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AFRPL-TR-67-136

MICROSCOPIC AND MICROCHEMICAL STUDY OF AGED SOLID PROPELLANT GRAINS

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May 1967

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FOREWORD

This technical report was prepared under Contract No. AF 04(611)-11637 as partial fulfillment of the requirements of Project No. 3148 of the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards, California. The work was done in the Advanced Propellants Department, Research and Technology Operations, Aerojet-General Corporation, Sacramento, California. This report was designated Aerojet-General Report 1082-81Q-3 and covers the results of work done during the interval 1 February to 31 April 1967. This project was monitored by Lt. Robert Bargmeyer.

Acknowledgment is made to the following persons who have contributed materially to the work performed during this period:

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Mr. Leo Granath

At Thiokol Chemical Corporation

Mr. Paden

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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ABSTRACT

Extensive analyses were made of the of the number, size, and distribution of refractive type reactive sites in model grains aged at 110, 120 and 130°F. Another grain aged at 180°F showed the formation of only very few aging sites. The analyses led to mapping of the sites on the bases of contours proportional to the volume concentration of the sites. The volume concentration was greatest in the samples aged at 110°F and decreased with increasing aging temperature. This effect was interpreted in terms of a volatile component whose residence time in the model grains was a function of the temperature.

A further analysis of colored reaction sites was made. A blue halo observed by dark field phase contrast optics was explained in terms of Rayleigh scattering from molecular size particles. The color of these sites seemed to be caused by the oxidation state of the iron compounds in the propellant and to be indicative of the oxidation state of the environment.

Chemical analyses by chromatography and infrared indicated that visibly degraded propellant differed from aged, non-degraded propellant only in the size of the fragments. Both propellants contained fragments which were chemically identical and typical for a polyurethane system.

AFRPL-TR-67-136

MICROSCOPIC AND MICROCHEMICAL STUDY OF AGED SOLID PROPELLANT GRAINS

I. INTRODUCTION

This is the third Quarterly Technical Report submitted in partial fulfillment of the requirements of Contract AF 04(611)-11637. The report covers the period 1 February 1967 to 30 April 1967.

The objectives of this study are to determine the course of the chemical aging process or processes in solid propellant formulations and to define the effects of these degradative chemical processes on the mechanical and ballistic properties of the propellant.

In accordance with these general objectives, the studies have been divided into two phases. The objectives in Phase I are to determine the structure, size and distribution of microscopic reaction sites in solid propellants as a function of age, formulation and storage environments; and to optically characterize and chemically analyze the reaction intermediates and products. In Phase II the mechanistic course of the aging process will be defined.

Work during the third quarter consisted of acquisition of samples from full-scale, field-aged motors, monitoring the accelerated aging in model grains, optical microscopic studies, and wet chemical studies.

II. PROPELLANT ACQUISITION

A. HAWK MOTOR 15121

Hawk Motor 15121 is part of a surveillance program and was retrieved for analysis after 5½ years. It has been cut into the major sections shown in Figure 1. Samples removed from the cutting face between sections 6 and 7 were examined and preliminary data are included in Section III.D.

B. MINUTEMAN MOTOR 76014

An 82-lb section (J-19) of Minuteman Motor 76014 was received from the Thiokol Chemical Corporation. Propellant samples were microtomed from the bore and case surface, and thin sections were prepared and studied with the microscope. No significant features were observed. The sample is being retained for chemical studies.

C. MODEL AGING GRAINS

In order to supplement the study of field propellants which were aged in an uncontrolled environment, some model grains were cast and aged in

SECTIONING DIAGRAM FOR HAWK FIELD MOTOR # 15121

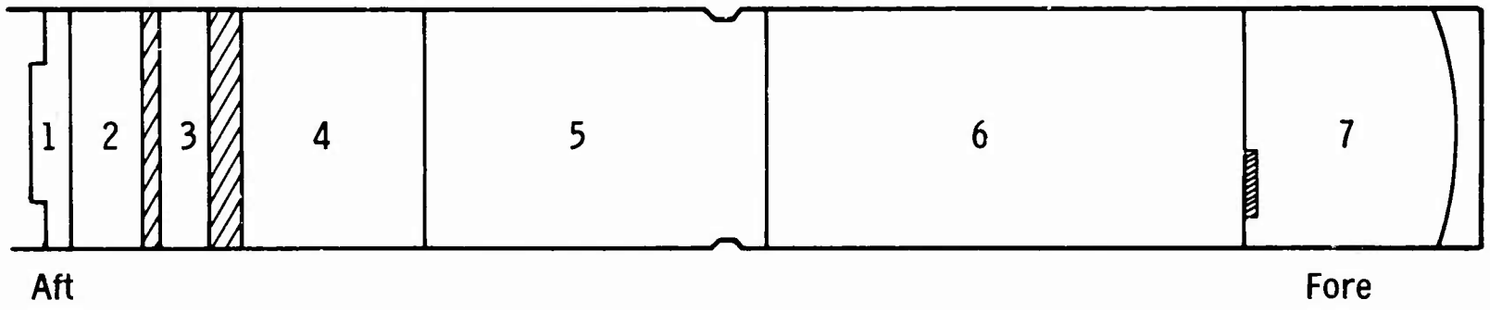


Figure 1

a controlled environment. The results have been fruitful and greater emphasis has been placed on their analysis.

Two types of polyurethane propellants were cast into six grains which were stored at various conditions and periodically sampled. The grains, storage conditions and age at sampling are given in Table I.

Table I

STORAGE CONDITIONS AND AGING TIME FOR MODEL GRAINS

Propellant Type	Grain No.	Storage Temp, °F	Age at Sample Time, Days	
			3 month[a]	6 month[a]
Igniter	1	180	89	169
	2	120	84	169
		50	85[b]	
	3	110	89	169
	4	130	84	169
Bipropellant	5	150	84	169
	6	120	99	169

[a]Nominal time of aging used to identify the samples in the text.
[b]Grain 2 was transferred from 120°F to 50°F storage at the end of the first sampling period.

Since the grain design and the position of the sample in the grain are pertinent to the studies, cross sections are shown at a scale of 1:1 for the model igniter (Figure 2) and bipropellant (Figure 3) grains.

D. POLARIS CYCLING UNIT

This grain is being studied by chemical methods because a zone of extensive binder degradation is present along the bore surface. Characteristics of this motor pertinent to this study have been described earlier(1).

III. OPTICAL AND MICROSCOPIC STUDIES

A. MICROSCOPIC REACTION SITES

1. General

The previous quarterly report AFRPL-TR-67-41 contained (1) an introductory description of the microscopic reaction sites and (2) an estimate of their relative concentration in the model grains after 3 months

CROSS SECTION OF MODEL IGNITER GRAIN

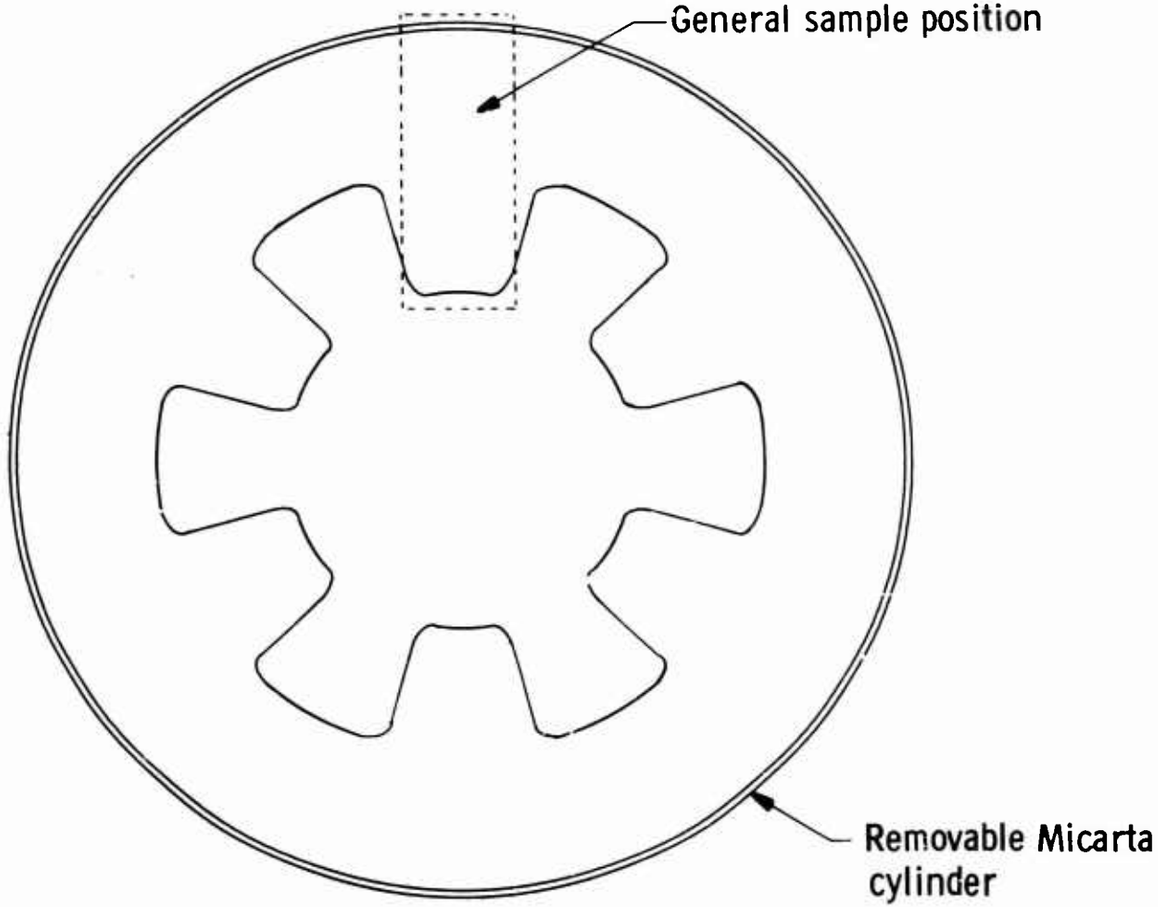
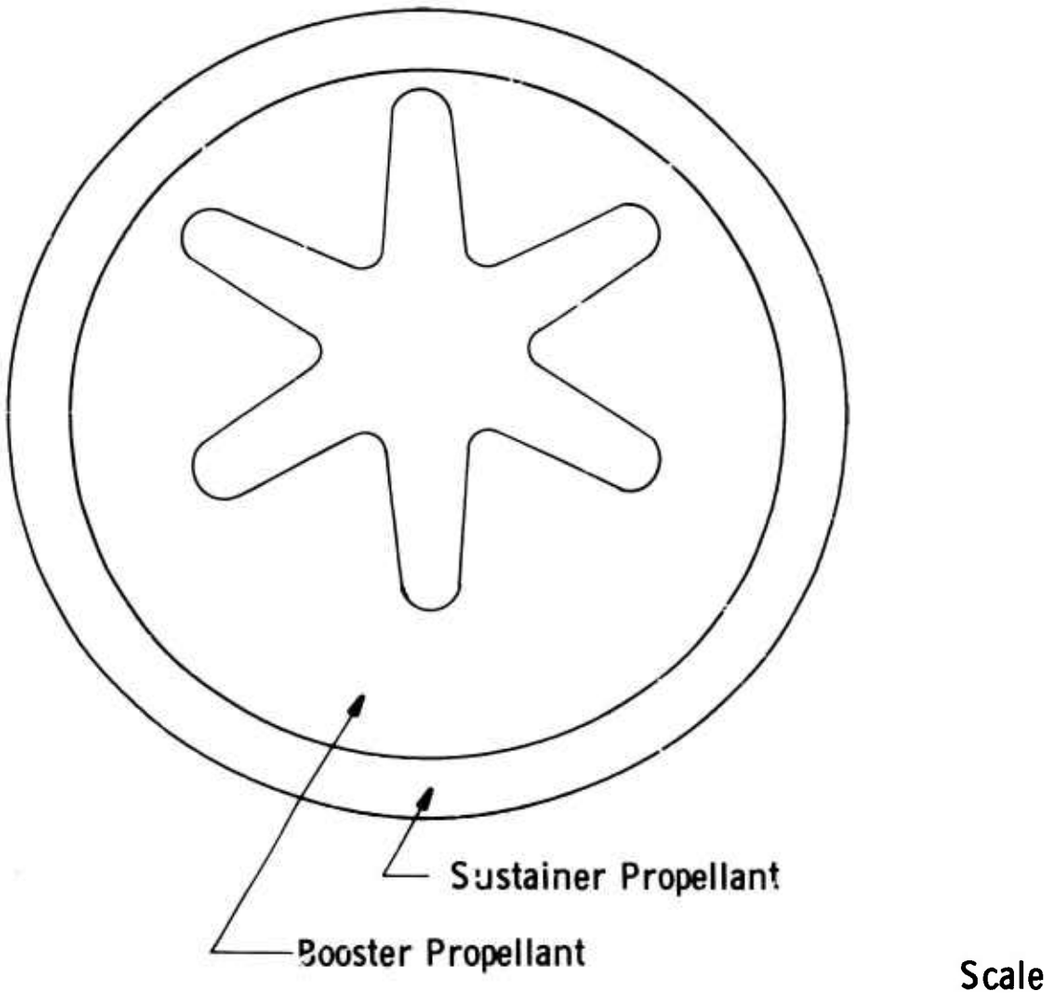


Figure 2

CROSS SECTION OF MODEL BIPROPELLANT GRAIN



Scale 1:1
Dia. 4-3/4

Figure 3

of aging. During this (third) quarter the colored reaction sites were further optically characterized and the relative concentration of the refractive type sites in the model grains was microscopically determined.

B. COLORED REACTION SITE

1. Dark Field Phase Illumination

The colored reaction site photographed in transmitted white light has an absorption halo caused by fine particles suspended in the binder around a central aluminum particle (Figure 4a). The same area is shown in Figure 4b in doubly polarized light. The absorption area is less birefringent which may be due to blocking of the light by the suspended particle plus possible loss of birefringent material. When the same area is viewed by dark field phase contrast, a characteristic blue light is seen to form a shell around the colored reaction site. The intensity of the blue light is nearly the same as the background white light from the surrounding area. Consequently the circles of varying light intensity are not seen in a black and white photograph (Figure 4c). When a blue filter is placed between the object and the photographic film, the white background is reduced relative to the blue and a weak image is obtained. A photographers' technique of enhancing weakly contrasting subjects by rephotographing the original was used to produce the photograph in Figure 4d. The bright ring is the halo of blue light surrounding the dark color absorption ring shown in Figure 4a. Surrounding the bright circle is a dark one observed on the photograph but not with the eye and microscope. An additional feature in this sequence of photographs is the bright spot of light in Figure 4c near the central aluminum. This is caused by a red-orange gel which has a high refractive index readily detected by the phase contrast optics, but which is not seen as an area of high intensity with plane light in Figure 4a. The phase contrast image (Figure 4d) of this bright red-orange zone is not observed because the red light is blocked by the blue filter on the exit pupil.

2. The Blue Light Ring

The ring of blue light observed by dark field phase illumination has not been reported in the periodical literature reviewed, nor in any standard text book.

The color of the light is specifically a sky blue. The color is uniform, does not depend upon its position relative to the position or number of the Liesegang ring, nor does it depend upon the absorption color or the location in the propellant of the reaction site. These facts suggest a form of Rayleigh scattering which gives the sky a blue color.

Further, in dark field phase contrast optics, light must be diffracted or bent to enter the objective. Any particle with a thickness and refractive index capable of bending the light sufficiently to enter the objective should be observed as a discrete particle. Since no such particles are observed, the bending is not the result of refraction of the light. The only other mechanism for bending the light is scattering by particles.

LIGHT SCATTERING AROUND COLORED REACTION SITES

-pol

a

+pol

b

d. f. phase

c

d. f. phase + blue filter

d

Figure 4

Discrete particles are not observed at the point source of the blue light in either plane or doubly polarized light. Inasmuch as the microscope has a resolution limit of 300 millimicrons and a detection limit of 50 millimicrons, the particles causing the light scattering must be of molecular size. Therefore, it is concluded that the blue light is a form of Rayleigh scattering by molecular size particles.

The blue light was originally observed in Hawk propellant 4½ years old. The analysis presented here is for the booster propellant from the model bipropellant grain aged three months.

C. DISTRIBUTION AND CONCENTRATION OF REFRACTIVE REACTION SITES IN MODEL IGNITER MOTORS

1. General

The objectives of this study were in part the application of microscopic methods for determination of reaction site concentration, distribution, and nucleation rate as a function of propellant storage temperature, time, and environment. Thus, numerical values are to be related to environmental variables for subsequent analysis in terms of chemical aging mechanisms.

The microscopic planimetric procedure for determining composition by volume was developed for mineral mosaics in rocks. Data obtained in this manner, and accurate to 1% of each component mineral, were first tabulated and then mapped. This was the procedure used to obtain the slightly less accurate data published on the propellant from the Polaris Unit[1]. In the model grains there is a concentration gradient within a single sample so that a procedure is under development to directly map the microscopic data and then to determine the volume by planimetric analysis of the mapped data. Variations of the procedure and accuracy limits will be tested as the work progresses.

2. Planimetric Analysis of Three Month Aging Samples

Samples were taken along a radial axis one inch from the end of the model igniter grain. These were microtomed and mounted on microscope slides so that there was a continuous series of thin sections from case wall to ray tip. Thin sections were prepared from three grains aged for three months at 110°F, 120°F and 130°F.

The thin sections were mounted on the mechanical stage of the microscope, the entire section was traversed and the coordinates of each refractive site recorded. A calibrated grid eyepiece was used to determine the size range of the site which was recorded along with the coordinates.

The coordinate data were plotted on a centimeter grid at a scale giving approximately a 1:10 enlargement, and a color code was used to designate size ranges. The procedure is demonstrated with the 120°F sample in Figure 5 where the points are plotted without any size designation. A transparent countout overlay and a 5/8" template circle were placed over Figure 5 and the points within the circle were totaled. This was repeated

LOCATION OF REACTIVE SITES IN SAMPLE FROM MODEL IGNITER GRAIN AGED 3 MONTHS AT 120°F

Figure 5

by moving the circle one centimeter at a time, until the whole figure was covered. The number of reaction sites for each position of the template circle was then recorded on a number overlay (Figure 6). A transparent overlay was placed on the number overlay and the points of equal concentration contoured in. The resulting map, Figure 7, shows the concentrations of reaction sites over the sample in question.

The site size was taken into account by assigning a number weight to each reaction site according to its area. The total weighted values of all the points within the counting circle were recorded on the volume concentration overlay, Figure 8, and then contoured on a map overlay, Figure 9. The weighted map overlay thus shows the concentration by volume of reaction sites per unit circle in a section of standard thickness. When Figure 9 is compared to Figure 5, the contours do not adequately portray the high frequency of points along the left side. Therefore, the plot grid was reduced to 1/4 cm squares and the counting circle size to 1.0 cm and the procedure repeated to produce the countout of Figure 10 and map in Figure 13. The area within each contour interval on the 1/4 cm grid maps was determined with a planimeter, summed, and divided by the total sample area, to yield a figure proportional to the concentration of reaction sites as volume percent of the sample. A correction factor, to be determined, must be applied to these values so that the mapped values will be percent reaction site volume on the thin section. These currently derived percent values permit comparison of the samples aged at different temperatures and time intervals.

3. Variation of Reaction Site Concentration with Storage Temperatures

The mapped data from the three igniter motors are shown in Figures 11, 12, 13 and 14. Figures 11 and 12 represent a continuous strip of propellant from case wall to ray tip for grain aged for 3 months at 110°F. The contour interval on Figures 13 and 14 for propellant aged 3 months at 120°F and 130°F, respectively, is 3% while on Figures 11 and 12 (the continuous strip) is 6%. In all figures the zero line is omitted and a 3% contour is the base line. Although a uniform contour interval is useful for comparison purposes, the contours are used here to serve as area boundaries. The contour intervals used are those expedient for examination of variables; for example, use of the 3% contour interval on Figure 11 would require doubling the scale and the labor and time of analysis.

The planimetric analysis yielded values of 37.9% at 110°F, 31.3% at 120°F and 21.2% at 130°F. These are plotted on a graph in Figure 15 showing reaction site concentration (in relative values) vs temperature for the first 3-month period. The point at 180°F is from the fourth model igniter grain where no reaction sites were visible in the ray section. The point at 150°F is an estimate from some previous work on a Polaris formulation. The dotted lines are projected changes with further aging. Although the six-month samples have been taken, it is not yet possible to estimate the changes that may have occurred. At the end of the 3-month period, the 120°F samples were transferred to a 50°F storage, and a point on the curve at that temperature may be derived for the sixth-month of aging.

NUMBER OF REACTION SITES PER UNIT CIRCLE
IN MODEL IGNITER
AGED 3 MONTHS, 120°F

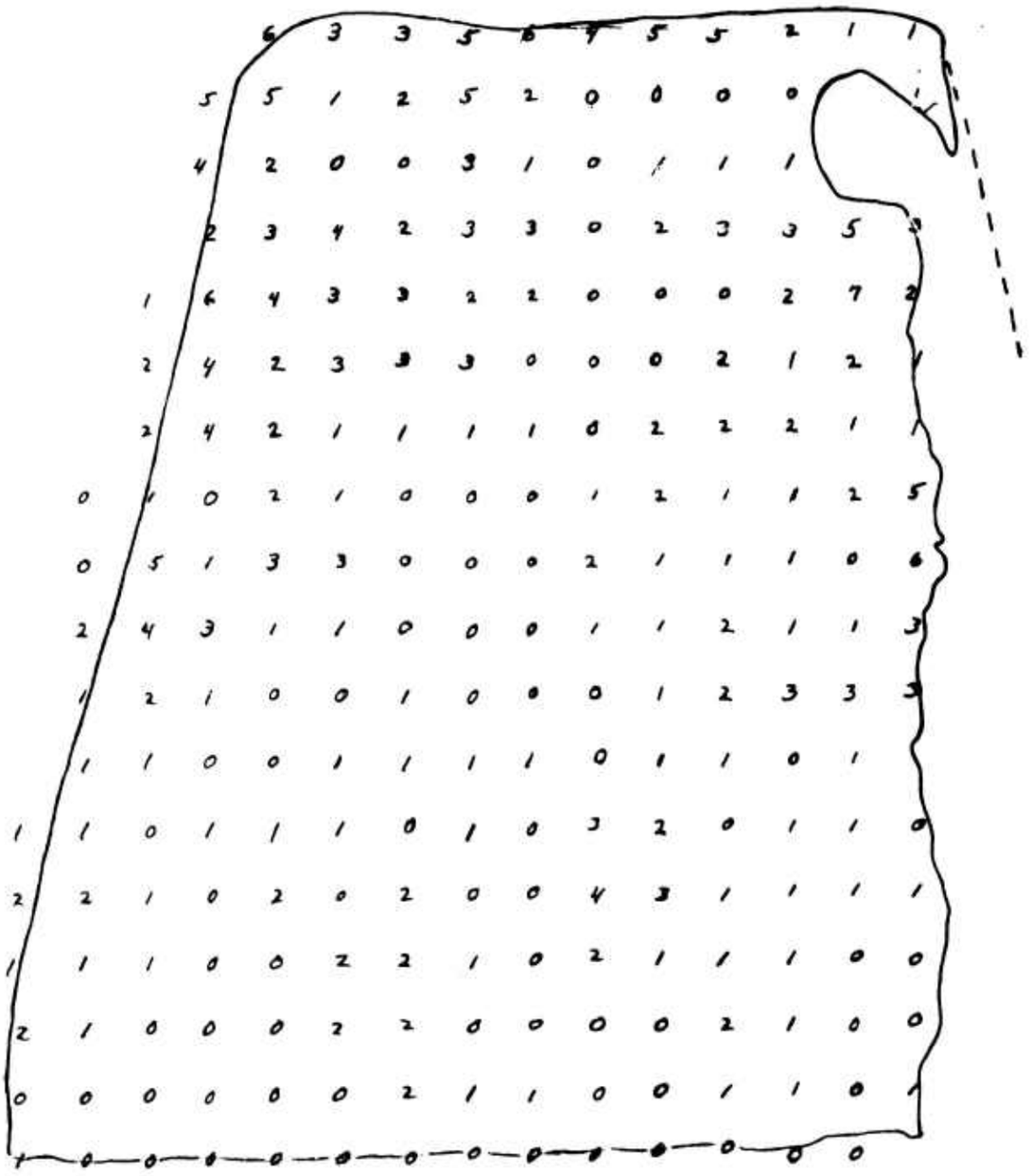


Figure 6

NUMBER FREQUENCY MAP, MODEL IGNITER GRAIN
AGED 3 MONTHS, 120°F

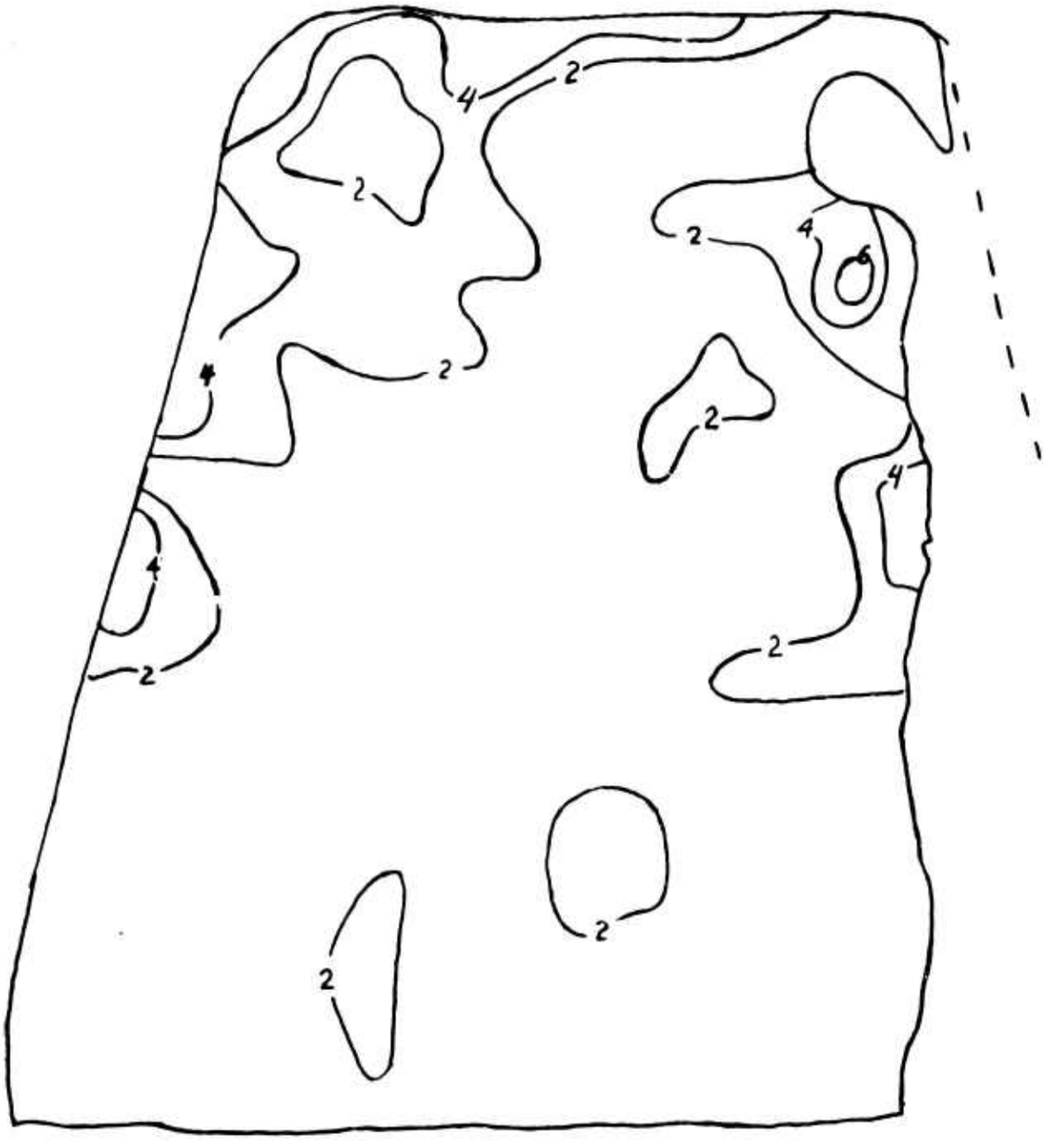


Figure 7

VOLUME CONCENTRATION MAP, MODEL IGNITER GRAIN AGED 3 MONTHS, 120°F

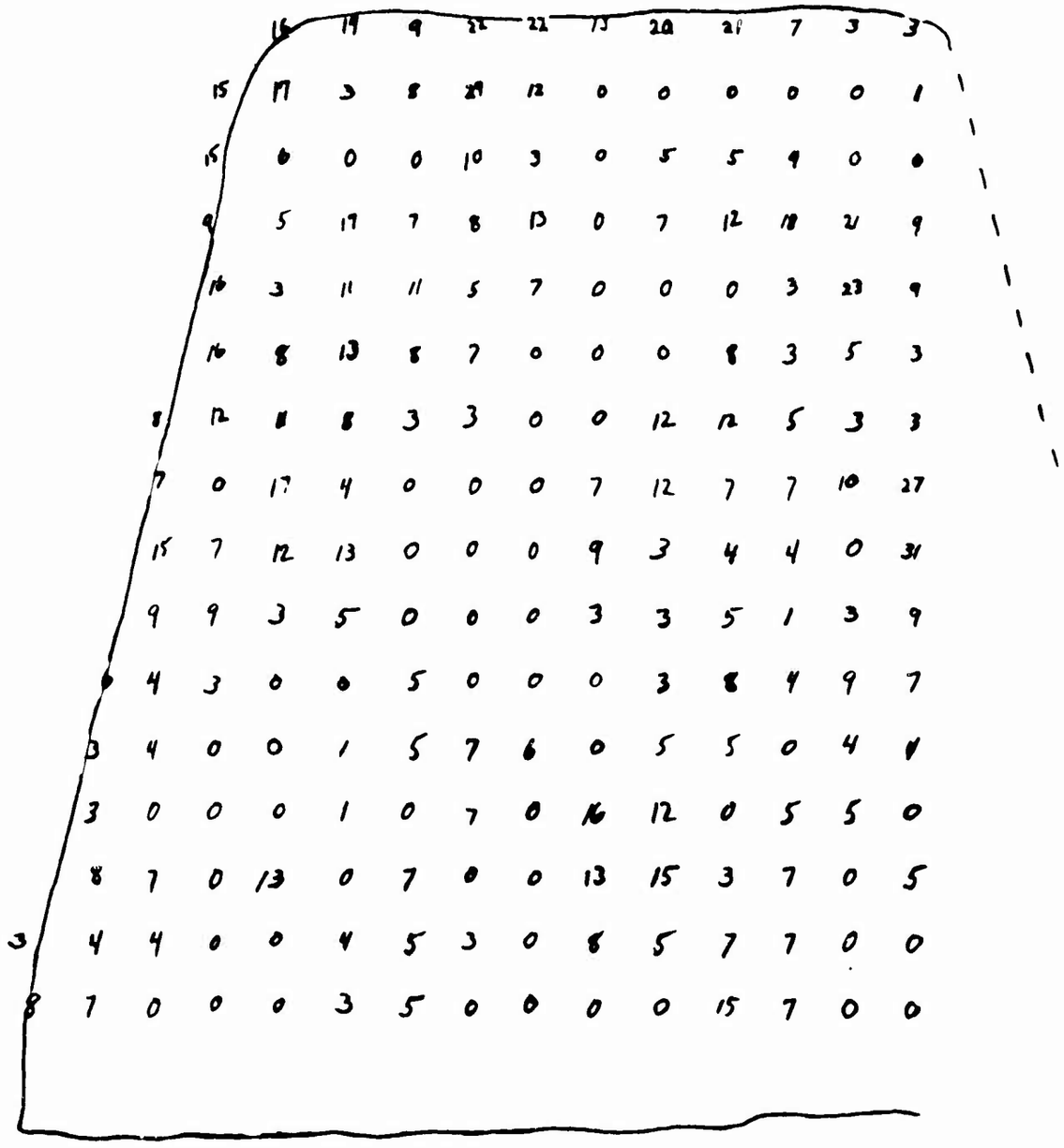


Figure 8

VOLUME CONCENTRATION CONTOUR MAP MODEL IGNITER GRAIN, AGED 3 MONTHS, 120°F

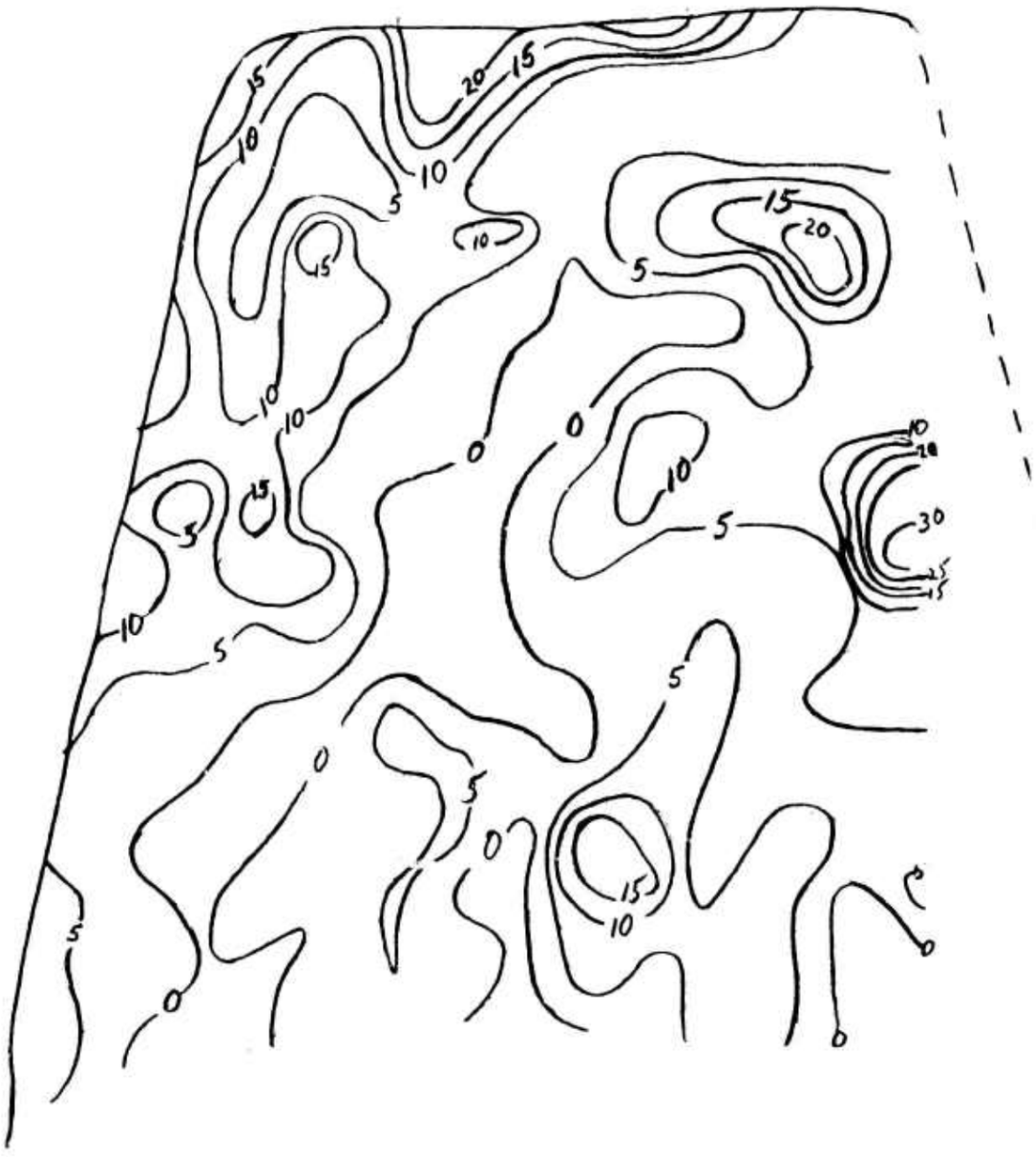


Figure 9

VOLUME CONCENTRATION MAP, MODEL IGNITER GRAIN AGED 3 MONTHS, 120°F

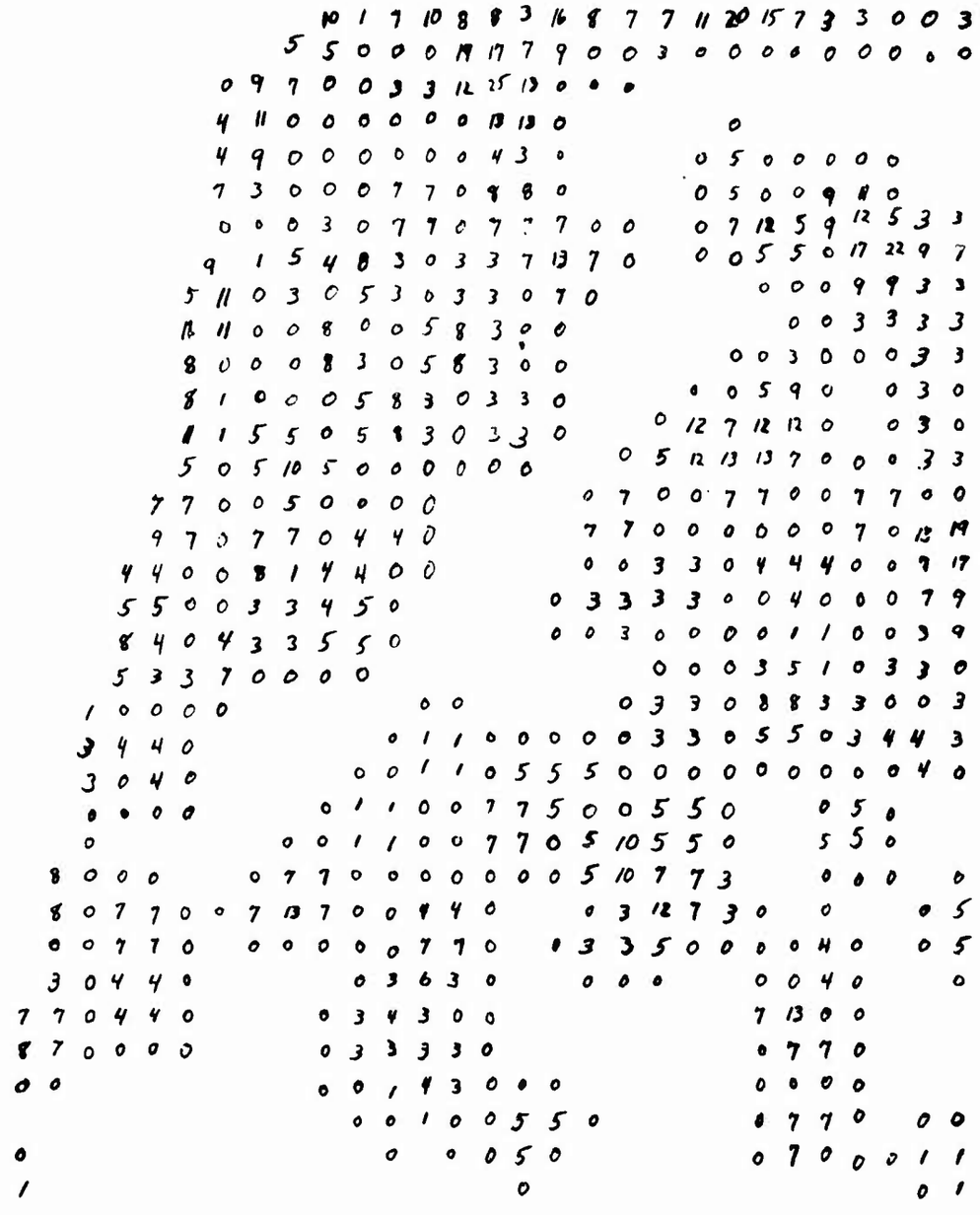
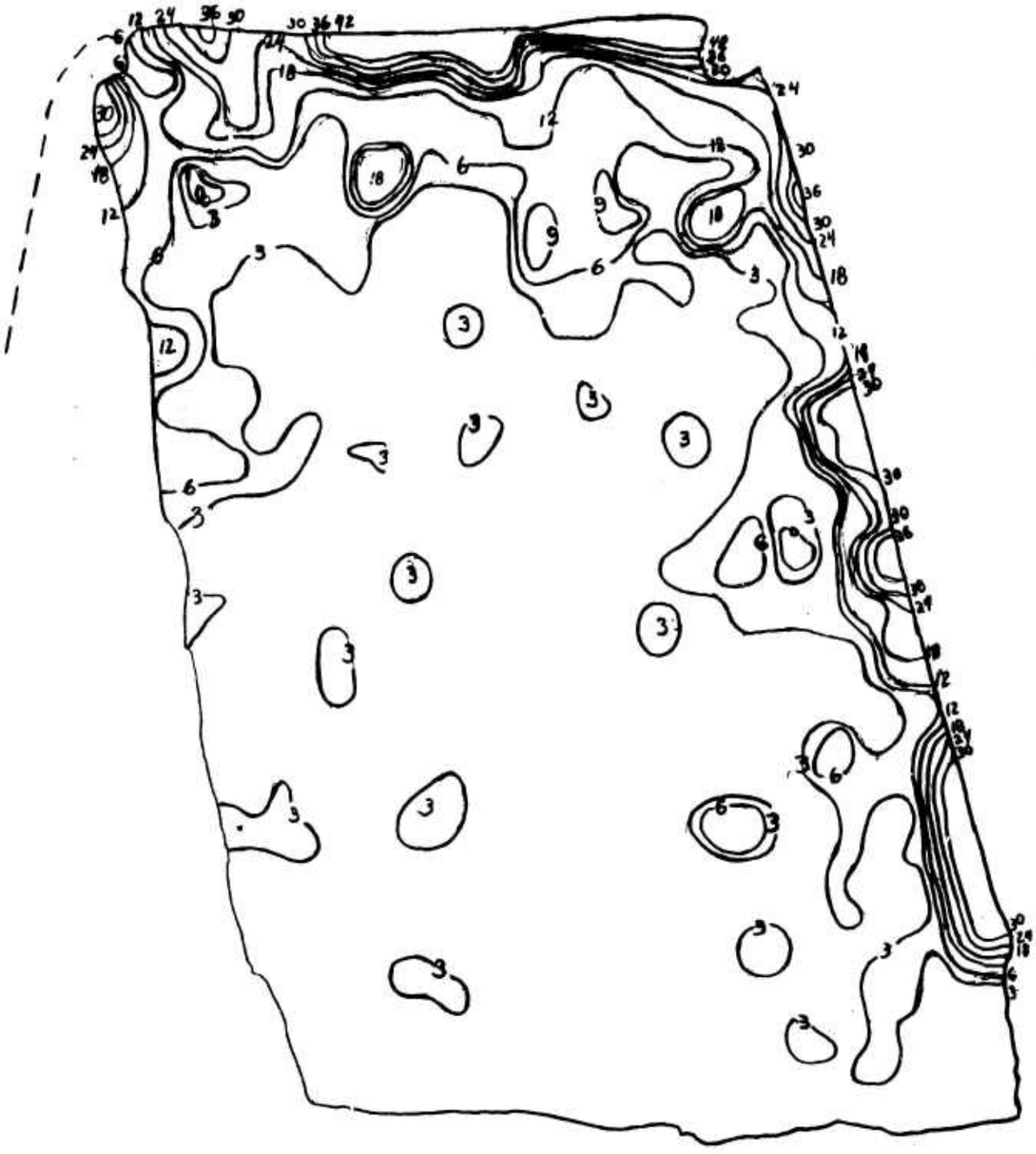


Figure 10

VOLUME CONCENTRATION CONTOUR MAP, MODEL IGNITER GRAIN
AGED 3 MONTHS, 110°F



Continued on Figure 12

Figure 11

VOLUME CONCENTRATION CONTOUR MAP, MODEL IGNITER GRAIN AGED 3 MONTHS, 110°F

Continuation of Figure 11

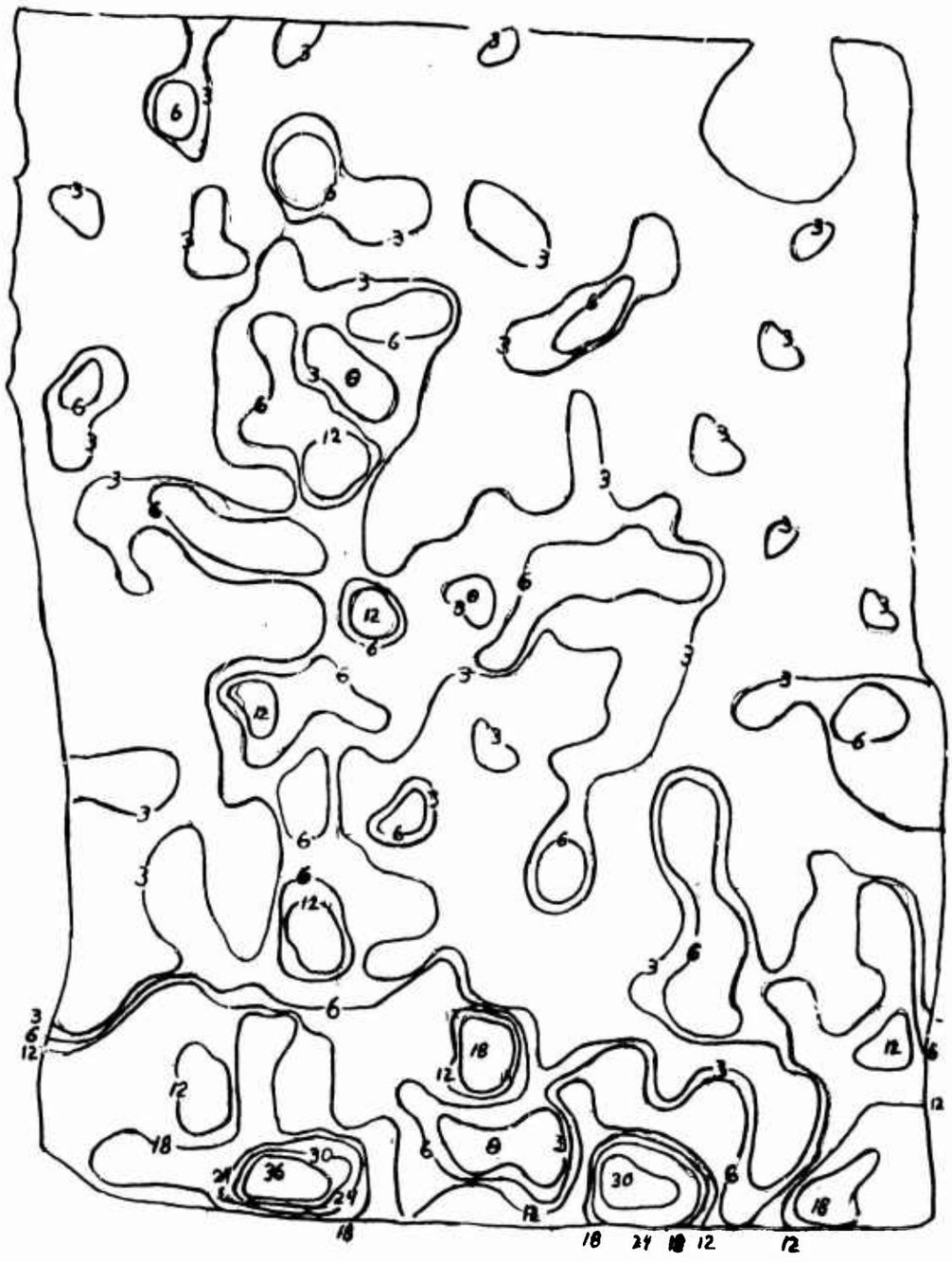


Figure 12

VOLUME CONCENTRATION CONTOUR MAP, MODEL IGNITER GRAIN
AGED 3 MONTHS, 120°F

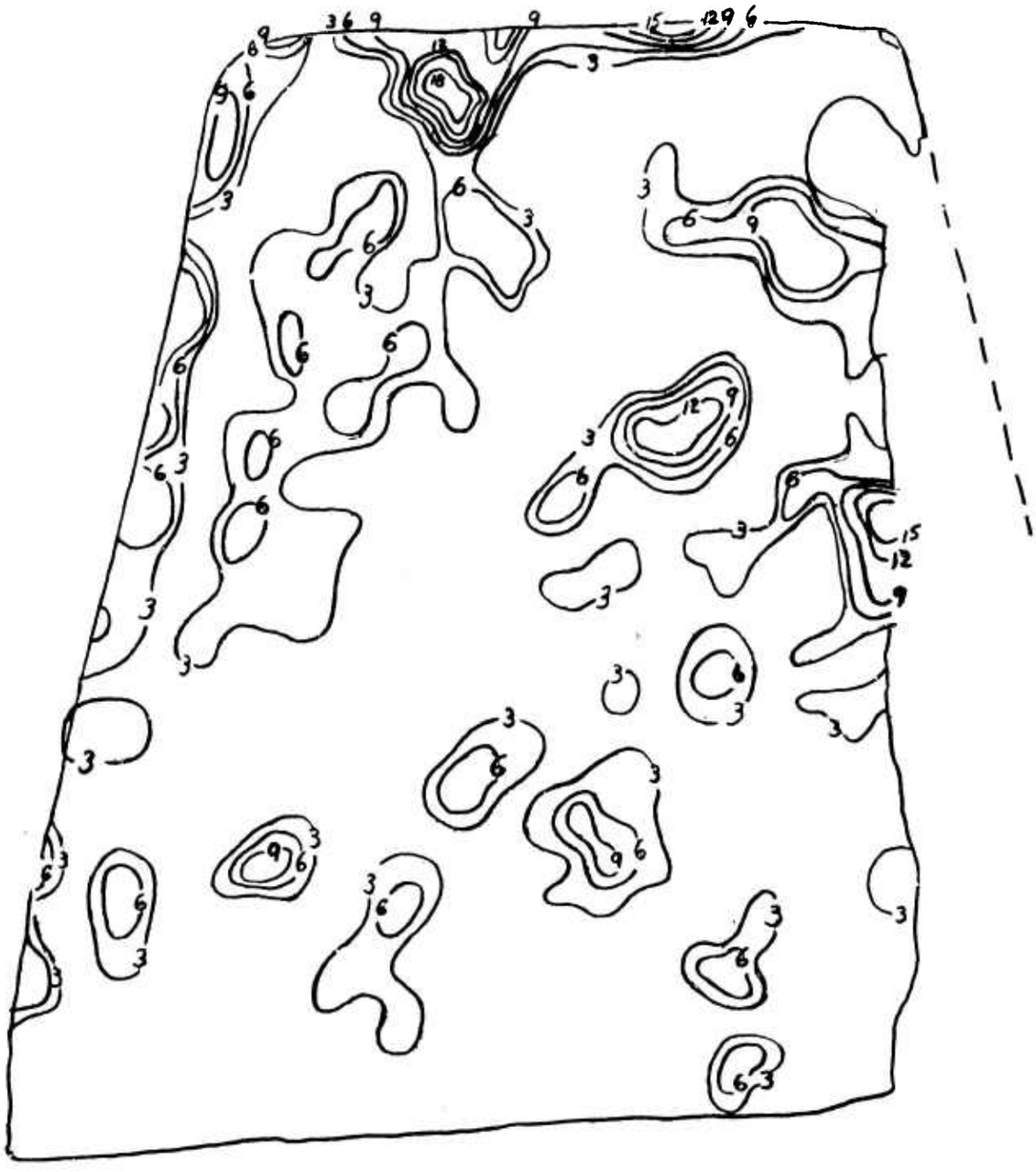


Figure 13

Volume Concentration Contour Map, Model Igniter Grain, Aged 3 months, 130°F

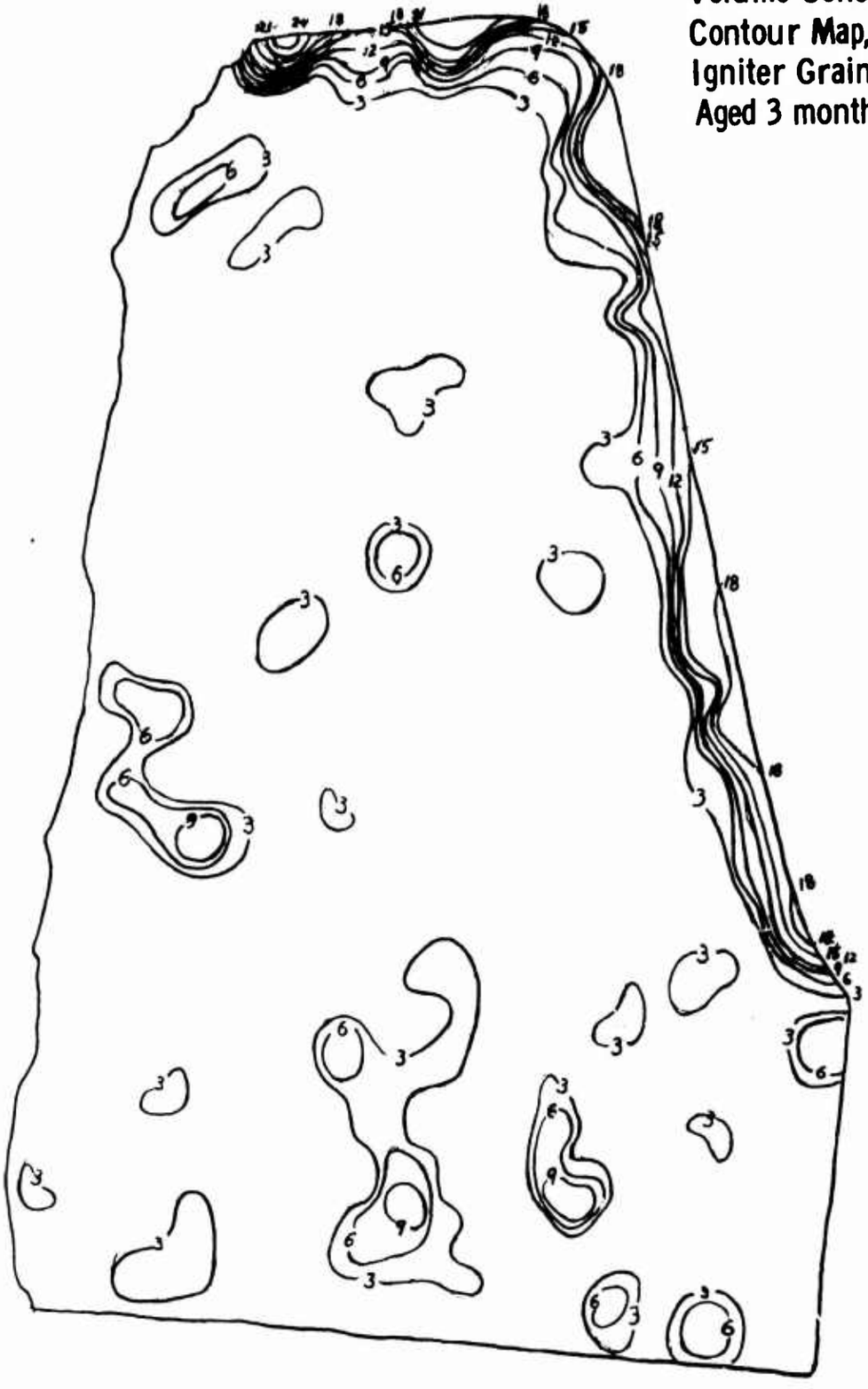


Figure 14

RELATIVE VOLUME CONCENTRATION OF REACTION SITES FOR A MODEL IGNITER GRAIN AGED FOR 3 MONTHS

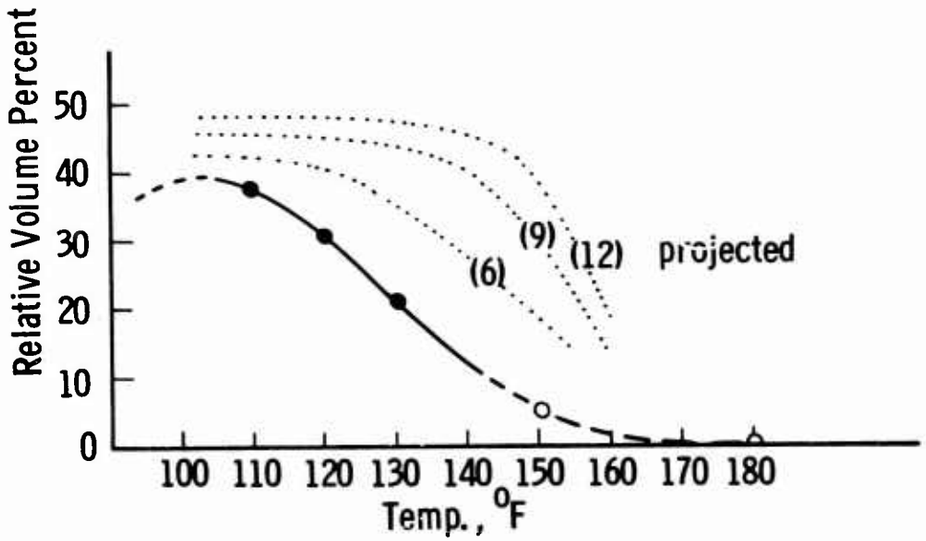


Figure 15

Figure 16 shows the location and size of refractive sites for a Minuteman Igniter Motor aged in a sealed atmosphere at 120°F for 3 months, and Figure 17 is a similar plot for a Minuteman Igniter Motor removed from a motor that had been in a silo for about one year. The scale in Figures 16, and 17 is the same as that in Figures 11-14. These two figures are from previous, unpublished work and are included because the formulations are the same as that of model grains and because the controlled atmosphere introduces another variable.

4. Discussion of Map Data

Various aspects of the reaction sites discerned from the mapped data are: size distribution, number and volume concentration and gradients.

Figures 16 and 17 display four reaction site size ranges. In the sealed motor the larger sizes appear internally (Figure 16) while in the field aged motor the larger sites are at the bore surface (Figure 17). In the model grains the distribution by size varies, but the variations have not been evaluated. A size gradation is a definite characteristic of field aged motors(1) (see Section D).

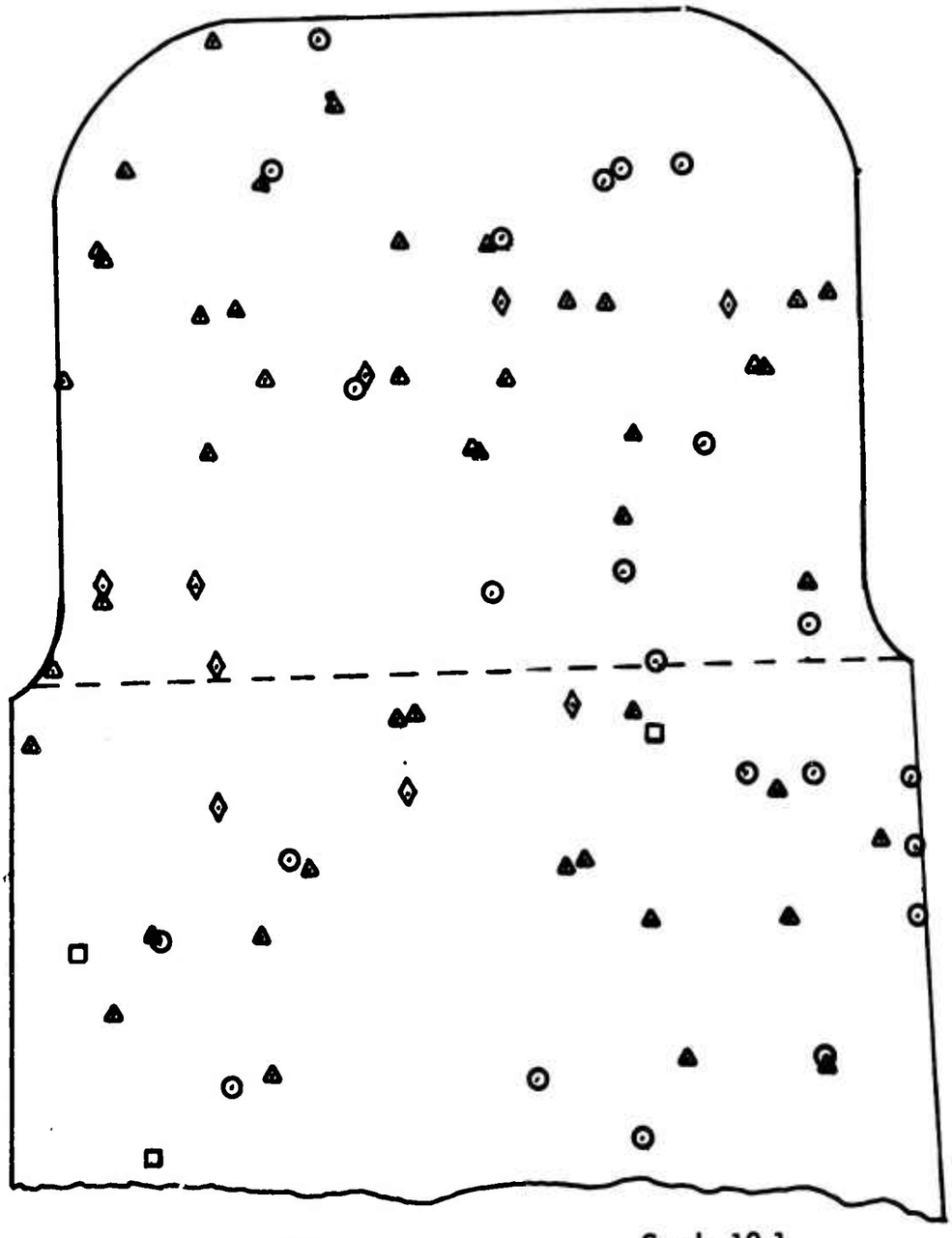
Volume concentration is a function of both site frequency and size, and is shown on the contour maps. It is apparent from Figures 11 and 12 that there is a high volume concentration of sites at both the bore surface and outer wall of the model grains. In the 180°F sample there are a few scattered sites along the case wall in a zone of complete binder degradation about one cm thick. Figure 15 shows that the reaction rate progressively decreases as the temperature increased from 110° to 180°F. Binders are known to progressively degrade with increasing temperature. These apparent opposite experimental results emphasize the difference between random binder degradation(1) and the localized reaction around the aluminum particle.

A study of the map distribution yields some new information on diffusion in the grain. The concentration of reaction sites is greatest at the bore surface in grains with an open bore (Figures 13, 11 and 17), but the distribution is random in the motor with the sealed bore (Figure 16). Thus, the reaction can occur independent of the proximity of a surface and diffusion of atmospheric agents is not a requirement for the reaction.

Furthermore, a relatively high concentration of reaction sites is distributed throughout the area between the base of the ray and case wall in Figure 12, while there is a low concentration in the center of the rays, Figures 8, 10 and 12. The areas of low concentration appear to be caused by depletion of material that has migrated to the bore and case surfaces.

The diffusion of compounds originating in the ingredients of the grain formulation appears to be a major factor in development of the refractive type reaction sites. The decrease in reaction site concentration with increasing temperature may be due to a volatile compound which escapes from the open bore surface, is trapped at the case wall, and exists in equilibrium with the bore atmosphere of the sealed motor. Development of the

DISTRIBUTION OF REFRACTIVE REACTION SITES IN SEALED IGNITER MOTOR, 3 MONTHS AT 125°F



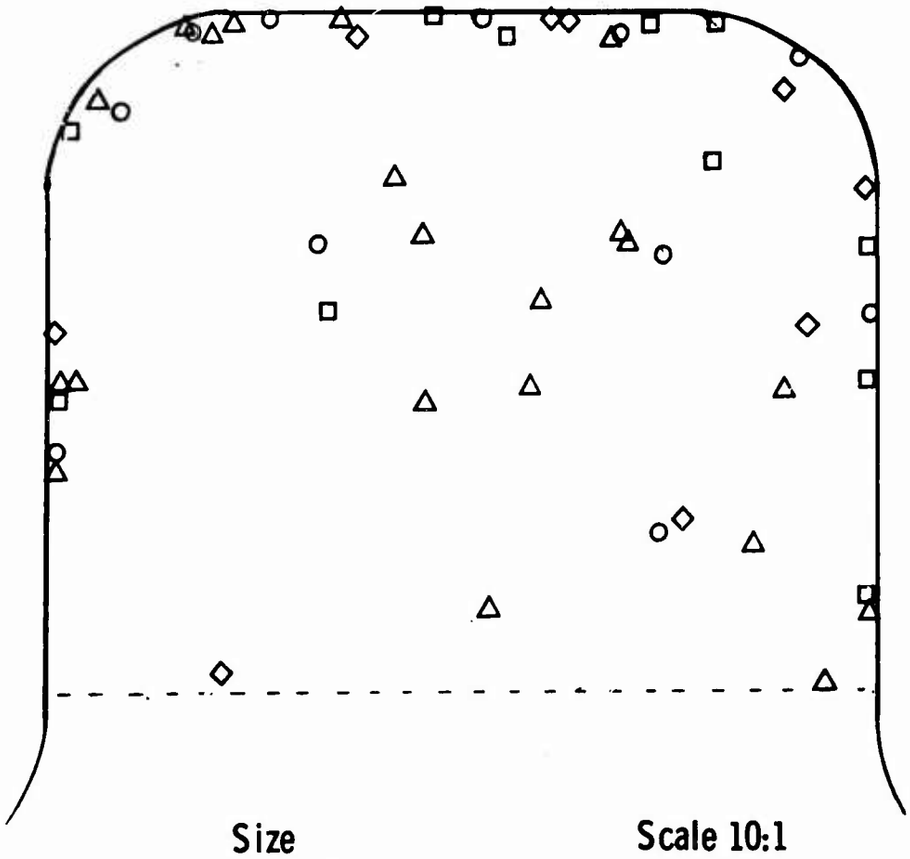
Scale 10:1

Size

△ ≤.025 mm^2
○ ≤.050 mm^2
◇ ≤.075 mm^2
□ ≤.100 mm^2

Figure 16

DISTRIBUTION OF REFRACTIVE REACTION SITES IN FIELD IGNITER MOTOR, 1 YEAR OLD



Size

Scale 10:1

△ ≤ .025 mm^2
○ ≤ .050 mm^2
◇ ≤ .075 mm^2
□ ≤ .100 mm^2

Figure 17

greatest reaction site concentration at lower temperatures is thus tentatively explained by a longer residence time of a volatile constituent in the grain.

D. DISTRIBUTION OF COLORED REACTION SITES IN THE HAWK MOTOR

1. Microscopic Studies

The distribution of colored reaction sites in the booster section of the 5½ year old Hawk grain is shown in Figure 18. The photograph is of a sample located in a radial position 18 inches from the fore end of the motor (Figure 1). The nearly opaque reaction sites were photographed in black and white by transmitted light. The frequency is greatest in Zone A adjacent to the sustainer, and there is a rather abrupt decrease in frequency and an increase in size at Zone B. Zone B shows a gradational decrease in size and an increase in frequency toward the surface. In Zone C a fairly uniform distribution of the smallest reaction sites is shown. Some refractive type sites have been observed in Zone C near the ray surface.

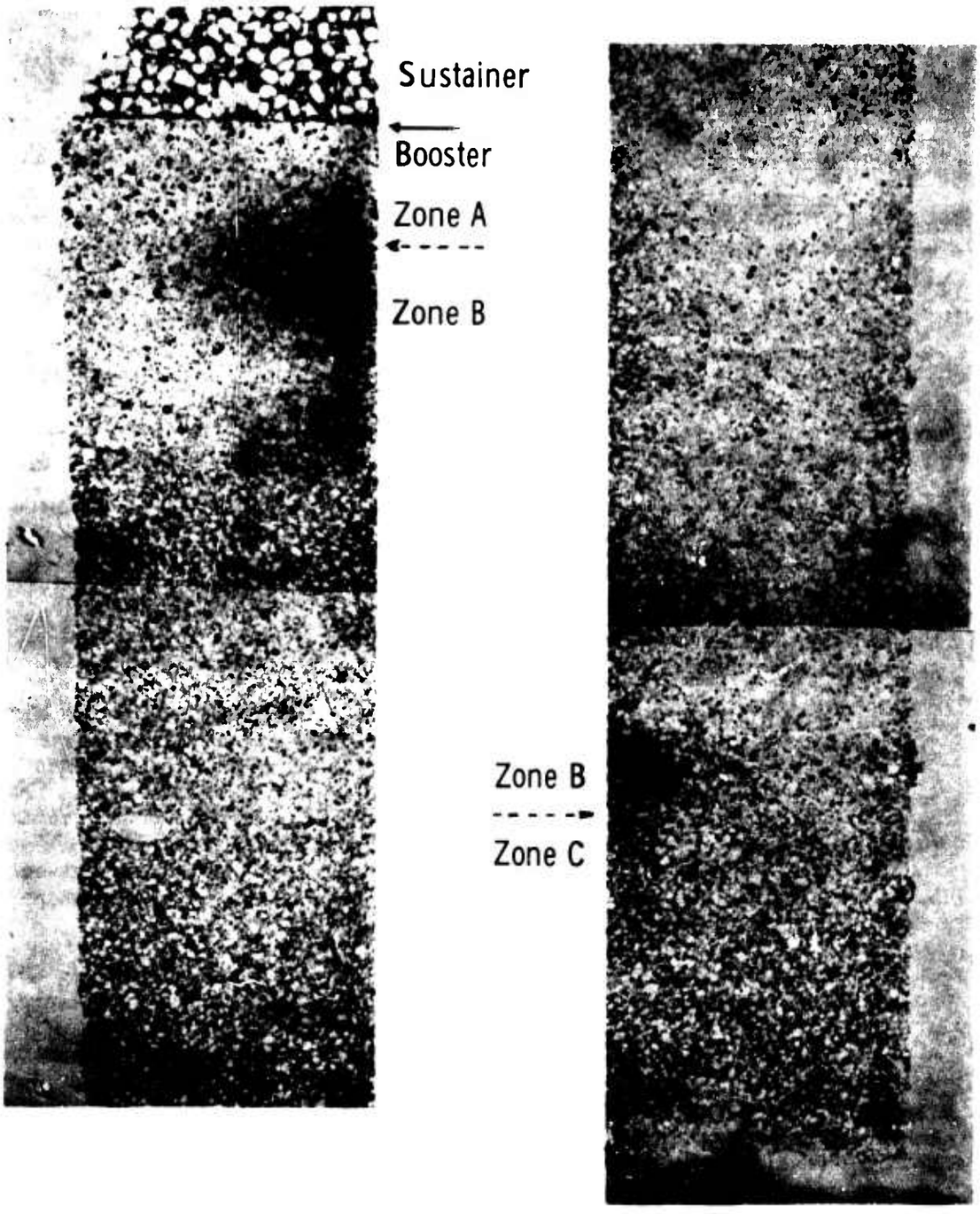
2. Discussion

The precipitation into the colored rings are the result of an iron complex formed within the formulation. Zone A has been influenced by the proximity of the adjacent sustainer, which contains more FeAA than the booster. Apparently, there has been bulk migration of iron across the bipropellant interface creating Zone A, but the actual iron concentrations have yet to be determined. The high frequency and small size of sites in Zone C at the surface represents a high rate of site formation with a slow rate of growth. There is a size and frequency gradient in Zone B. The size of the sites increase and their size frequency decrease approaching Zone A. Possibly Zone C nearer the bore surface was more completely exposed to maximum thermal cycling (heat flow) with thermal gradients decreasing toward the B/C Zone line. Zone B was exposed to a relatively more constant thermal environment with the most thermally stable environment near the B/A Zone line. Any specific changes eventually detected in Zone C may be considered possible intrusion of atmospheric agents.

E. SUMMARY OF MICROSCOPY GRAIN AGING

In comparing the distribution of refractive type sites to the colored sites, it is shown that a large radial concentration gradient exists for the refractive site and the gradient is much less or even reversed for the colored site. This is true for the refractive sites in the model grain as well as those in the full scale 5½-year old Polaris Cycling Unit[1] (see also Figure 2 and 11). Incidently, this illustrates the good correlation between the microscopic aging characteristics of model grains and full scale motors. In the Hawk field motors, a radial color gradient from red-orange near the bipropellant interface to the blue-green near the bore surface was observed at the 4½-year period. (The red-orange color shells are not observed in the model grain.) The color gradient possibly due to iron in different oxidation states, was indicative of a reducing environment at the bore end of Zone B and of an oxidizing environment at the bipropellant interface. At the end of 5½ years, the color rings had developed characteristic black shells indicating a change of the oxidizing media to a stronger reducing environment.

HAWK FIELD MOTOR, 5-1/2 YRS, DISTRIBUTION OF COLORED REACTION SITES AT FORWARD END



Magnification 6X

Ray Surface

Figure 18

In summary, reactive compounds contained in the formulation appear to diffuse locally or throughout the propellant, in part, driven by a thermal gradient, and react or precipitate in a transient oxidation gradient, at a reaction rate dependent upon their residence time. Interaction with inwardly diffusing atmospheric agents also may occur. These various reactions result in modification which could affect both mechanical and ballistic properties. The more exact nature of these reactions must be defined.

IV. CHEMICAL STUDIES

Chemical analysis of the propellant from a Polaris Cycling Unit was continued. Further attempts were made to separate into components the degraded portion of the binder. Thin layer chromatography (TLC) of the ethylene dichloride soluble fraction showed that the mixture was more mobile on alumina (basic) than on silica gel (acidic), demonstrating that the components are basic. A more quantitative analysis of the degraded binders was attempted by gas chromatography of the soluble fraction. A sample was injected into a chromatograph and passed through a 2-ft column containing a non-polar silicone coated support which was heated at a constant rate to 300°C. No detectable amount of material passed through the column showing that the molecular weights of the degraded fragments are still too large for gas chromatography.

In order to obtain larger amounts of material for chemical analyses, a portion of the soluble degraded binder was chromatographed through a column containing alumina (pH = 4) and another portion through a column containing alumina (pH = 10). Each column successfully resolved the original mixture into at least three components which have identical infrared spectra (Figure 19) and thus are similar chemically. This experiment will be repeated on a larger scale to obtain enough sample size for further chemical analysis.

A soluble fraction from a sample of the non-degraded binder was also examined by thin-layer chromatography. The mobility of the mixture from the non-degraded binder was lower than that of the mixture from the degraded portion. This would indicate that the average molecular weight of the fragments in the degraded binder was lower. The infrared spectra of the various fractions from either the degraded or non-degraded binder are identical and are typical for a polyurethane. It appears that the major differences between the degraded and non-degraded sections is the presence of longer polyurethane fragments in the non-degraded section of propellant.

A set of experiments is underway with the objective of defining the chemistry of the phenomena observed by microscopic examination. Attempts will be made to define the minimum number of chemical components that are required to produce the phenomena cited above. For this purpose, a stock polyurethane binder, with a composition similar to that used in a Minuteman igniter formulation, has been chosen as the reaction matrix. Into this uncured binder will be added, individually and then in combination, the following compounds: Al, NH_4ClO_4, FeAA, copper chromite. Each of the test samples will be examined microscopically at intervals for evidence of color centers, high refractive index material, etc. Those samples that show evidence of unusual behavior will be investigated chemically.

TYPICAL INFRARED SPECTRUM OF MATERIAL FROM DEGRADED POLARIS BINDER CHROMATOGRAPHED ON Al_2O_3 COLUMN

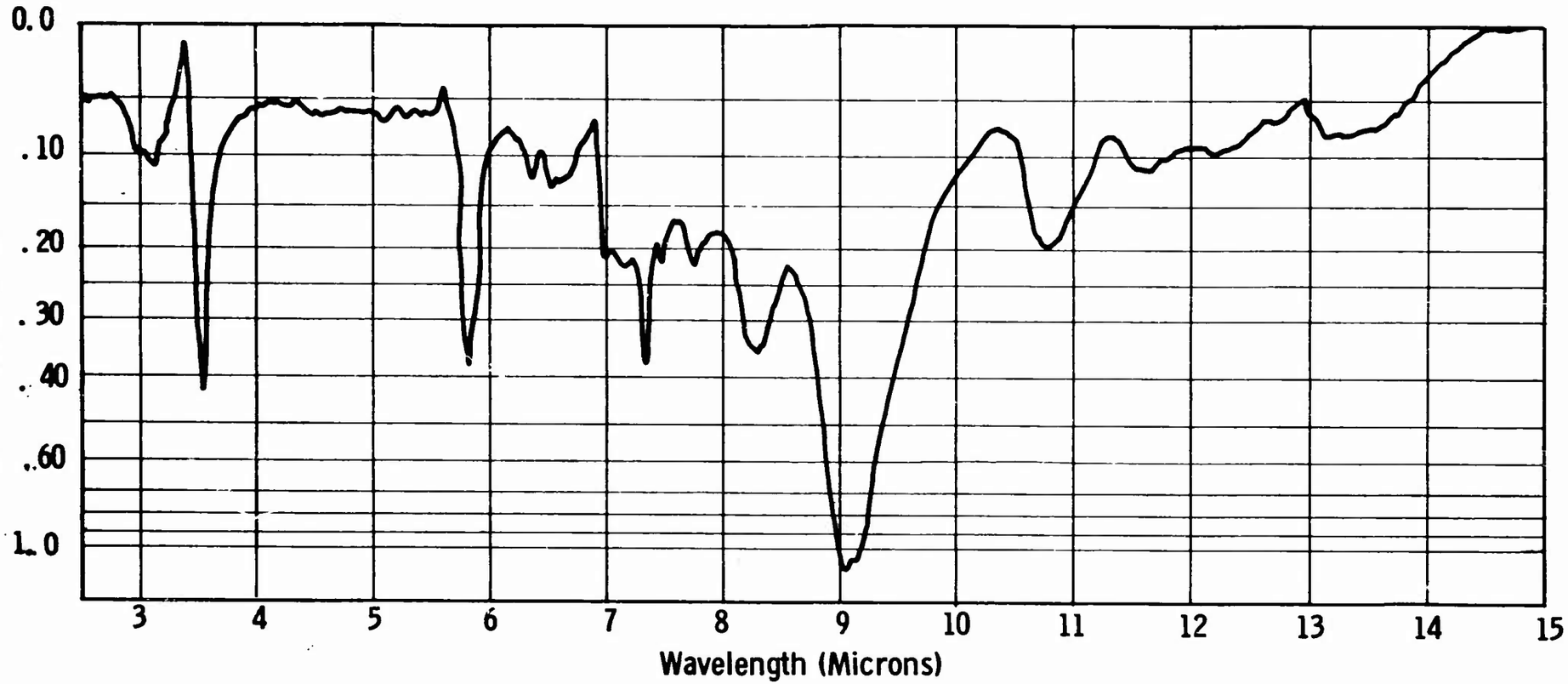


Figure 19

V. FUTURE WORK

The concentrations and distribution of various sites will be determined and compared to those from subsequent sampling periods and from field motors. Special attention will be devoted to changes observed in the model grains. The chemical analyses will be continued and attempts will be made to obtain an analysis of an actual aging site.

VI. REFERENCES

(1) J. L. McGurk, "Microscopic Determination of Near Solid State Changes in Aged Propellants", A.A.I.A. Journal, 3, 1890-95 (1965)

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13. ABSTRACT

Extensive analyses were made of the number, size, and distribution of refractive type reactive sites in model grains aged at 110, 120 and 130°F. Another grain aged at 180°F showed the formation of only very few aging sites. The analyses led to mapping of the sites on the basis of contours proportional to the volume concentration of the sites. The volume concentration was greatest in the samples aged at 110°F and decreased with increasing aging temperature. This effect was interpreted in terms of a volatile component whose residence time in the model grains was a function of the temperature.

A further analysis of colored reaction sites was made. A blue halo observed by dark field phase contrast optics was explained in terms of Rayleigh scattering from molecular size particles. The color of these sites seemed to be caused by the oxidation state of the iron compounds in the propellant and to be indicative of the oxidation state of the environment.

Chemical analyses by chromatography and infrared indicated that visibly degraded propellant differed from aged, non-degraded propellant only in the size of the fragments. Both propellants contained fragments which were chemically identical and typical for a polyurethane system.

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