive



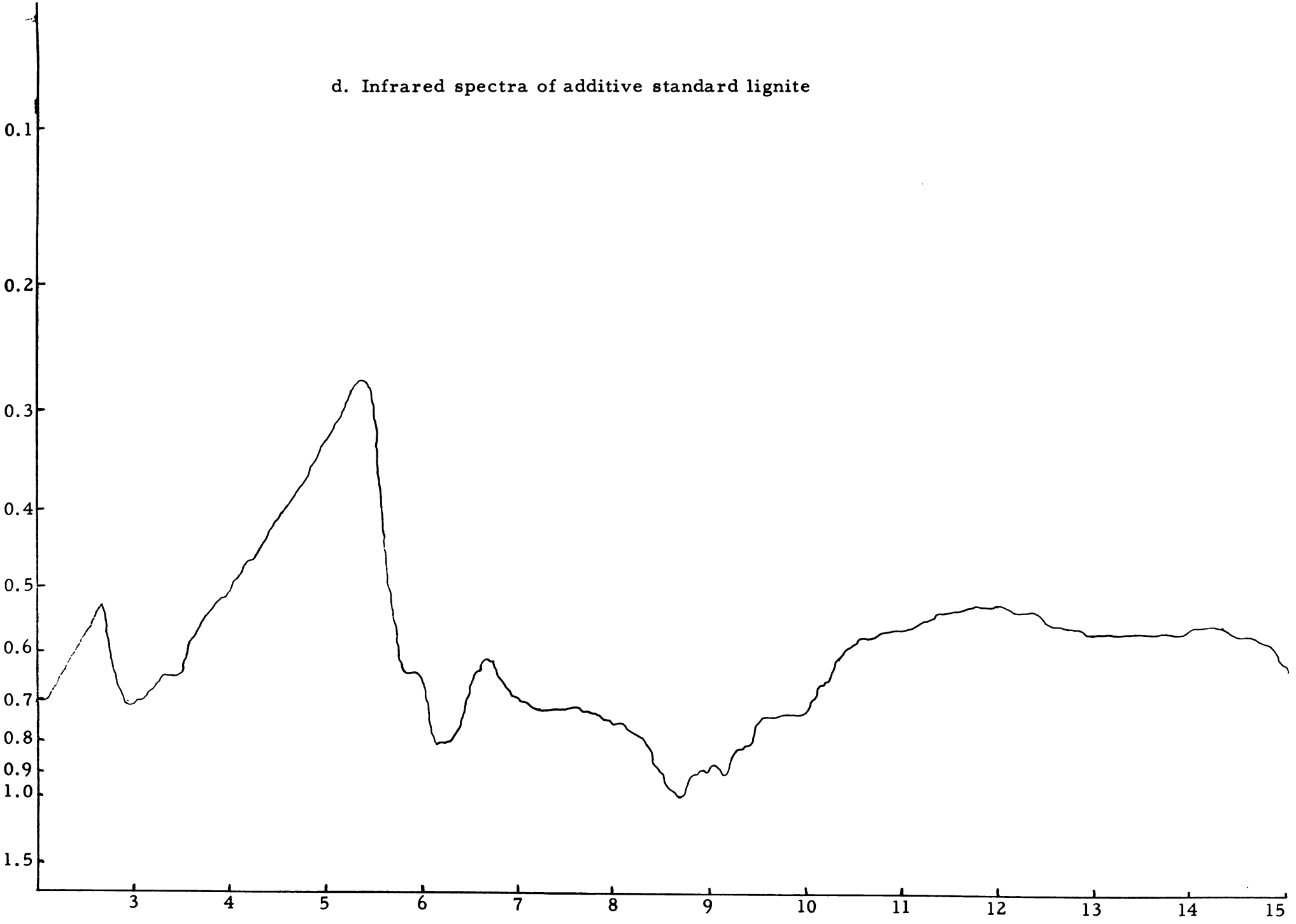
c. Infrared spectra of sludge obtained using Palconate as additive (i) Lower layer.



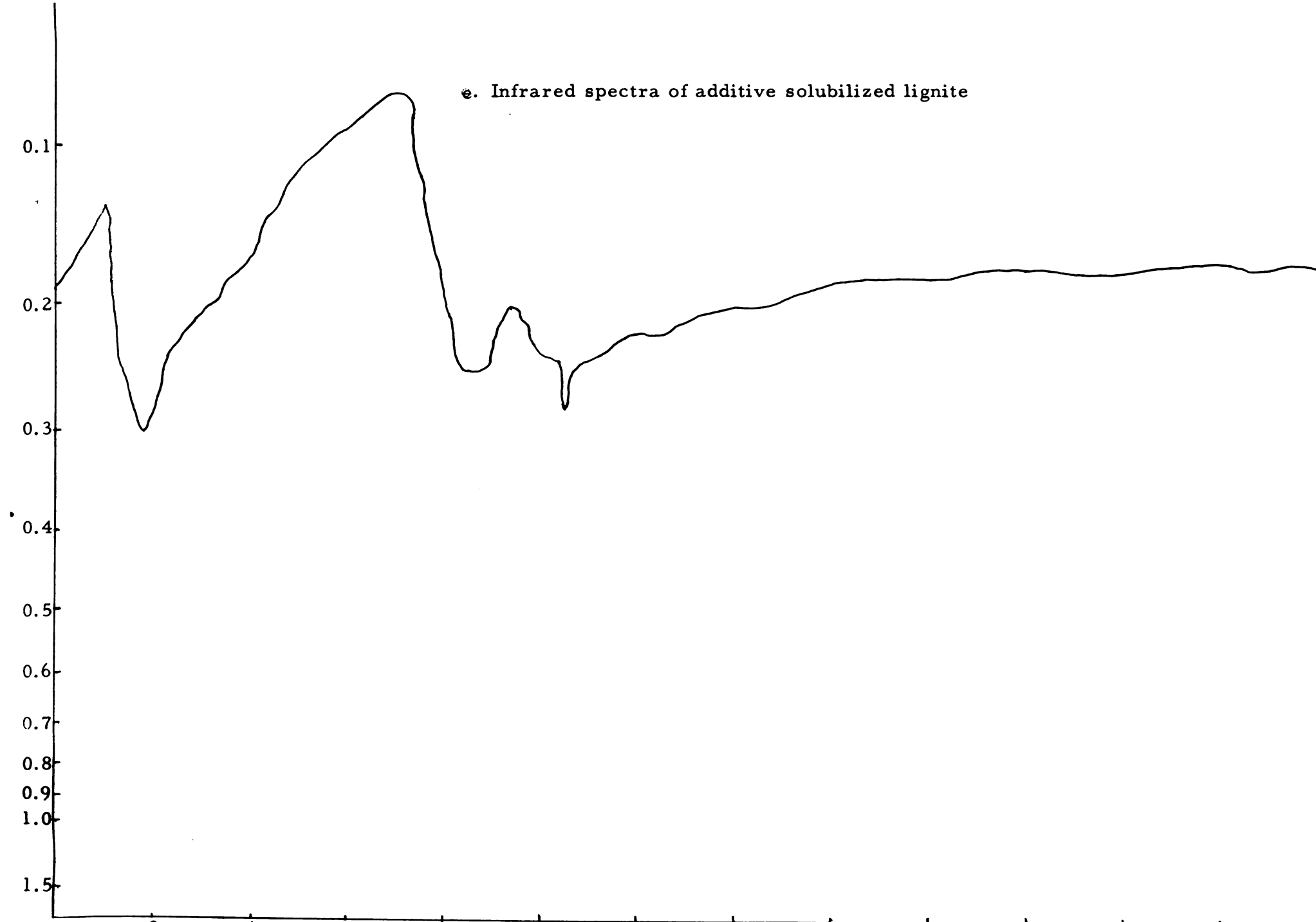
c. Infrared spectra of sludge obtained using Palconate as additive. (ii) Middle layer.



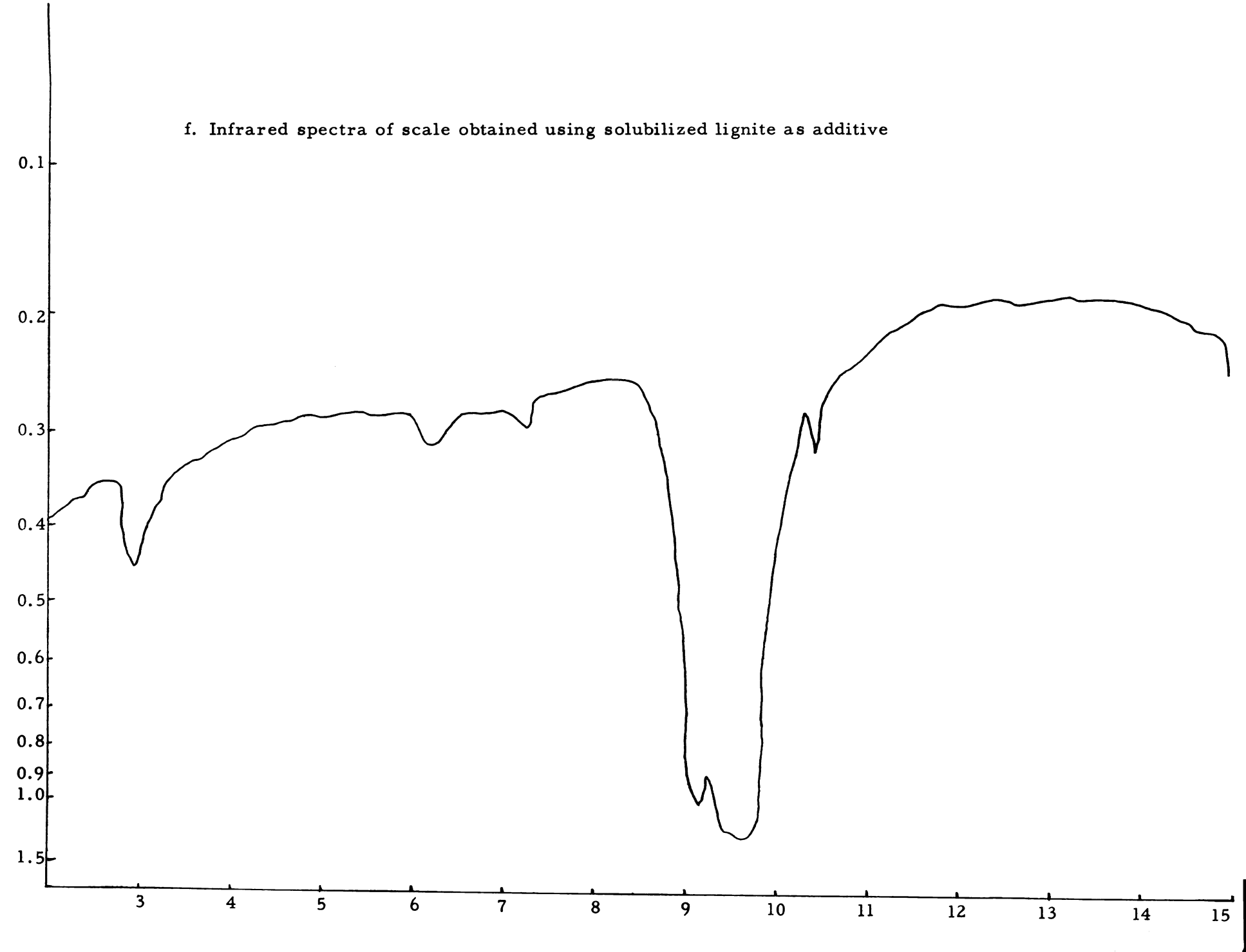
d. Infrared spectra of additive standard lignite



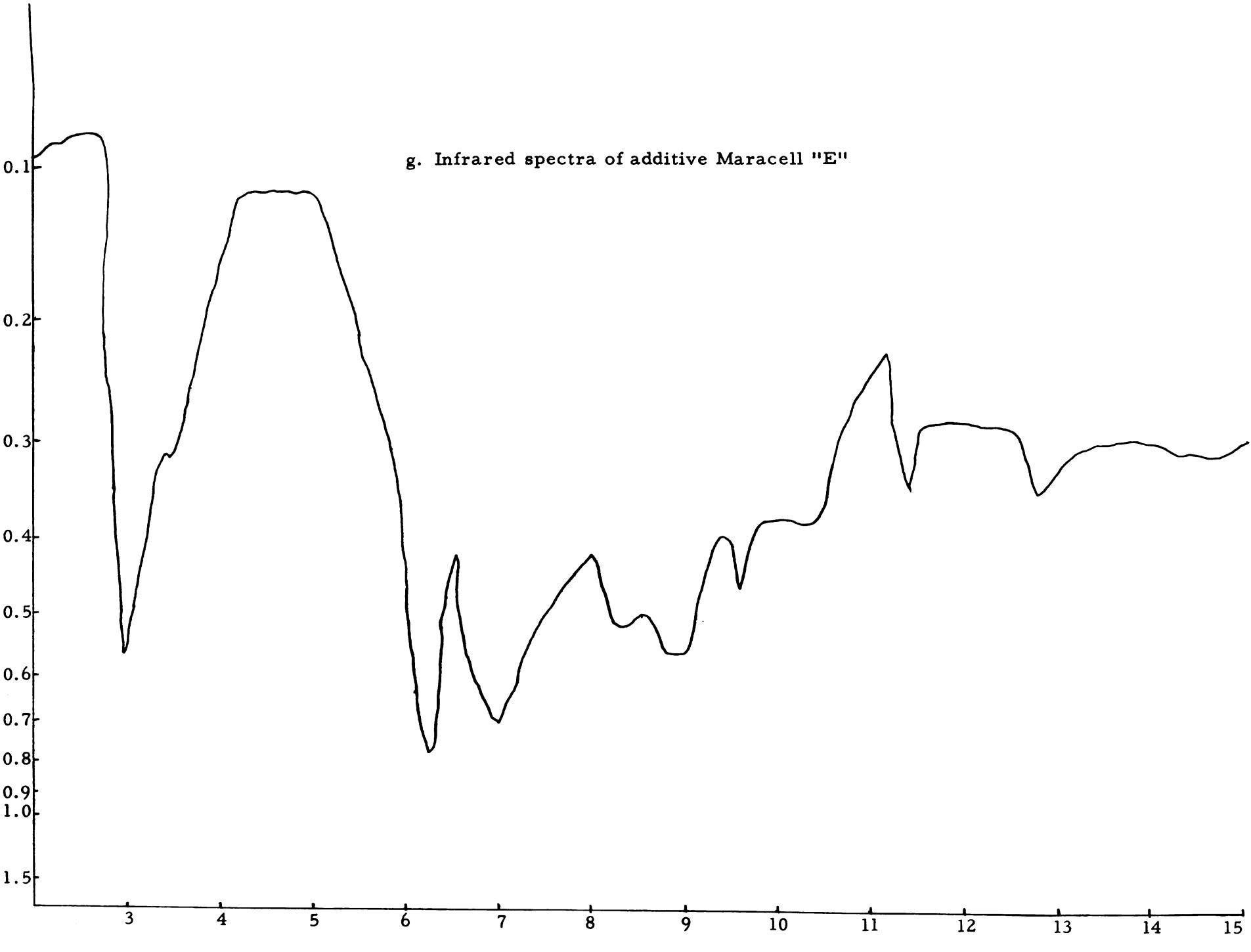
e. Infrared spectra of additive solubilized lignite



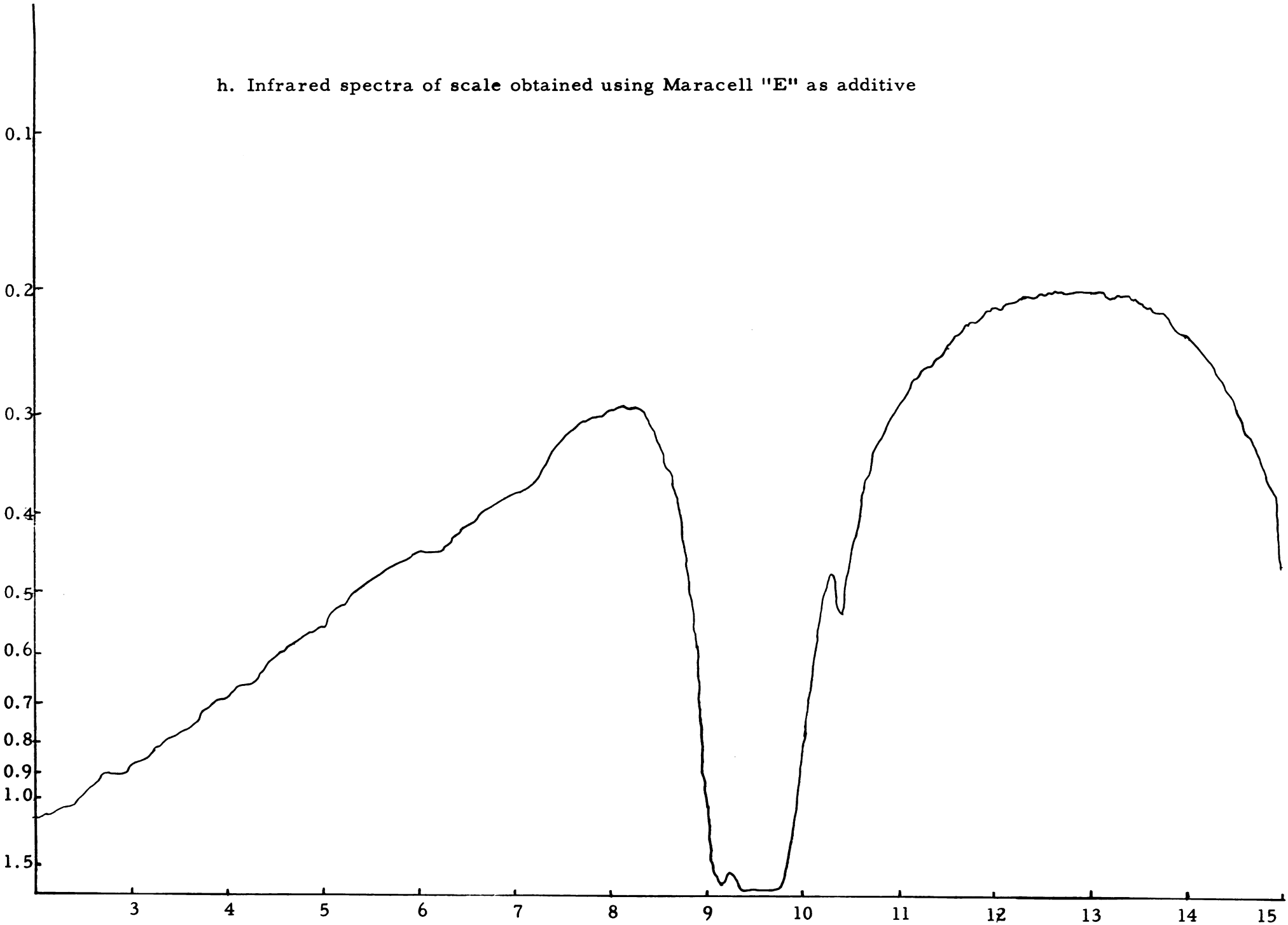
f. Infrared spectra of scale obtained using solubilized lignite as additive



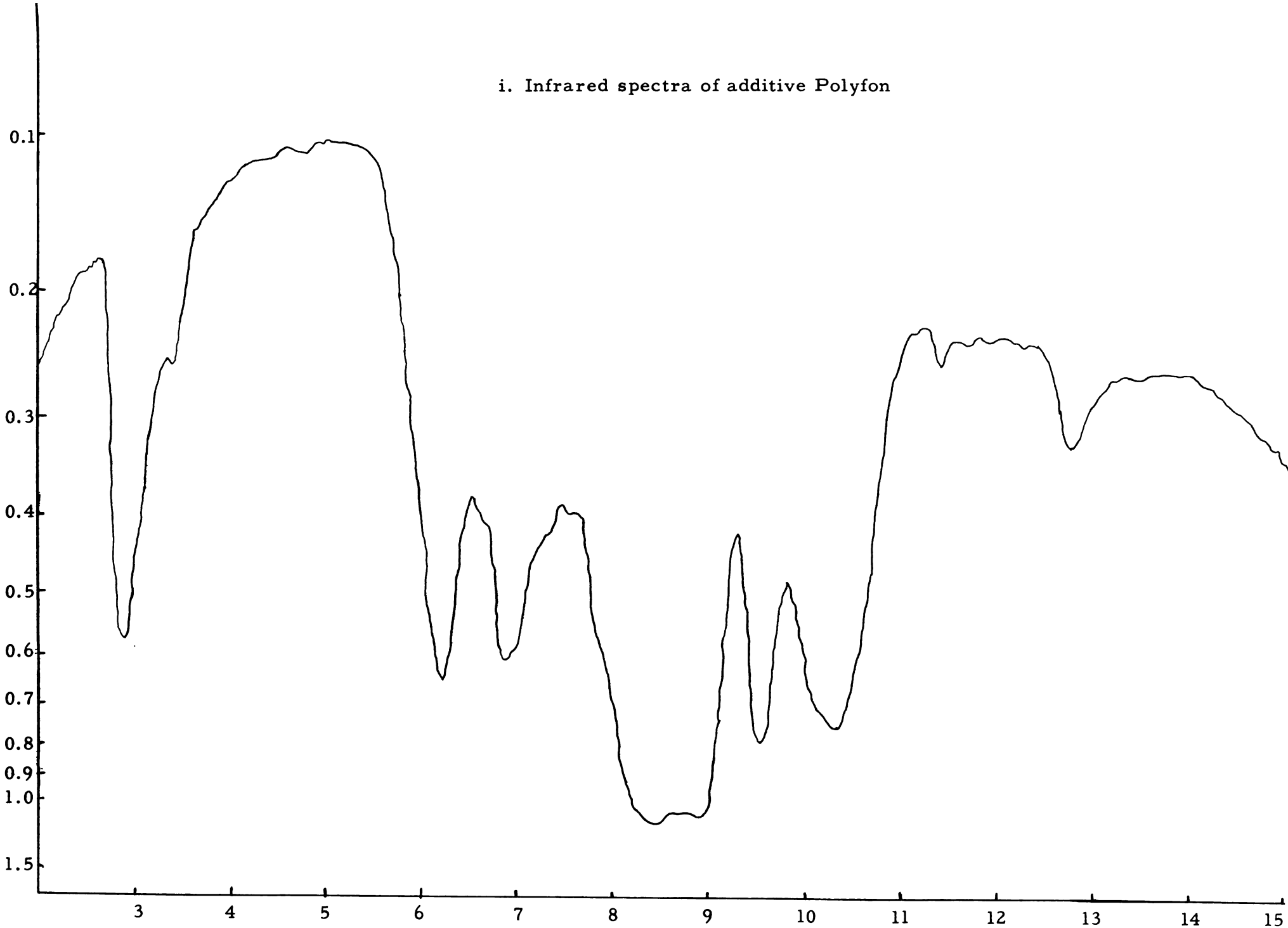
g. Infrared spectra of additive Maracell "E"



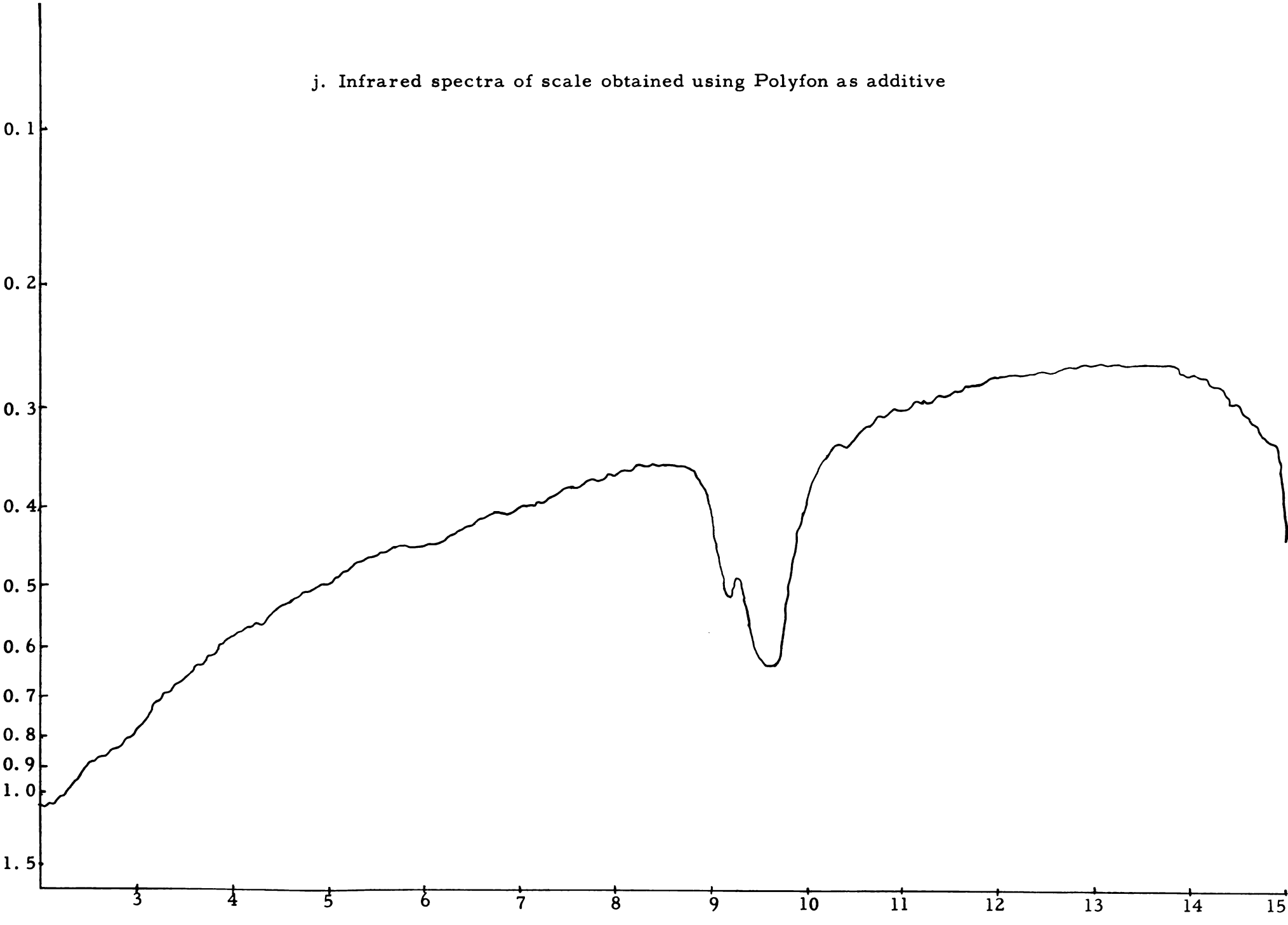
h. Infrared spectra of scale obtained using Maracell "E" as additive



i. Infrared spectra of additive Polyfon



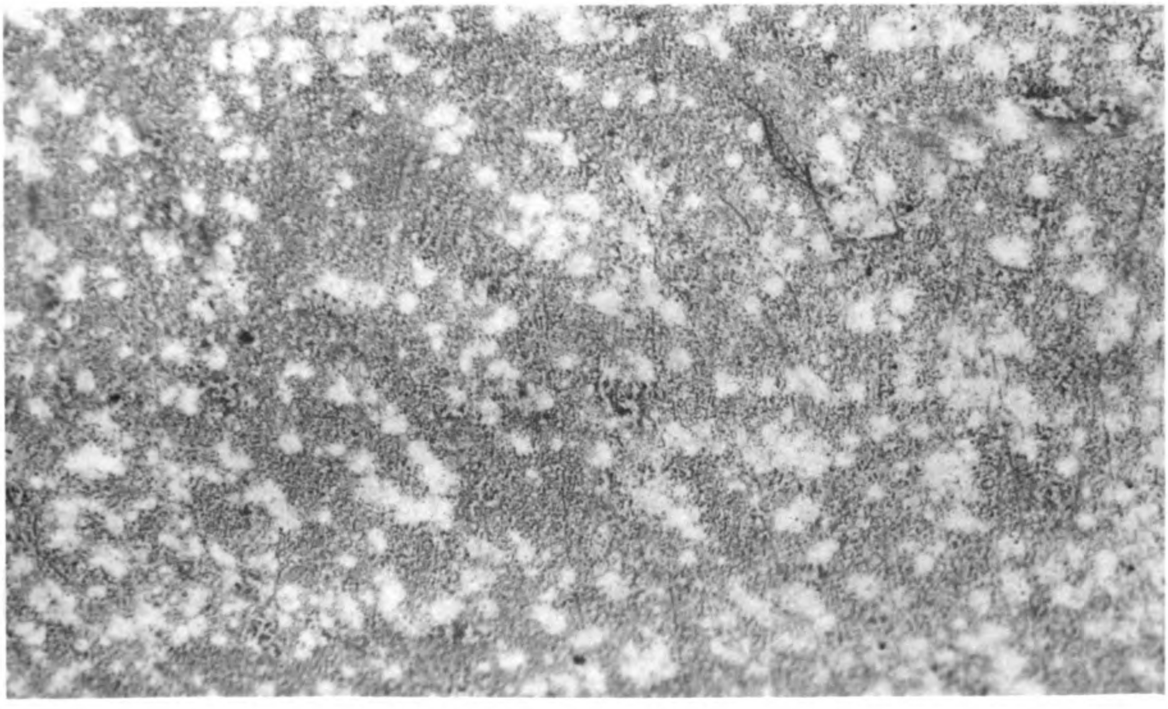
j. Infrared spectra of scale obtained using Polyfon as additive



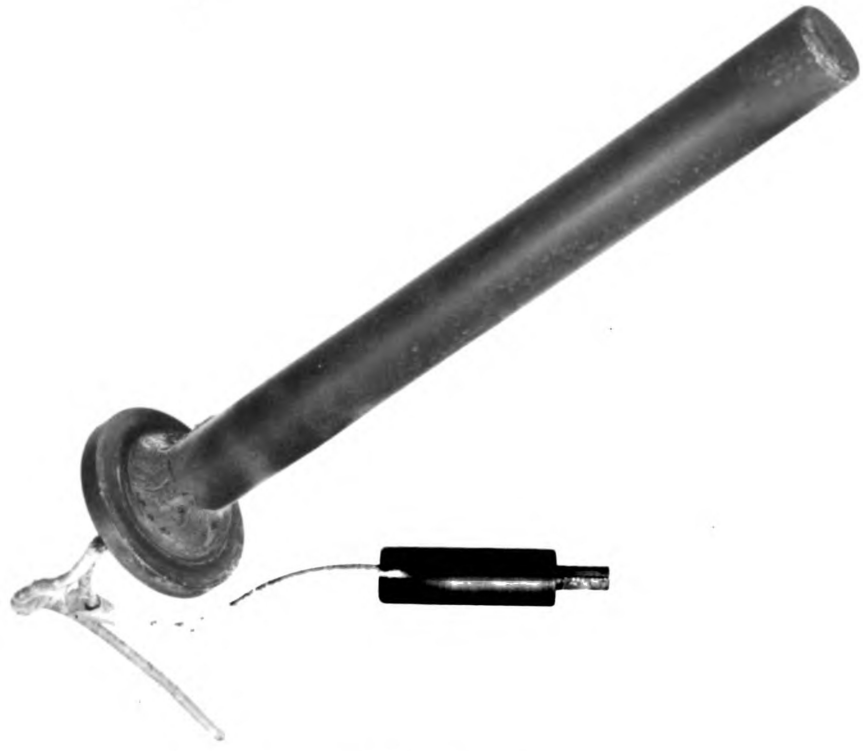
APPENDIX 4

PHOTOGRAPHS OF HEATING SURFACES USING METHACRYLIC ACID POLYMERS OF VARIOUS MOLECULAR WEIGHTS

a. Molecular weight 127, 000



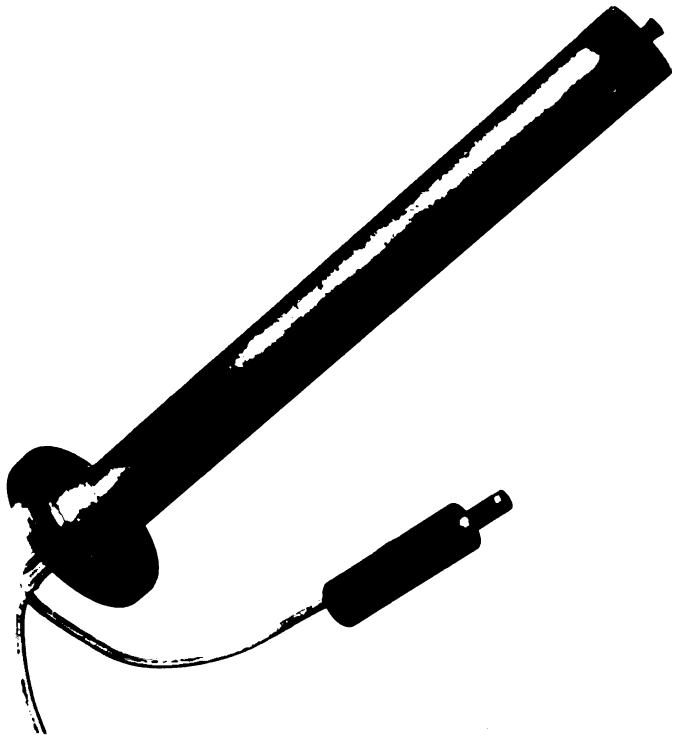
b. Molecular weight 86
Magnification 20



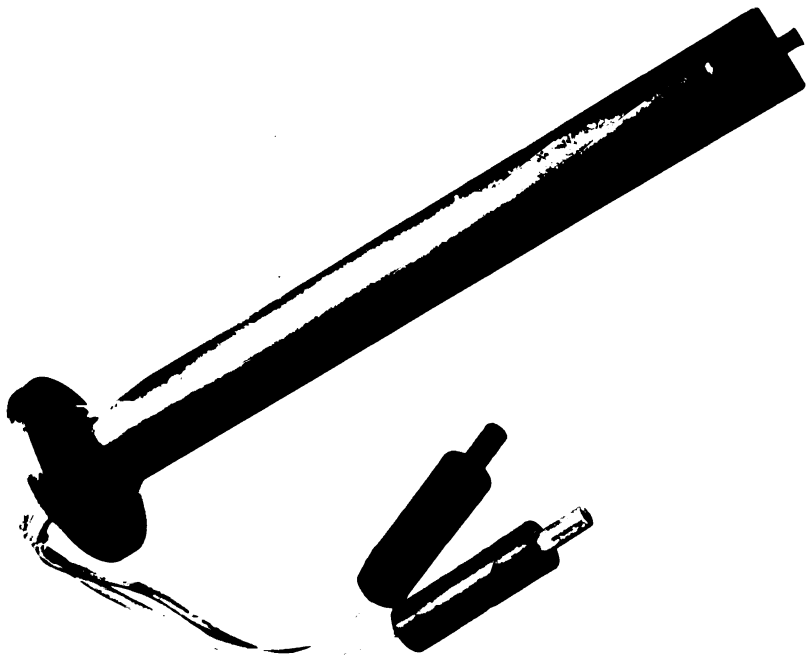
(i) Heat flux 93, 000

(ii) Heat flux 52, 000

c. Molecular weight 12, 400



(i) Heat flux 90, 000



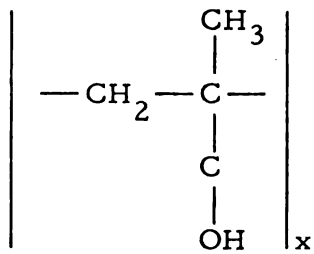
(ii) Heat flux 50, 000

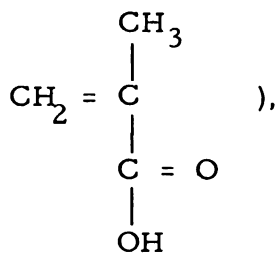
d. Molecular weight 6, 500

APPENDIX 5

SYNTHESIS OF METHACRYLIC ACID POLYMERS AND THEIR MOLECULAR WEIGHT DETERMINATION

a. Method of Synthesis

The methacrylic acid polymers of formula 

were synthesized in a nitrogen atmosphere in a batch reactor placed in a controlled temperature bath. The monomer (molecular weight 86) formula  ,

distilled water, methanol, catalyst, and chain transfer agent were mixed continuously by bubbling oxygen-free nitrogen through the solution. The appearance of a cloudy and viscous solution indicated completion of the reaction. The solution was filtered and the filtrate dried in a vacuum at 110°C for 48 hours and then ground to a fine powder. The proportions of distilled water, methanol, catalyst, and chain transfer agent used, and the reaction temperature were varied to obtain polymers of different molecular weights. Appendix 5c is a summary of the proportions of chemicals used.

b. Method for Molecular Weight Determination

Molecular weights were determined by measuring the viscosity of solutions of various concentrations of polymers in 2N NaOH, by calculating the intrinsic viscosity from these results, and by use of an intrinsic viscosity-degree of polymerization plot for methacrylic acid polymers. The time required to flow the solution between two marks of a Ubbelholde viscometer (Canon and Fenske modification) was measured at 30.00 $\pm$ 0.02°C. The relative viscosities were calculated from the following formula assuming $\rho_1 = \rho_0$,

$$N_{rei} = \frac{\rho_1(t_1 - C/t_1)}{\rho_0(t_0 - C/t_0)} \approx \frac{(t_1 - C/t_1)}{t_0 - C/t_0}$$

where

N_{rei} = relative viscosity

ρ = density of solution

ρ_0 = density of solvent

t_1 = time required for solution to flow

t_0 = time required for solvent to flow

C = viscometer constant (135)

The intrinsic viscosity was calculated by extrapolating a plot of concentration versus specific viscosity per unit concentration to zero concentration. Thus, intrinsic viscosity = $\lim_{C \to 0} \frac{\text{specific viscosity}}{\text{concentration}}$ and specific viscosity = relative viscosity - 1. By multiplying the degree of polymerization by 86, the monomer molecular weight, the molecular weight of the polymer was obtained.

TABLE 5. Summary of proportions of chemicals used to synthesize methacrylic acid polymers

Sample	Grams of monomer	ml of methanol	ml of water	Grams of catalyst*	Grams of mercapto-ethanol	Gms of N butyl mercaptan	Temperature °C
A	50	150	150	0.25	----	-----	70
B	40	200	200	0.20	----	-----	70
C	50	150	150	0.50	----	-----	70
D	25	150	150	1.00	----	-----	70
E	50	200	200	5.00	----	-----	70
F	50	400	400	10.000	----	-----	70
G	25	200	200	3.00	1.00	-----	80
H	25	200	200	5.00	4.00	-----	80
I	25	200	200	10.00	----	19.00	70

*α, α'-Azodi-iso-butyronitrite

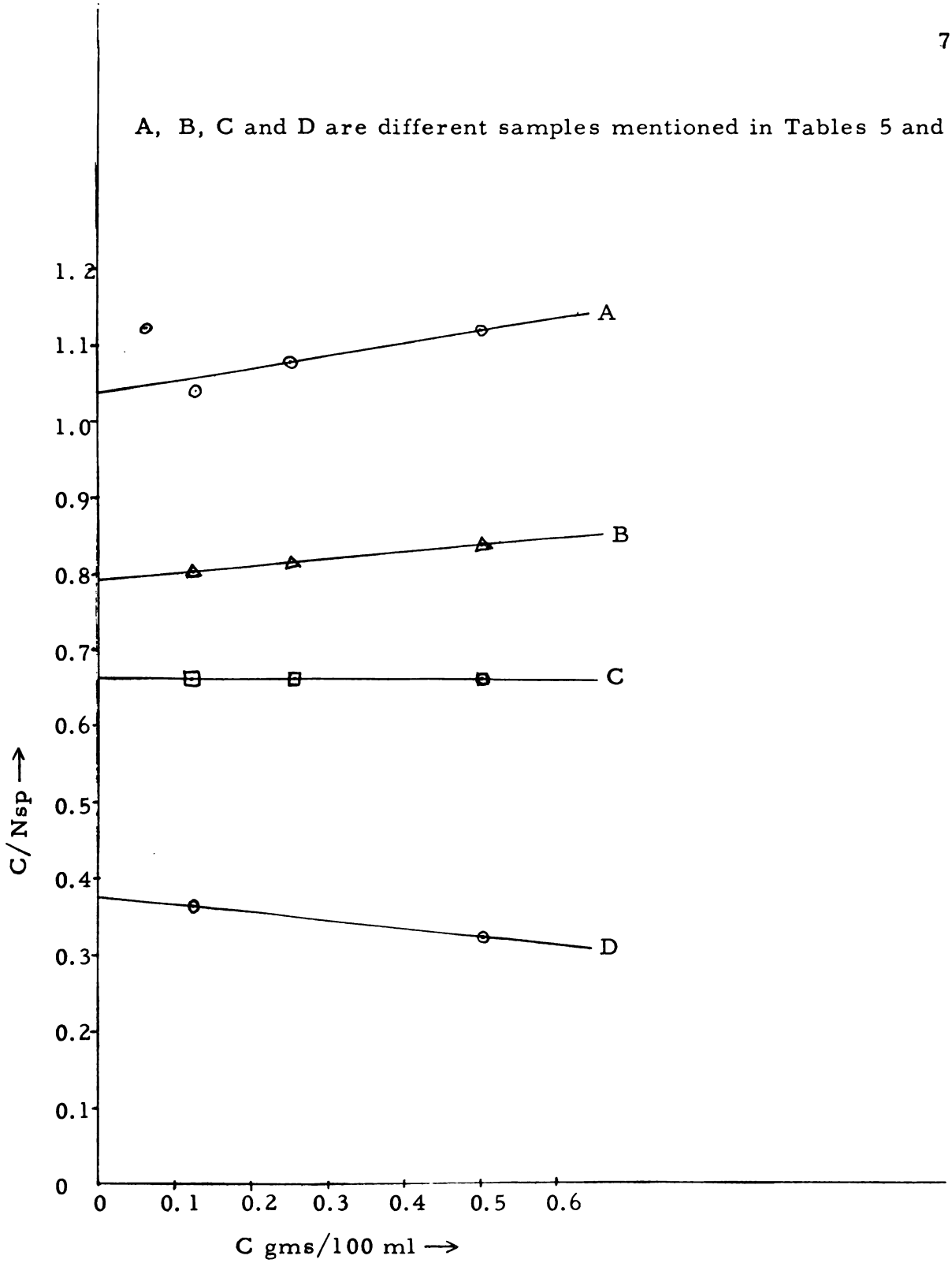
TABLE 6. Intrinsic viscosity measurements for molecular weight determinations

Sample	Concentration C gm/100 ml	Time sec.	N relative	N sp/C	Intrinsic viscosity [N]	Degree of polymerization	Mol. wt.
NaOH	2N	142.75					
A	0.5	221.85	1.56	1.12			
	0.25	180.85	1.27	1.08			
	0.125	161.00	1.13	1.04	1.04	1478	127,000
	0.0625	152.62	1.07	1.12			
B	0.5	202.14	1.421	0.842			
	0.25	171.40	1.203	0.812			
	0.125	157.00	1.101	0.808	0.794	1090	94,000
	0.0625	150.70	1.055	0.880			
C	0.5	189.70	1.332	0.664			
	0.25	166.20	1.167	0.668			
	0.125	154.65	1.083	0.664	0.664	920	79,000
	0.0625	149.40	1.046	0.736			
D	0.5	165.60	1.161	0.322			
	0.25	154.55	1.083	0.332			
	0.125	149.17	1.046	0.368	0.370	500	43,000
	0.0625	147.40	1.032	0.512			

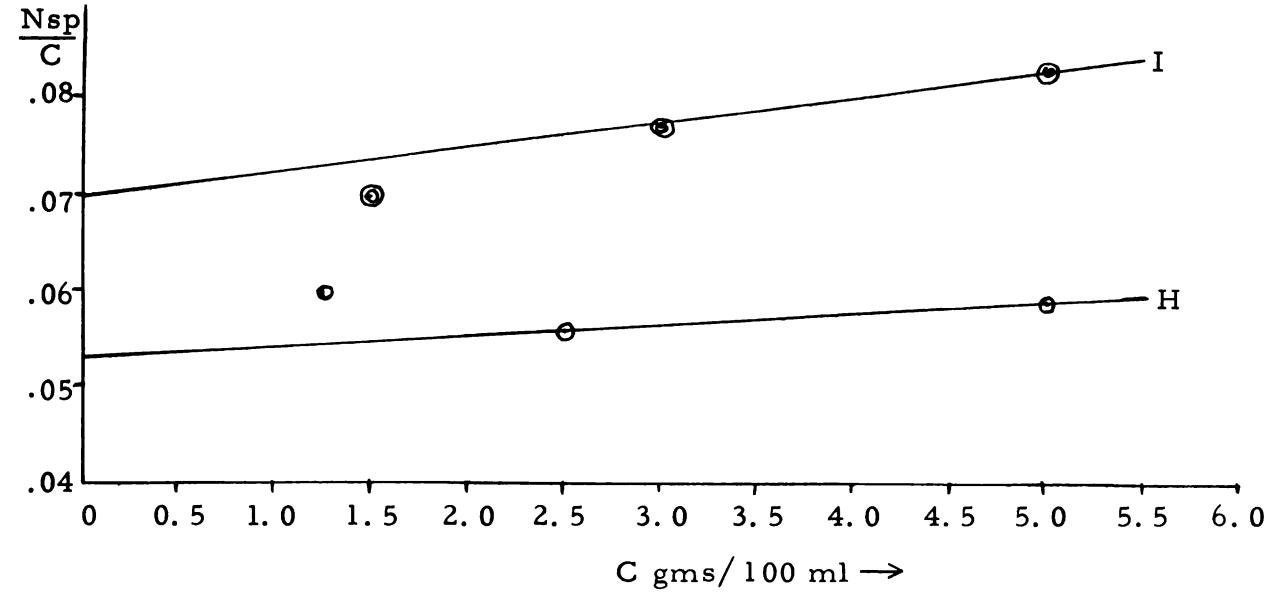
(Table 6 Continued)

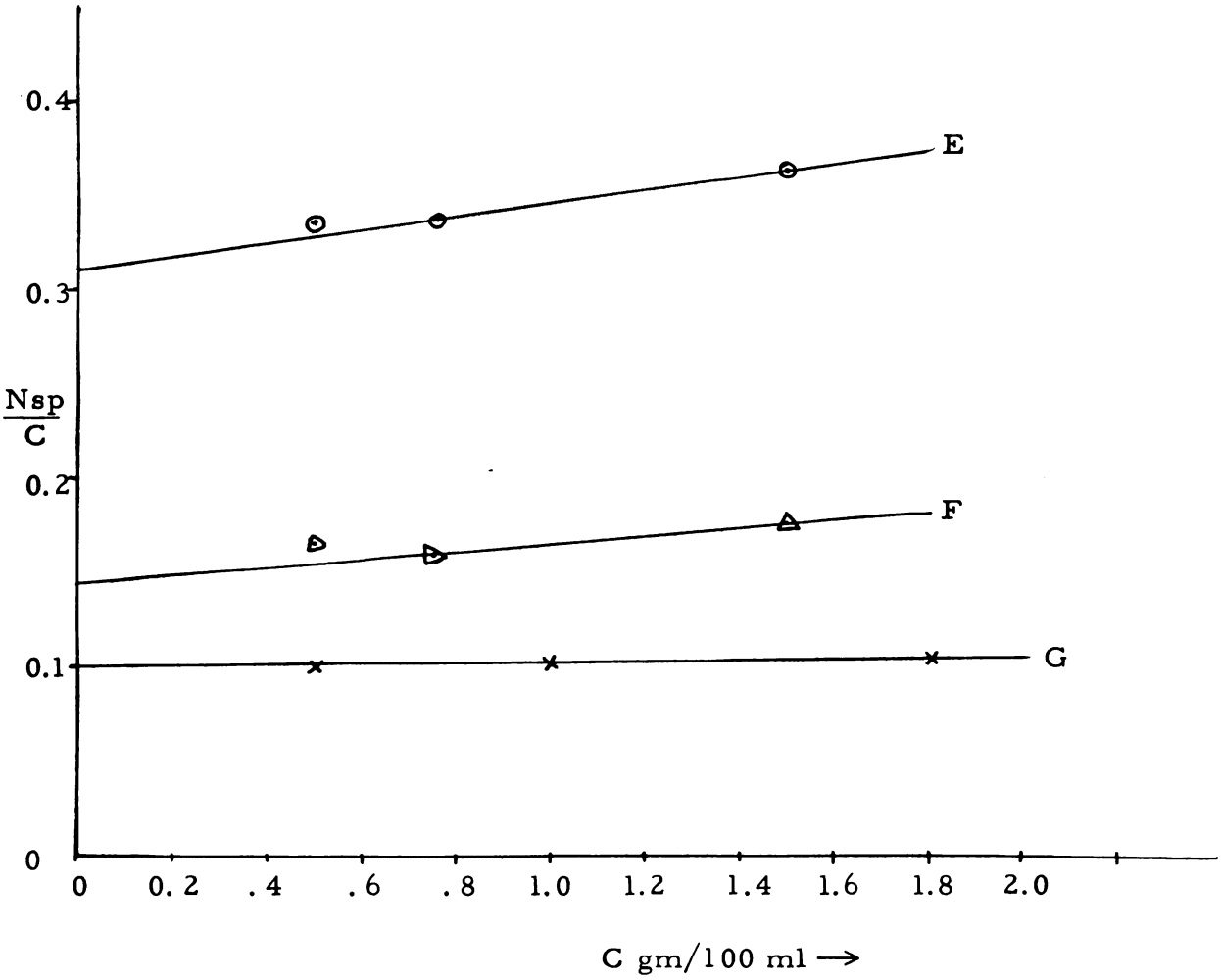
Sample	Concentration C gm/100 ml	Time sec.	N relative	N sp/C	Intrinsic viscosity [N]	Degree of polymerization	Mol. wt.
NaOH	2N	143.45					
E	1.5	220.00	1.547	0.365			
	0.75	178.55	1.253	0.3375	0.31	410	35,000
	0.5	166.37	1.168	0.336			
F	1.5	180.038	1.265	0.177			
	0.75	159.75	1.120	0.160	0.1425	200	17,000
	0.5	154.45	1.083	0.166			
G	2.0	172.10	1.21	0.105			
	1.0	157.23	1.103	0.103	0.10	140	12.400
	0.5	149.93	1.05	0.1			
H	5.0	184.23	1.295	0.059			
	2.5	162.05	1.14	0.056	0.053	80	6,500
	1.25	153.11	1.075	0.060			
I	6.0	213.3	1.50	0.0834			
	3.0	175.0	1.23	0.0767	0.070	105	9,000
	1.5	157.6	1.105	0.070			

A, B, C and D are different samples mentioned in Tables 5 and 6



6. A plot of concentration versus specific viscosity per unit concentration.

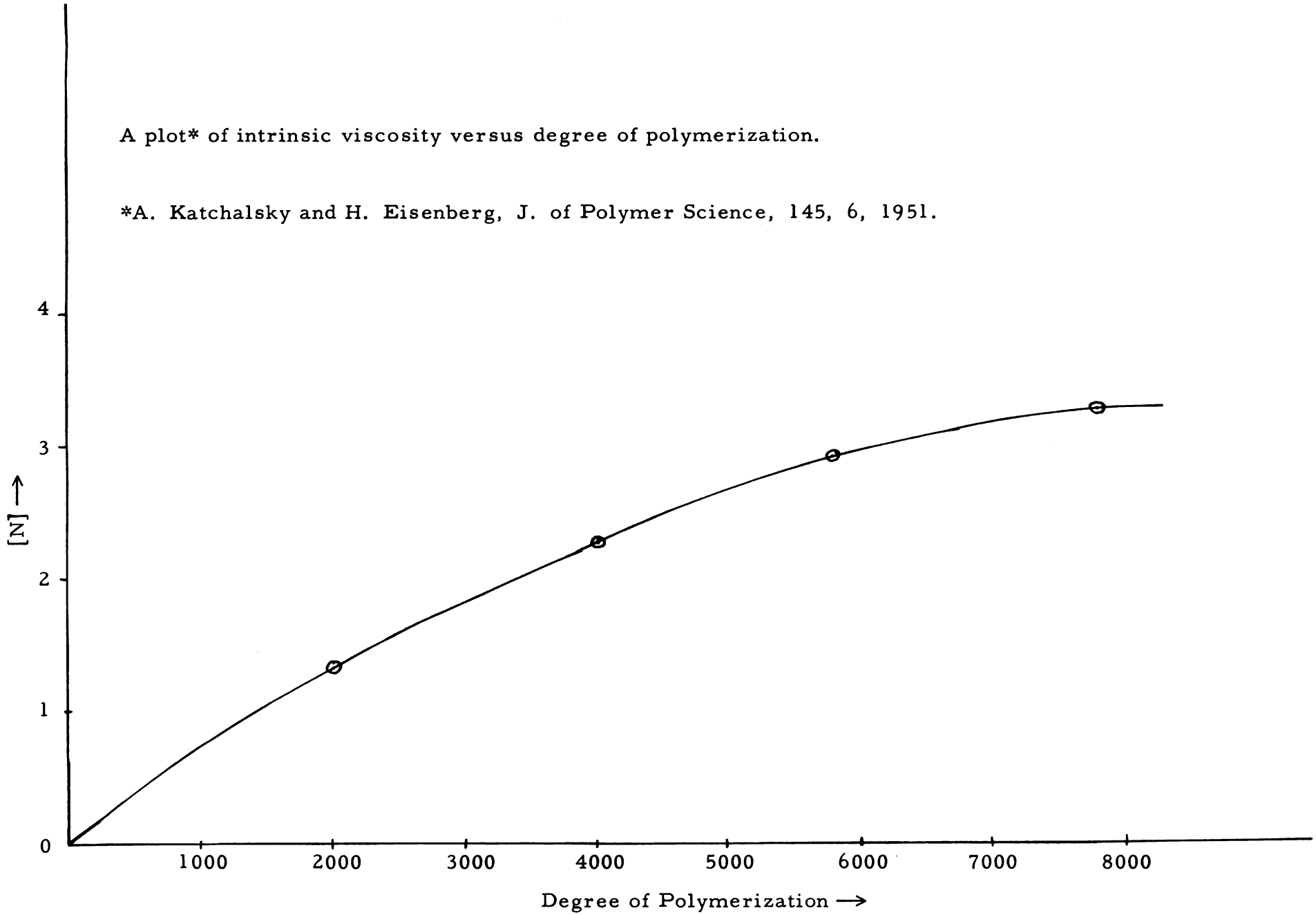




E, F, G, H and I are different samples mentioned in Tables 5 and 6.

A plot* of intrinsic viscosity versus degree of polymerization.

*A. Katchalsky and H. Eisenberg, J. of Polymer Science, 145, 6, 1951.



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