AD-763 879

PREDICTION OF SAFE LIFE OF PROPELLANTS

N. S. Garman, et al

Picatinny Arsenal
Dover, New Jersey

May 1973

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

AD 763879

COPY NO. 20

TECHNICAL REPORT 4505

PREDICTION OF SAFE LIFE OF PROPELLANTS

N. S. GARMAN
J. P. PICARD
S. POLAKOSKI
J. M. MURPHY

MAY 1973

DDC
JUL 31 1973

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

PICATINNY ARSENAL
DOVER, NEW JERSEY

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Picatinny Arsenal, Dover, New Jersey 07801	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED
	2b. GROUP

3. REPORT TITLE

PREDICTION OF SAFE LIFE OF PROPELLANTS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5. AUTHOR(S) *(First name, middle initial, last name)*

N. S. Garman J. M. Murphy
J. P. Picard
S. Polakoski

6. REPORT DATE May 1973	7a. TOTAL NO. OF PAGES ~~25~~ 31	7b. NO. OF REFS 5

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S) Technical Report 4505
b. PROJECT NO.	
c. AMCMS Code 4810.16.2954.1	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

10. DISTRIBUTION STATEMENT

Approved for Public Release: Distribution unlimited

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY

13. ABSTRACT

The measure of chemical stability and the prediction of safe storage life is of prime interest to the manufacturer and use of propellants. This report will discuss the results obtained with standard artillery propellant when exposed to artificial ageing at various temperatures. The measurements of residual stabilizer versus time have been used as the criteria for propellant deterioration. A kinetic interpretation of this deterioration phenomena employing Berthelot's Law demonstrates that a family of straight lines can be plotted characterizing the length of time necessary at the various test temperatures to obtain a given variation of stabilizer content. By establishing realistic cut-off points in regard to stabilizer content, propellant safe life may be safely calculated at any storage temperature.

DD FORM 1 NOV 65 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

UNCLASSIFIED

Security Classification

1A

UNCLASSIFIED
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Propellant						
Safe storage life prediction						
Propellant chemical stability						
Artificial ageing						
Propellant stabilizers						
Berthelot's Law of deterioration						
Propellant stabilizer analysis						
Propellant surveillance practices						
Propellant temperature resistance						

UNCLASSIFIED
Security Classification

Technical Report 4505

PREDICTION OF SAFE LIFE OF PROPELLANTS

By

N. S. Garman
J. P. Picard
S. Polakoski
J. M. Murphy

May 1973

Approved for Public Release: Distribution Unlimited

AMCMS Code 4810.16.2954.1

Propellants Division
Feltman Research Laboratory
Picatinny Arsenal
Dover, New Jersey 07801

IC

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont)

Page

Figures

Distribution List

ABSTRACT

The measure of chemical stability and the prediction of safe storage life is of prime interest to the manufacturer and user of propellants. This report will discuss the results obtained with standard artillery propellant when exposed to artificial ageing at various temperatures. The measurements of residual stabilizer versus time have been used as the criteria for propellant deterioration. A kinetic interpretation of this deterioration phenomena employing Berthelot's Law demonstrates that a family of straight lines can be plotted characterizing the length of time necessary at the various test temperatures to obtain a given variation of stabilizer content. By establishing realistic cut-off points in regard to stabilizer content, propellant safe life may be safely calculated at any storage temperature.

OBJECT

To apply standard analytical methods to propellant stabilizer determination in order to establish the rate of loss of stabilizer during periods of high temperature propellant ageing, applying Berthelot's Law of deterioration phenomena to the resulting data in an effort to predict propellant chemical safe life at any storage temperature.

SUMMARY

As part of a project entitled "Long Range Study of Prediction of Safe Life of Propellants", benefits which may be derived by the application of testing procedures or concepts are reviewed and evaluated to determine their relevance. To this end, the testing technique described in this report and the kinetic interpretation of the resulting test data have shown much promise as a method of forecasting propellant chemical safe life on small samplings of standard single-, double- and triple-base U. S. Army artillery propellant formulations. However, work must be expanded to make a more comprehensive review of propellants of U. S. Army interest and to study and refine the approach so that full application of this testing routine can be included in the propellant surveillance effort.

INTRODUCTION

One of the major problems concerned with the manufacture and use of propellants is the measurement of their chemical stability and the prediction of their safe storage life. The U. S. Army has substantial quantities of artillery propellants in storage. These various artillery propellants are subject to degradation with ageing, the end result being spontaneous ignition. Therefore, it is mandatory that a continuous knowledge of the stability status of this stock be acquired. The Propellants Division, Picatinny Arsenal, has the responsibility for this mission, and currently maintains control over these stocks by conducting the 65.5°C. Surveillance Test and the propellant stock activity described in references (1) and (2) respectively. These two programs involve all lots of artillery propellant manufactured for the U. S. Army.

The 65.5°C. Surveillance Test depends upon an end-point which is defined as the appearance of visible red fumes of nitrogen dioxide over the propellant sample stored at 65.5°C. It has been established through years of experience that the development of the end-point in 20 days or less denotes a storage hazard of the ambient stored stock but with an ample safety margin for disposition action on any remnant of that lot of propellant.

The propellant stock program has only very recently been implemented, the scope of this activity now relating to propelling charges and/or bulk propellant actually on hand in Field Service and Industrial Stock installations. Stabilizer content determinations of representative samples of each lot forwarded to this installation from the storage facilities form the basis for safe life determinations of this active stock. From the data developed by this program, in addition to those results observed in the 65.5°C. Surveillance Test, a sound, comprehensive stability control of all U. S. Army propellant stock is accomplished.

The benefits derived from such programs far outweigh the costs of testing, in that these measurements are the controlling factor in preventing loss of property and possibly life. The results of these programs can be translated into money, material and manhour savings by insuring the use of only acceptable propellant in loading and reblending operations, and by reducing storage costs through the disposal of unserviceable propellants. Additionally, a technical advantage is realized from conducting the 65.5°C. Surveillance Test in that opportunity is provided to perform related studies concerned with the safe life properties of propellants.

It is widely recognized in the study of propellant chemical deterioration that the measurement of residual stabilizer content offers the best means of establishing the stability potential of these materials. The method of analysis is, of course, of the greatest importance. It must be analytically sound, reproducible, relatively simple and capable of providing results which can be meaningfully interpreted. In the last few years, such a method was developed and is presently replacing some of the older wet chemical methods whose results were questionable when applied to aged propellants. This method is described in detail in Reference 3. The available propellant stabilizer is separated from hot alkali by steam distillation and analyzed spectrophotometrically. For this, the distillate is diluted to a standard volume with ethanol and the absorbance of the solution measured at 285 and or 247 mμ for the determination of available stabilizer as diphenylamine or ethyl centralite respectively. This method of analysis is employed to accomplish the surveillance activity described in Reference 2.

Recently the NATO countries were in need of an evaluation procedure that would assure acceptor countries that propellants received from others would have a proven chemical stability for a given period of time when stored at ambient conditions. After many stability tests were reviewed and evaluated through the conduct of round robins to insure that strict analytical agreement could be realized among world-wide participating laboratories, the above mentioned method for the determination of available stabilizer content was accepted, with the establishment of suitable cut-off points. It was assumed that if a propellant withstood a heating period of 60 days at 65.5°C., without undue depletion of available stabilizer content, then that propellant would have a proven chemical stability for 5 years storage at ambient conditions.

Once it was demonstrated that a reliable method of analysis had been established, capable of predicting the safe life of propellants for a five year period, it was of interest to attempt to apply this technique to predict the safe life of propellants for a much longer time. It was felt that by the establishment of realistic cut-off points in regard to stabilizer content, it should be possible to calculate safe life of propellant at any storage temperature with some degree of accuracy and with an ample margin of safety.

In March 1964, the French delegation at one NATO meeting suggested that kinetic interpretation of decomposing propellant could be interpreted by the use of Berthelot's Law of deterioration phenomena (References 4 and 5). With these tools and funds made available under project title, "Long Range Study of Prediction of Safe Life of Propellants", this study was initiated.

RESULTS

The formulations of the propellants studied under this program are tabulated in Table 2. In order to verify the agreement between the experimental results developed by the application of Berthelot's Law and the actual decomposition occurring under normal storage conditions, data representing propellants of different ages are presented in Table 3.

For each temperature investigated, curves were plotted showing the variation of the stabilizer content with time (plotting the stabilizer content along the ordinate and the time along the abscissa) thus representing these two variables in linear coordinates. These curves are shown in Figures 1 and 2 representing single-base M6 formulation, Figures 3 and 4 representing double-base M9 formulation, Figures 5 and 6 representing triple-base M30 formulation and Figures 7 and 8 representing single-base M10 formulation.

The graphical expressions applying Berthelot's Law to the developed data for M6, M9, M30 and M10 propellant formulations are shown in Figures 9, 10, 11 and 12 respectively.

Figure 13 shows data comparing Arrhenius' vs. Berthelot's equations.

DISCUSSION

Characteristics of the formulations under study, the compositions of which are shown in Table 2, are generally that single- and triple-base propellants will resist deterioration at high temperature exposure better than double-base propellant formulations. Conditioning temperatures for this study were, therefore, chosen at 10°C. intervals between 60° and 100°C. for single- and triple-base propellants, and between 60° and 90°C. for double-base propellants. These conditions are considered realistic for the three types of propellants considered. The behavior of the compositions heated at these different temperatures was determined by means of stabilizer analysis performed at specific time intervals in order to obtain a basis for extrapolation to lower storage temperatures. Therefore, through artificial ageing of the propellants at various temperatures and measuring the residual stabilizer content spectrophotometrically as described in Reference 3, the deterioration rate curves shown in Figures 1 through 8 were developed. In general the shapes of these curves are quite similar and display a rapid and relatively linear depletion rate up to approximately 70% of the overall deterioration pattern. As ageing progresses the curves exhibit a point of inflection and then proceed very slowly to approach 100% dissipation of the stabilizer. This apparent change of reaction rate can no doubt be attributed to the relatively high concentrations of the deterioration products of the stabilizer at this stage which themselves are capable of stabilization. Conditioning and stabilizer analysis were halted when the stabilizer level reached 0.1%, since it was found that at this point the propellant at these high temperatures was approaching hazard. It is likely that the reaction mechanisms are influenced by temperature and that the results of many high temperature tests are not reliable for safe life studies. However, since reaction mechanisms and rates decrease at lower storage temperatures, extrapolations derived from this high temperature work leave an ample margin of safety for disposition action of potentially hazardous propellants.

The points of interest on these graphs are the intersections of the lines corresponding to the consumption of 10, 20, 30, 40 and 50% of the stabilizer with the deterioration rate curves for each storage temperature. For convenience sake, alpha (α_X) defines the length of time (measured in days) necessary for obtaining a decrease of X% of the stabilizer content. Such values may be used for kinetic interpretation employing Berthelot's Law of the deterioration phenomena.

Berthelot's Law is applied to develop curves reflecting the variation of the rate of reaction with temperature. It is written as follows:

$$\log K = aT + b \qquad (1)$$

where T is the reaction temperature in degrees Kelvin, a and b are coefficients characteristic of the product under study; K is the rate constant at temperature T.

Constant K can be calculated only when the mechanism of the reaction, and especially the latter's order, is known; this is not the case in the thermal decomposition of propellants. When K cannot be determined, it is possible to replace it with time t, which is inversely proportional to K.

$$K = c/t \tag{2}$$

where t is the time necessary to obtain a given variation of a constituent, and c is the concentration of that constituent (for example a 50% decrease in stabilizer content) for the product under study at temperature T. Then formula (1) can be written as:

$$\log c/t = aT + b \qquad \text{or}$$

$$T = -1/a \log t + 1/a\ (\log c - b) \tag{3}$$

Formula (3), represents Berthelot's mathematical expression of the deterioration phenomena, which is a straight line function. By referring back to the experimental data plotted for each propellant formulation at the various test temperatures, the points α_x, representing the times for the consumption of a specific amount of stabilizer can be extracted. If these experimental data then satisfy Berthelot's Law, this will be shown by plotting these points (α_x) with T as ordinate and log t as abscissa, and the development of a family of straight lines. This will characterize the length of time necessary for the propellant to consume 10, 20, 30, 40 and 50% of the initial amount of its stabilizer. These graphical expressions for M6, M9, M30 and M10 propellant formulations are shown in Figures 9, 10, 11 and 12 respectively. In viewing the graphs for the M6, M9 and M30 propellants, it is evident that the experimental data conforms quite satisfactorily with Berthelot's Law. However, the results for the M10 Propellant show lines of varying slopes, indicating a change in the reaction mechanism for certain temperature intervals. It is felt that these variations are not so critical as to prevent the determination and use of an average slope for the M10 Propellant. The slope of these lines can be defined by a coefficient gamma (γ_{10}) corresponding to the increase of the reaction rate for a temperature change of 10°C. Therefore, to determine γ_{10}, it is sufficient to take the duration t_1 and t_2 corresponding to a temperature difference $(T_2 - T_1) = 10°C.$, where $\gamma_{10} = t_1/t_2$.

Mathematically, it can be shown that equation (4) below can be derived from (3)

$$T_2 = -1/a \log t_2 + 1/a(\log c-b)$$

$$T_1 = -1/a \log t_1 + 1/a(\log c-b)$$

$$T_2-T_1 = 1/a \log t_1/t_2$$

$$\log t_1/t_2 = a(T_2 - T_1)$$

By setting $\gamma_{10} = 10^{10a}$

Then $\log t_1/t_2 = \log \gamma_{10} x \ (T_2-T_1)/10$

and that $$t_1/t_2 = \gamma_{10}^{\frac{T_2-T_1}{10}} \qquad (4)$$

Therefore, by knowing points (α_x) and the slope γ_{10}, then

$$D_x = \frac{\alpha_x \gamma_{10}^{\frac{T_2-T_1}{10}}}{365} \qquad (5)$$

where α_x is the time, in days, necessary for obtaining an X% decrease in stabilizer content at T_2, γ_{10} is the increase of the rate of reaction for a 10°C. temperature change, and D_x is the prediction of safe life expressed in years to obtain an X% decrease in stabilizer content at T_1.

The literature reveals that investigators have used both Berthelot's and Arrhenius' Laws freely to represent propellant deterioration phenomena. Table 1 shows that there are similarities in their graphic expressions, but also shows differences, mainly in their linear representation of T.

TABLE 1

Representation of Arrhenius' and Berthelot's Law

		Representation	
	Formula	K	T
Berthelot	$\log K = aT + b$	Log Scale	Linear Scale
Arrhenius	$\log K = a-b/T$	Log Scale	1/T, Linear Scale

As a matter of interest, a formula similar to equation (5) can be derived from Arrhenius' Equation, which employs the data to determine the activation energy (E) rather than Berthelot's coefficient (γ_{10}). Since it is not possible to determine exactly which of these two equations is more appropriate to describe the deterioration of propellants, the choice is left to the discretion of the investigator.

When the data were graphically expressed for both laws as shown in Figure 13, it was found that the predicted safe life of the propellant according to Arrhenius' Law was much longer. Therefore, since this study is related to propellant safe life prediction and safety in storage of propellant stocks, the use of Berthelot's Law for this application is preferred.

The calculated life duration is only a crude approximation of the real life. Coefficients α_x, γ_{10} and D_x have mainly a comparative value, but at the present time they represent a method of estimating the chemical stability of a given composition. In order to verify the agreement between the experimental results and the decomposition under normal storage conditions, formula (5) has been applied to several propellants of different ages. This data is presented in Table 3 and shows that ageing has resulted in the loss of stabilizing potential (X%). By referring to any of the high temperature deterioration rate curves developed for these propellants, the time necessary for the loss of X% stabilizing potential (α_x) can be determined. The coefficient γ_{10} has beer established for these formulations as shown; therefore, by substituting these values into formula (5) the time necessary to obtain the same stabilizer decrease (D_x) at 20°C. (ambient conditions) can be calculated. The relative agreement between the experimental results and the actual ages of the propellants would indicate that this technique is an aid in predicting the safe life of propellants. In the field of propellant stability there are many applications of this predicting technique. A few of these applications are enumerated and discussed below.

In the work dealing with NATO activities, it was assumed that a 60 day storage period at 65.5°C. could be equated to 5 years storage for a propellant, regardless of formulation, at ambient conditions. It was also assumed that new propellant formulations containing 1.00% stabilizer or less should retain no less than 0.3% of that stabilizer after 60 days storage at 65.5°C. in order to be acceptable. Similarly, propellant formulated with more than 1.00% stabilizer should retain at least 0.5% under the same storage conditions.

This study has established that the deterioration rates of propellants of different formulation stored at both high and low temperatures vary greatly; nonetheless it can be shown that the criteria established by the NATO countries are not unrealistic and provide for an ample safety margin in their favor. Working with the most extreme case of all the propellants tested during this study, the M30 Propellant, and calculating its equivalency, ambient temperature storage (20°C.), based on 60 days at 65.5°C., results in a prediction of 8 years. This indicates that the 5 year assumption is reasonable. The lower acceptance limits established are also reasonable and safe, since it has been determined that propellants approach hazard at a 0.1% stabilizer residue.

As stated earlier, the 65.5°C. Surveillance Test is conducted continuously on each and every lot of artillery propellant manufactured for the U. S. Army. In addition, many lots of small arm and rocket propellants are undergoing the same test. In all, there are currently approximately 22,000 lots being evaluated. For some new and stable propellants the length of time necessary for the appearance of red fumes may be in excess of 5 years, as is probable for the M6 formulation, while other formulations are less heat resistant and fume much sooner. Since many years of effort and much repetitive testing is required to maintain the necessary control over these propellant stocks, there is an urgent need for a relatively short term, reliable test to aid in the prediction of safe storage life for all propellants.

It is relatively easy to link the fume time with the change in stabilizer content, since experience has shown that the red fumes of nitrogen dioxide appear very shortly before the propellant has consumed the entire amount of available stabilizer. For convenience we shall call α_N the time elapsed until the appearance of red fumes, and it can therefore be written that α_{100} is greater than or equal to α_N at any high temperature storage condition. The fume times for the M6 Propellant were recorded at various temperatures and when this data is plotted, as shown in Figure 9, it is noted that the slope of this α_N line differs from the other lines, indicating that the reaction mechanism for the overall depletion of stabilizer content is different than the initial through the loss of 50% stabilizer. This fact is particularly evident in the rate curves developed for the M6 Propellant as well as for all the formulations, regardless of the stabilizer involved. This information is of particular interest if used for the prediction of fume times applicable to the 65.5°C. Surveillance Test and enables the currently used surveillance test to be simplified.

Triple-base formulations have, since their inception, presented problems in their safe life control. These propellants do not produce the red fumes of nitrogen dioxide when tested under the conditions cited for the performance of the 65.5°C. Surveillance Test. Therefore, control by means of this test is not maintained through fuming but rather by the appearance of evidence of physical breakdown of the propellant grain. This is not entirely satisfactory. The introduction of this newly developed technique into the surveillance activities offers a distinct advantage in the safe life control over those formulations.

CONCLUSIONS

Analysis of stabilizer content and kinetic interpretation of the resulting data provide a testing technique for measuring the chemical stability of propellants and a tool for forecasting safe storage life.

RECOMMENDATIONS

It is recommended that work of this nature be expanded to include a more comprehensive coverage of propellants of U. S. Army interest. It is also suggested that in future work much closer temperature control be maintained in the high temperature storage chambers, and studies be made to evaluate the extent of temperature control required. In addition, future work should employ supplementary analytical techniques such as thin layer and gas chromatography to evaluate the benefits that might be realized from additional knowledge of the type and concentration of degradation products of the stabilizers involved. Finally, it is recommended that this work and any additional work be closely correlated with propellant surveillance efforts currently in progress at this Arsenal in an effort to coordinate and evaluate the test data pertaining to propellant safe life.

REFERENCES

1. Clear, Arthur J., "Standard Laboratory Procedures for Determining Sensitivity, Brisance, and Stability of Explosives, Picatinny Arsenal Technical Report 3278 Rev. 1, April 1970.

2. Department of the Army Supply Bulletin SB 742-1300-2, "Charge, Propelling, Various Propellant, Bulk Ammunition Surveillance Procedures", 28 July 1971.

3. MIL-STD-286B, Notice 2, Method 201.4.2, "Propellants, Solid: Sampling, Examination and Testing", dated 30 June 1971.

4. Tranchant, J., "Contribution a L'Etude des Proprietes' Chimiques et Physico-Chimiques des Poudres", Memorial des Poudres 44, Annexe (1962).

5. Tranchant, J. and Brun, J., "Etude Generale de la Stabilite' Chimique des Poudres", Memorial des Poudres 41, 189 (1959).

TABLE 2

Propellant Compositions

Ingredients, %	Propellant Type: M6	M10	M9	M30
Nitrocellulose	87.00	98.00	57.25	28.00
Nitroglycerin			40.00	22.50
Nitroguanidine				47.70
Dinitrotoluene	10.00			
Dibutylphthalate	3.00			
Diphenylamine	1.00*	1.00		
Ethyl Centralite			0.75	1.50
Potassium Sulfate		1.00		
Potassium Nitrate			2.00	
Cryolite				0.30
Graphite		0.10**	0.15*	

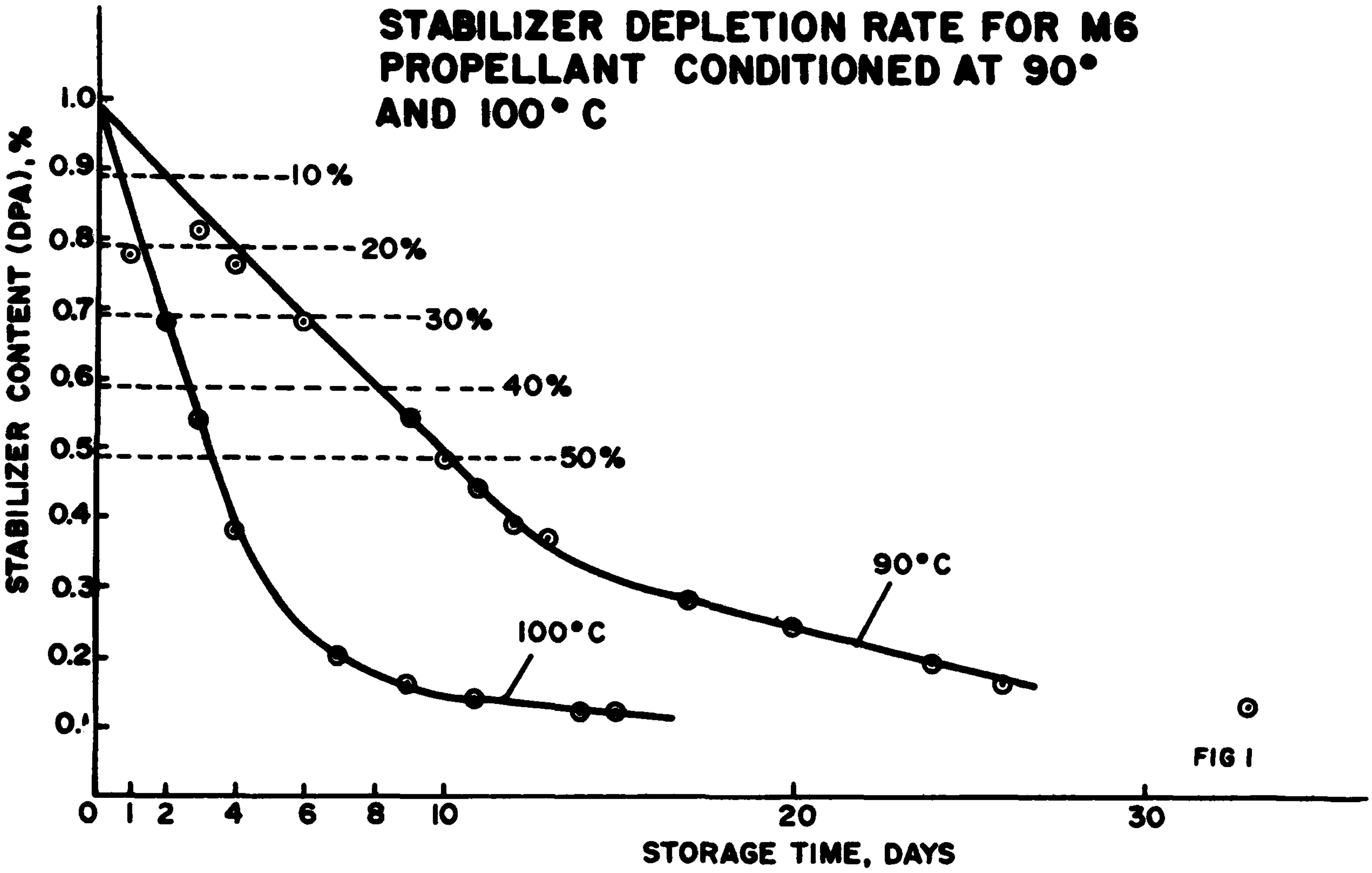
*Added

**Glazed

TABLE 3

Prediction of Propellant Safe Life

Propellant Type	Stabilizer Loss, %	γ_{10}	α_x, Days at T_2	D_x, Years	Actual Age, Years
M1	10	3.83	12.5 at 70°C.	25	28
M1	11	3.83	14.5 at 70°C.	25	33
M6	13	3.29	2.5 at 90°C.	21	29
M6	15	3.29	2.9 at 90°C.	34	33
M5	8	3.75	1.3 at 80°C.	7	10
M5	9	3.75	1.5 at 80°C.	7	11
M7	5	4.49	0.2 at 90°C.	18	20



STABILIZER DEPLETION RATE FOR M6 PROPELLANT CONDITIONED AT 90° AND 100° C

FIG I

STABILIZER DEPLETION RATE FOR M6 PROPELLANT CONDITIONED AT 60°, 70°, AND 80° C

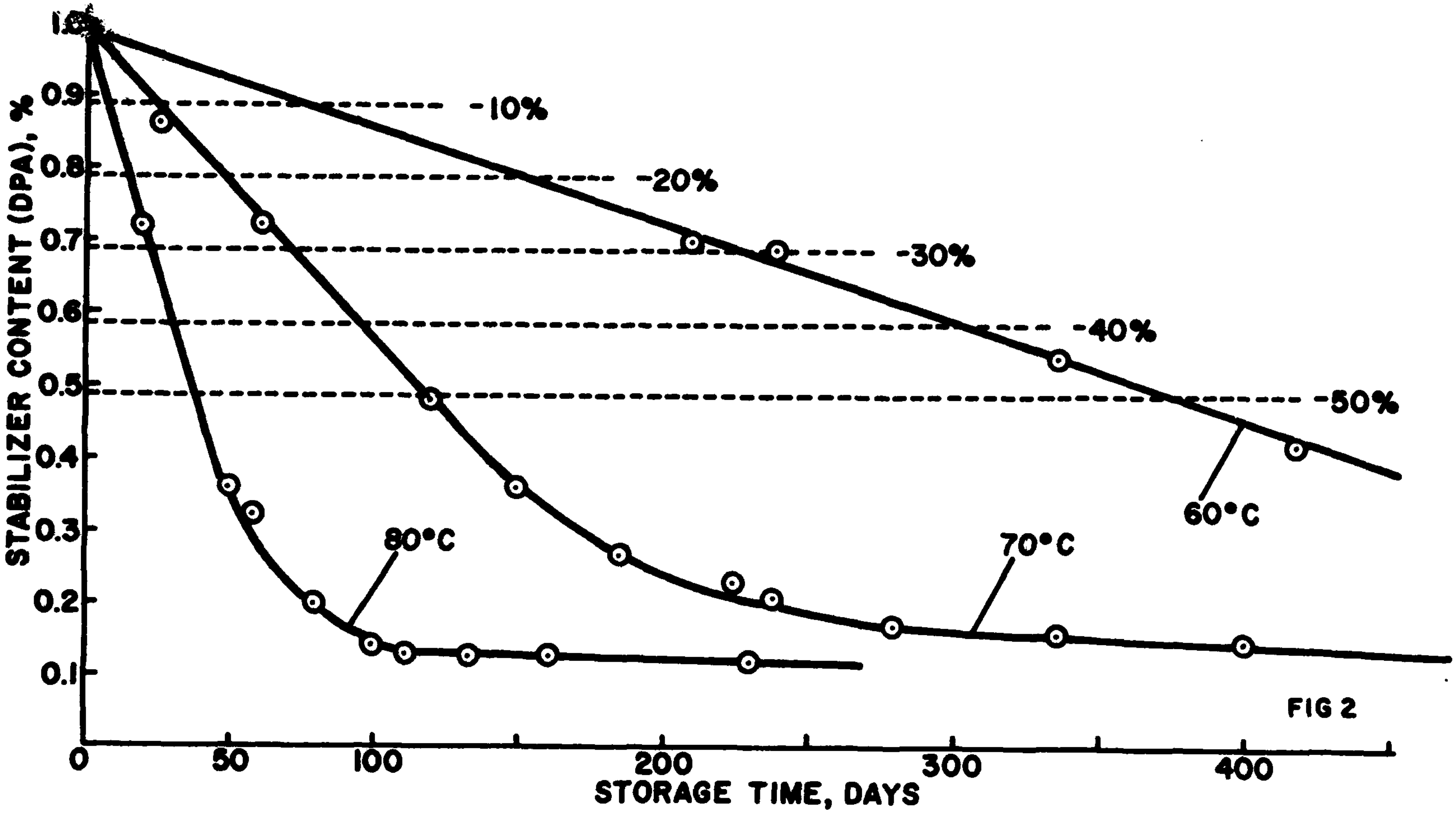


FIG 2

STABILIZER DEPLETION RATE FOR M9 PROPELLANT CONDITIONED AT 80° AND 90°C

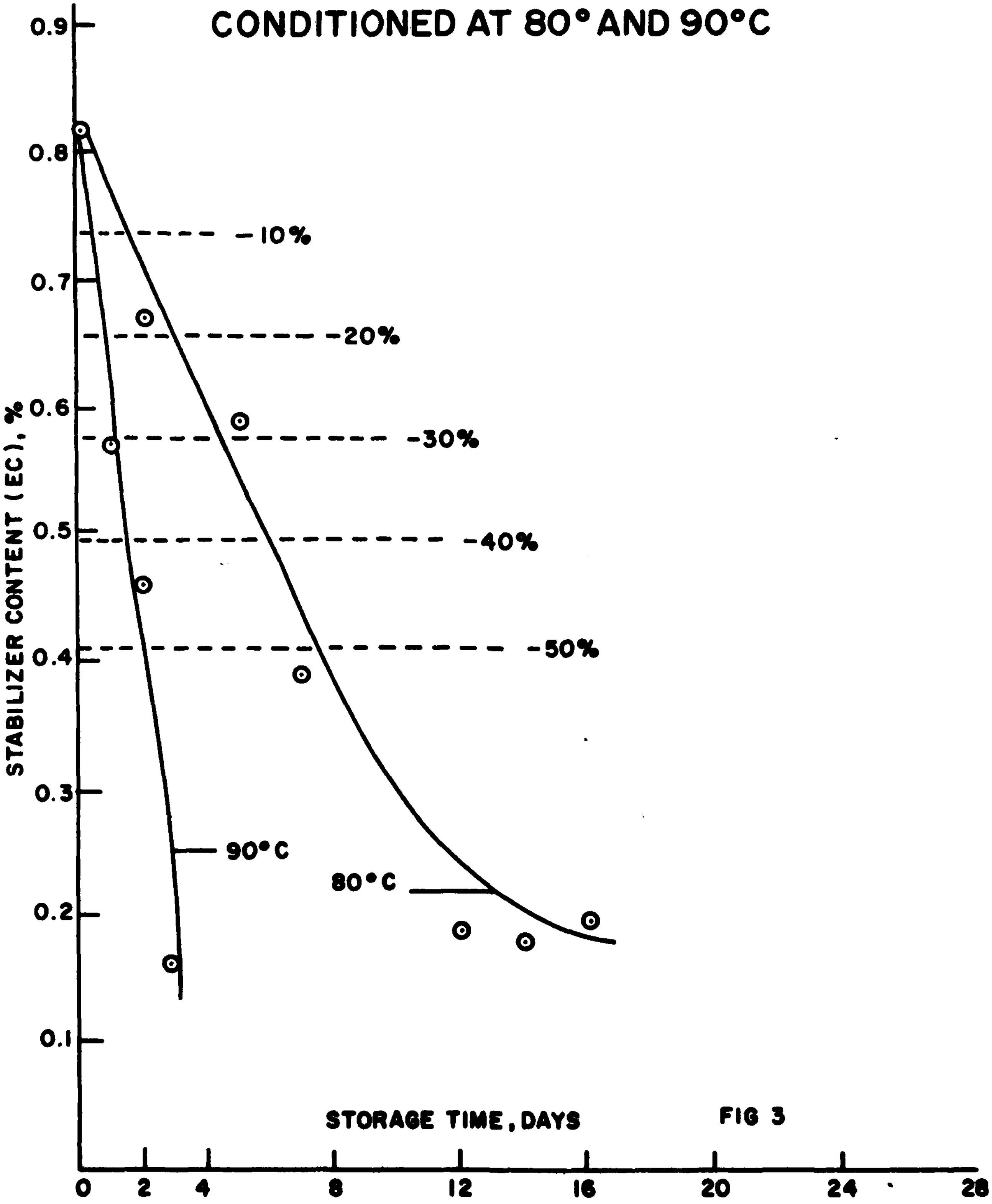


FIG 3

STABILIZER DEPLETION RATE FOR M9 PROPELLANT CONDITIONED AT 60° AND 70°C

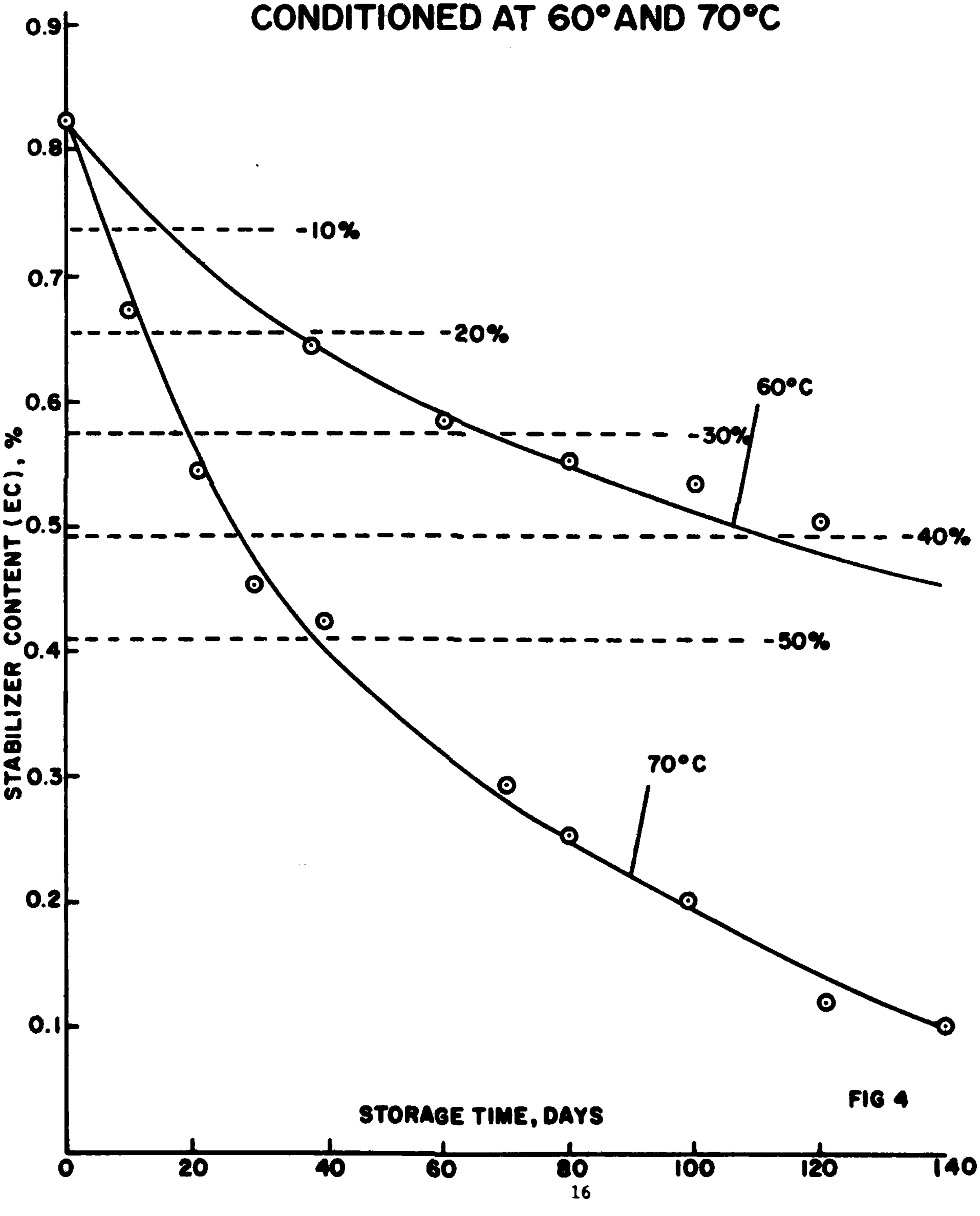
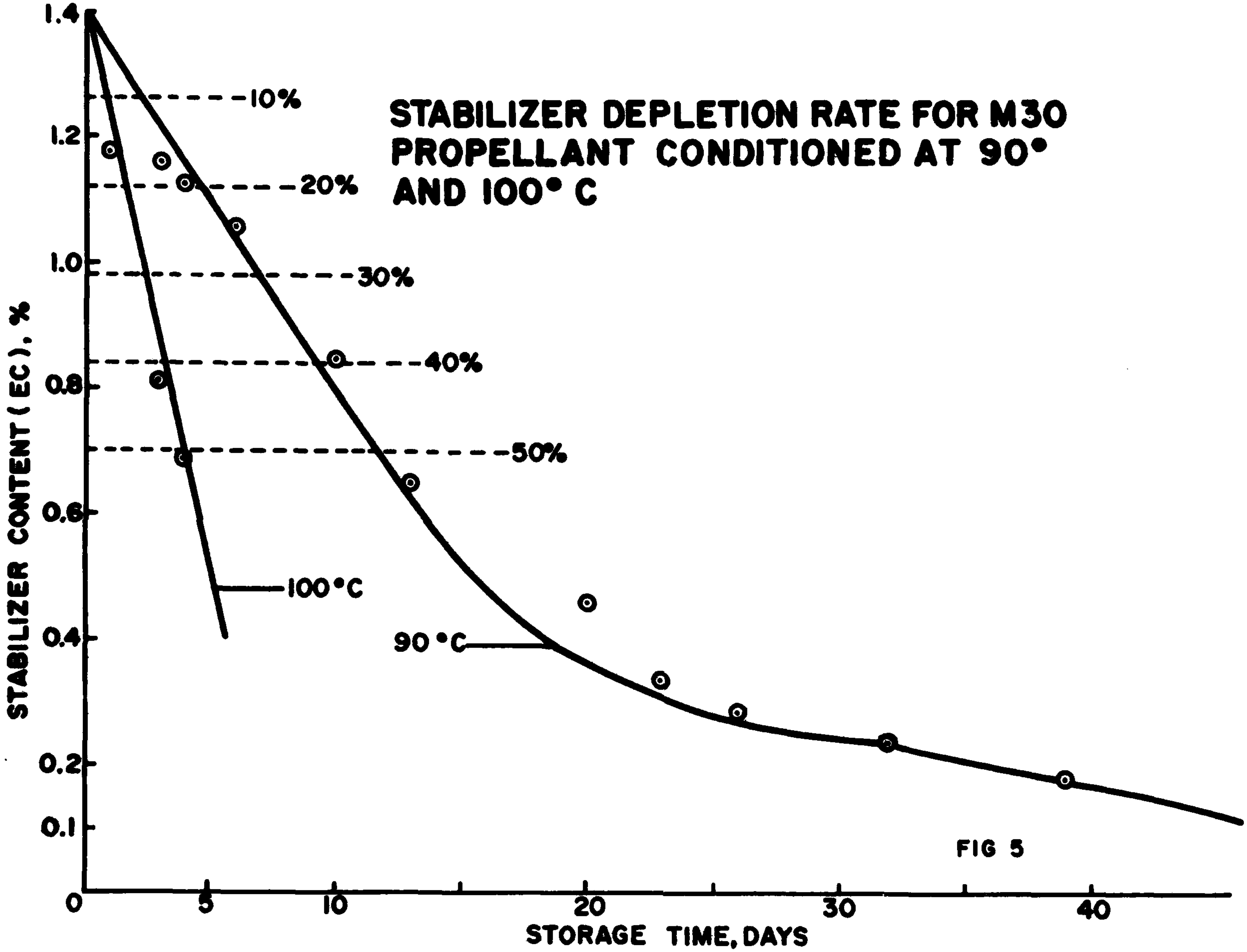
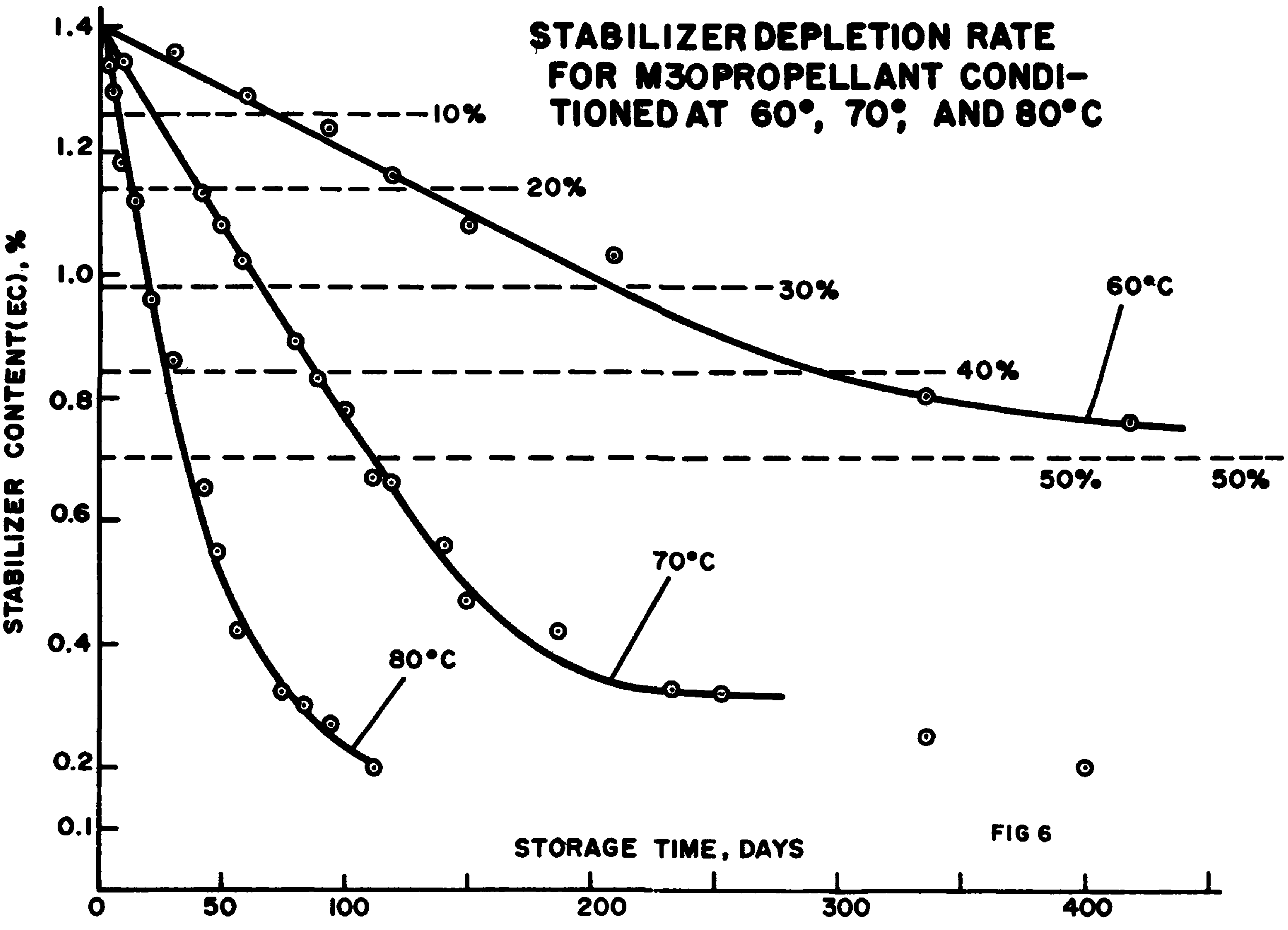


FIG 4



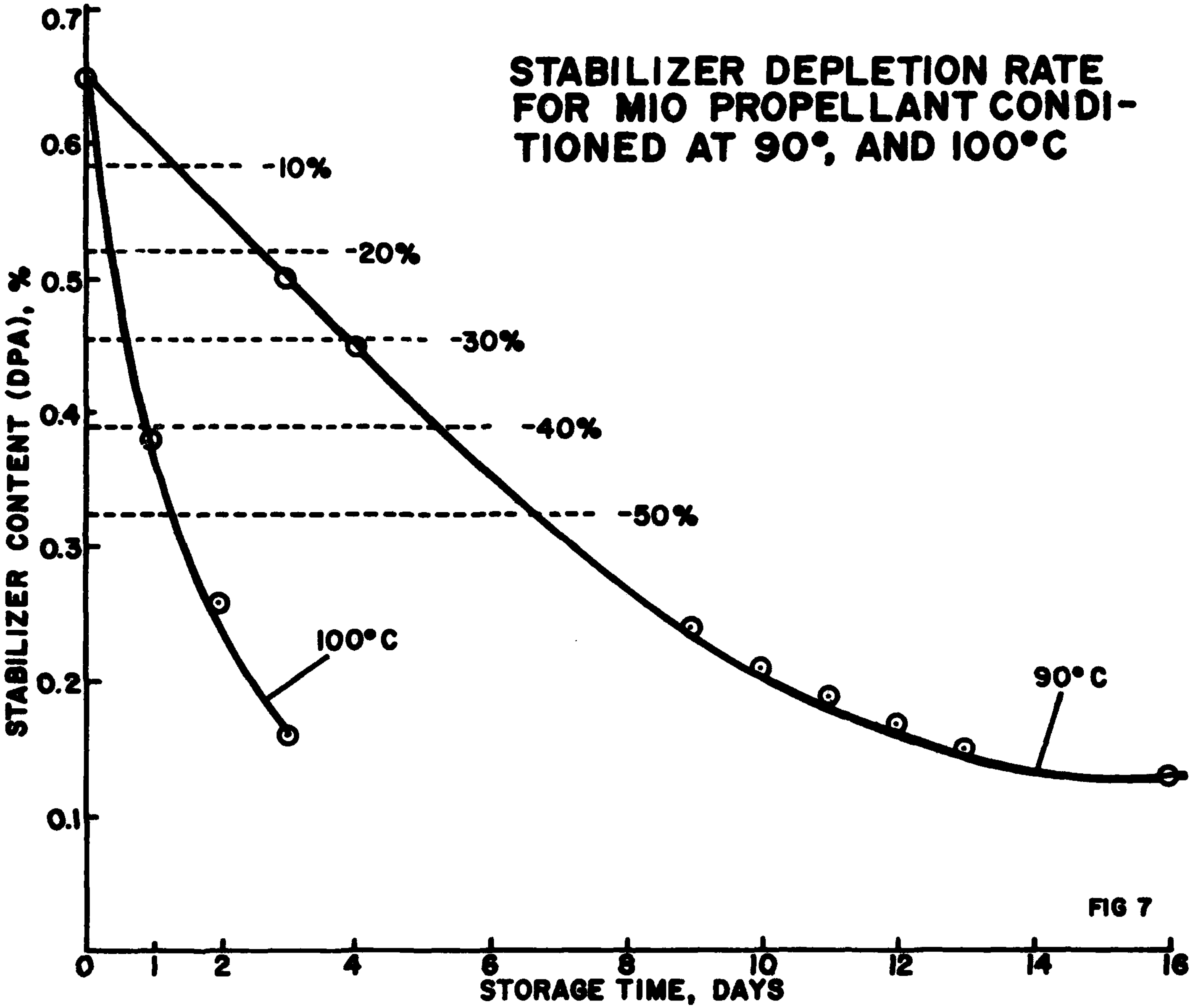
STABILIZER DEPLETION RATE FOR M30 PROPELLANT CONDITIONED AT 90° AND 100° C

FIG 5



STABILIZER DEPLETION RATE FOR M30 PROPELLANT CONDITIONED AT 60°, 70°, AND 80°C

FIG 6



STABILIZER DEPLETION RATE FOR MIO PROPELLANT CONDITIONED AT 90°, AND 100°C

FIG 7

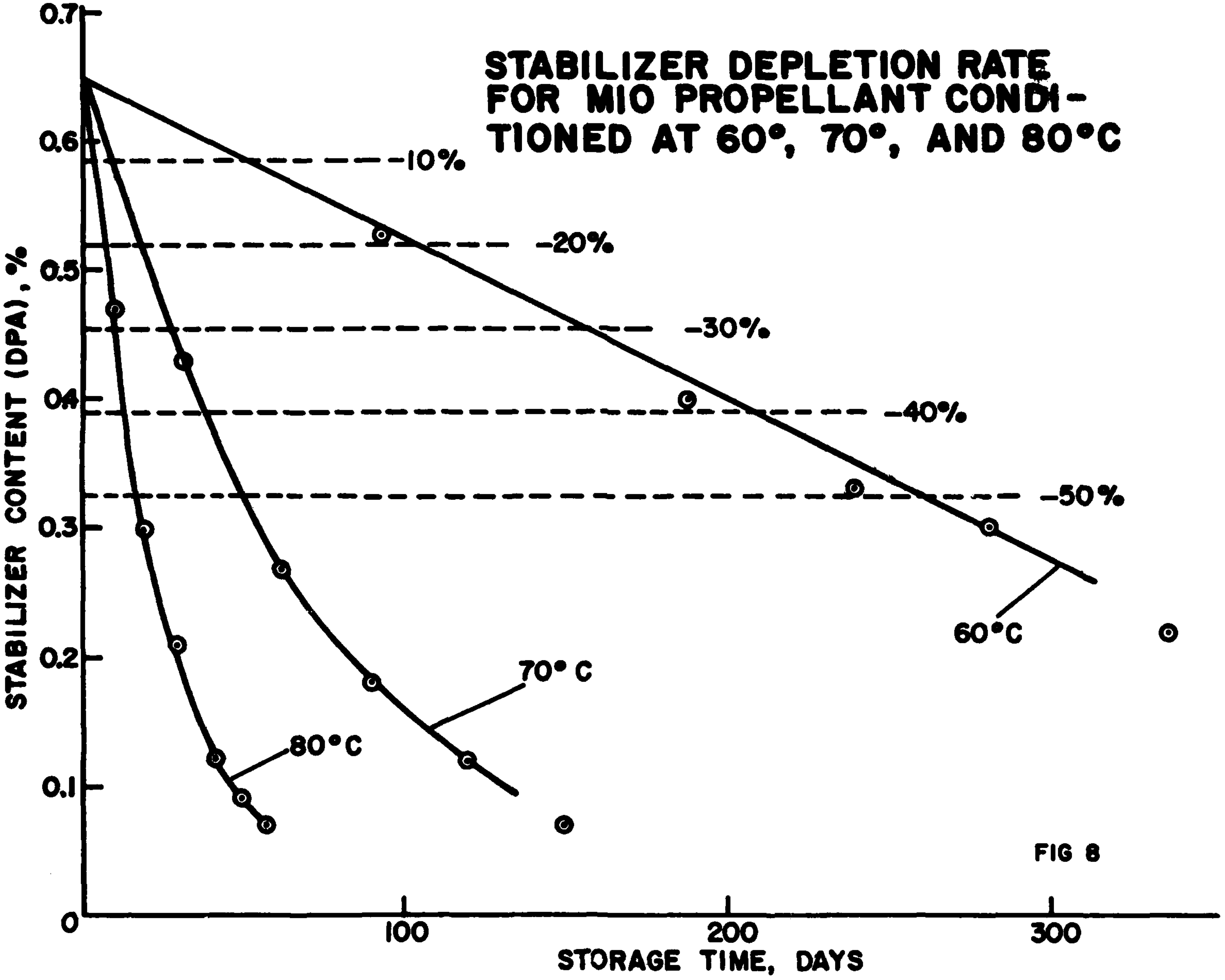
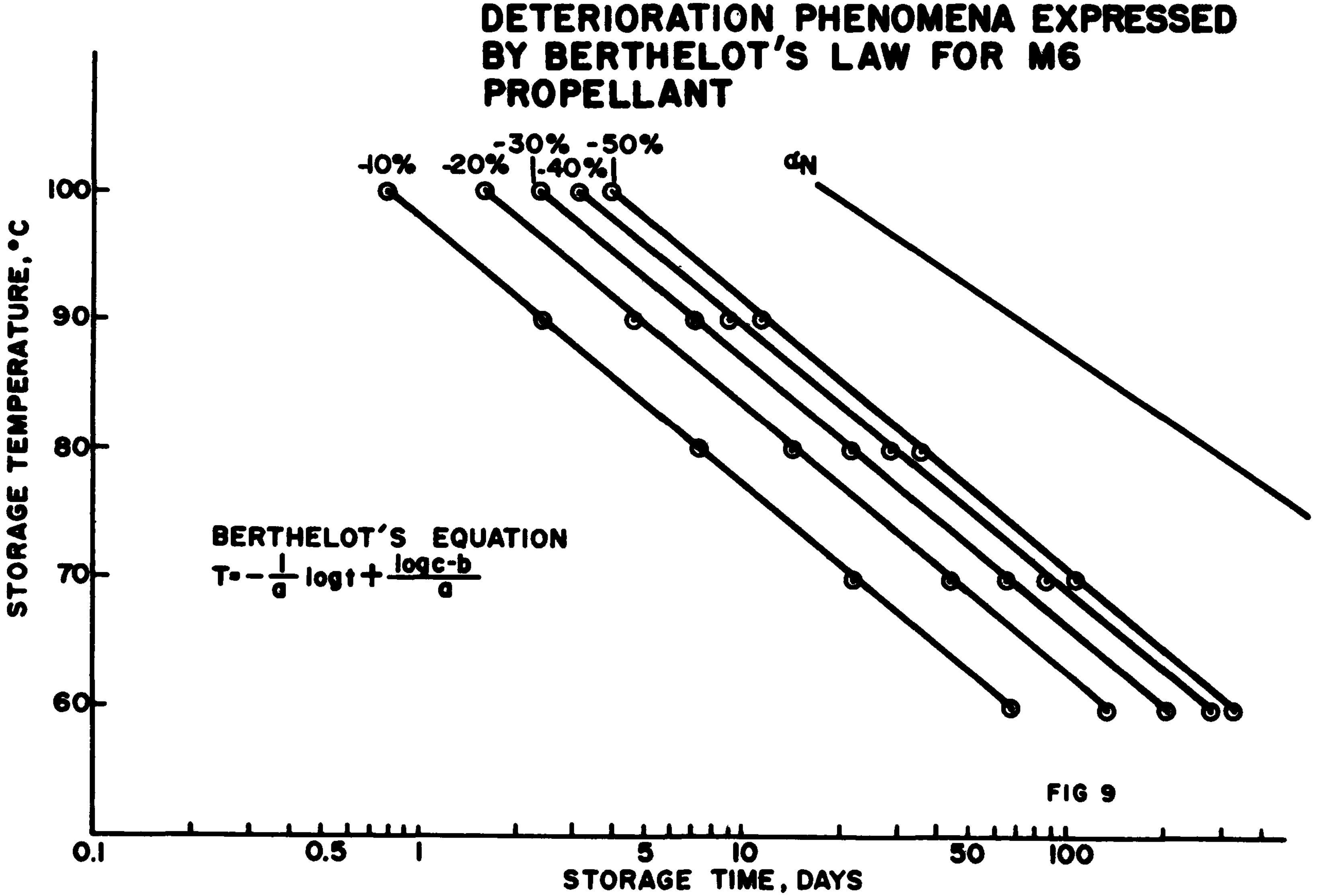
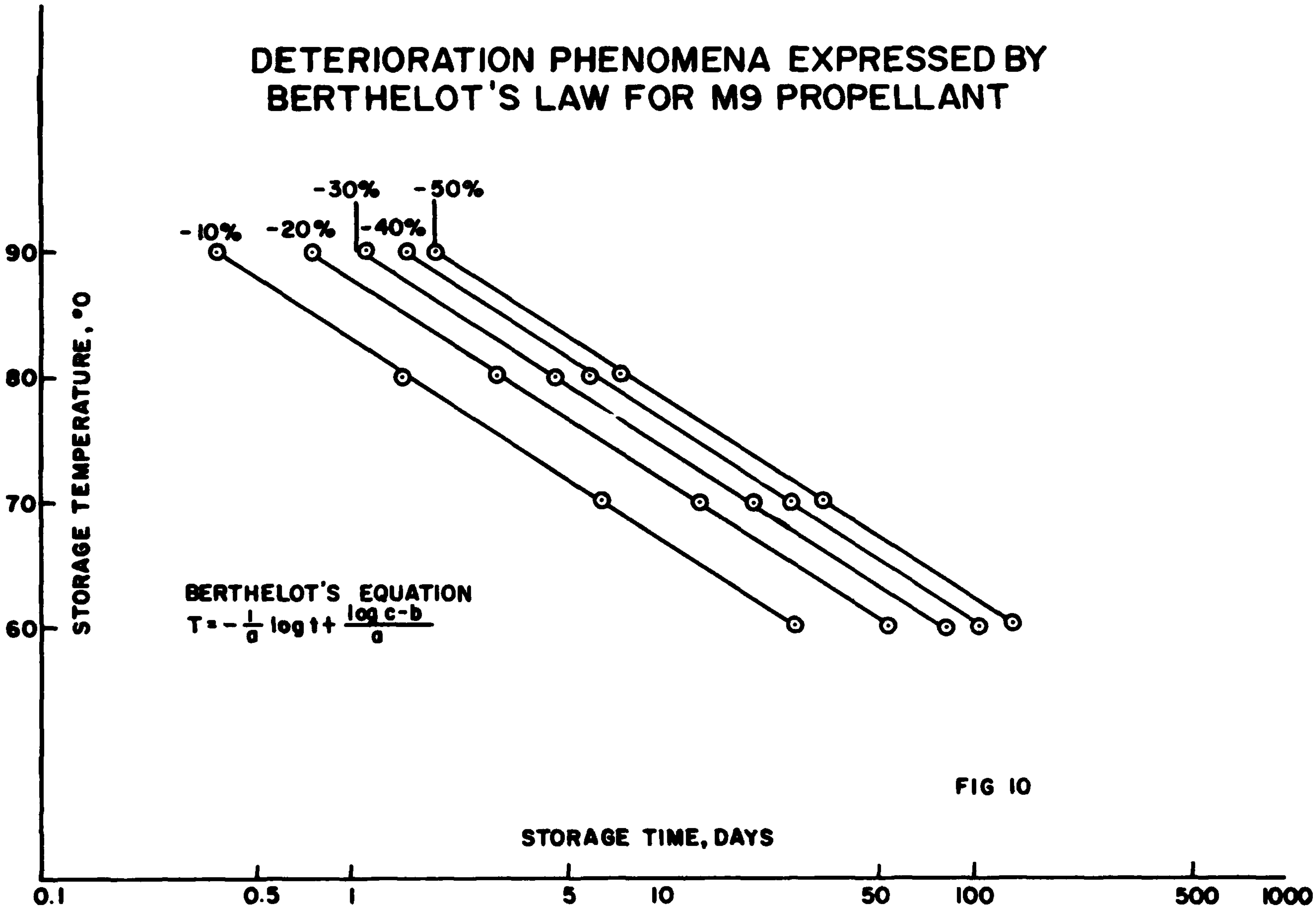

STABILIZER DEPLETION RATE FOR M10 PROPELLANT CONDITIONED AT 60°, 70°, AND 80°C

FIG 8



DETERIORATION PHENOMENA EXPRESSED BY BERTHELOT'S LAW FOR M6 PROPELLANT

FIG 9



DETERIORATION PHENOMENA EXPRESSED BY BERTHELOT'S LAW FOR M9 PROPELLANT

FIG 10

DETERIORATION PHENOMENA EXPRESSED BY BERTHELOT'S LAW FOR M30 PROPELLANT

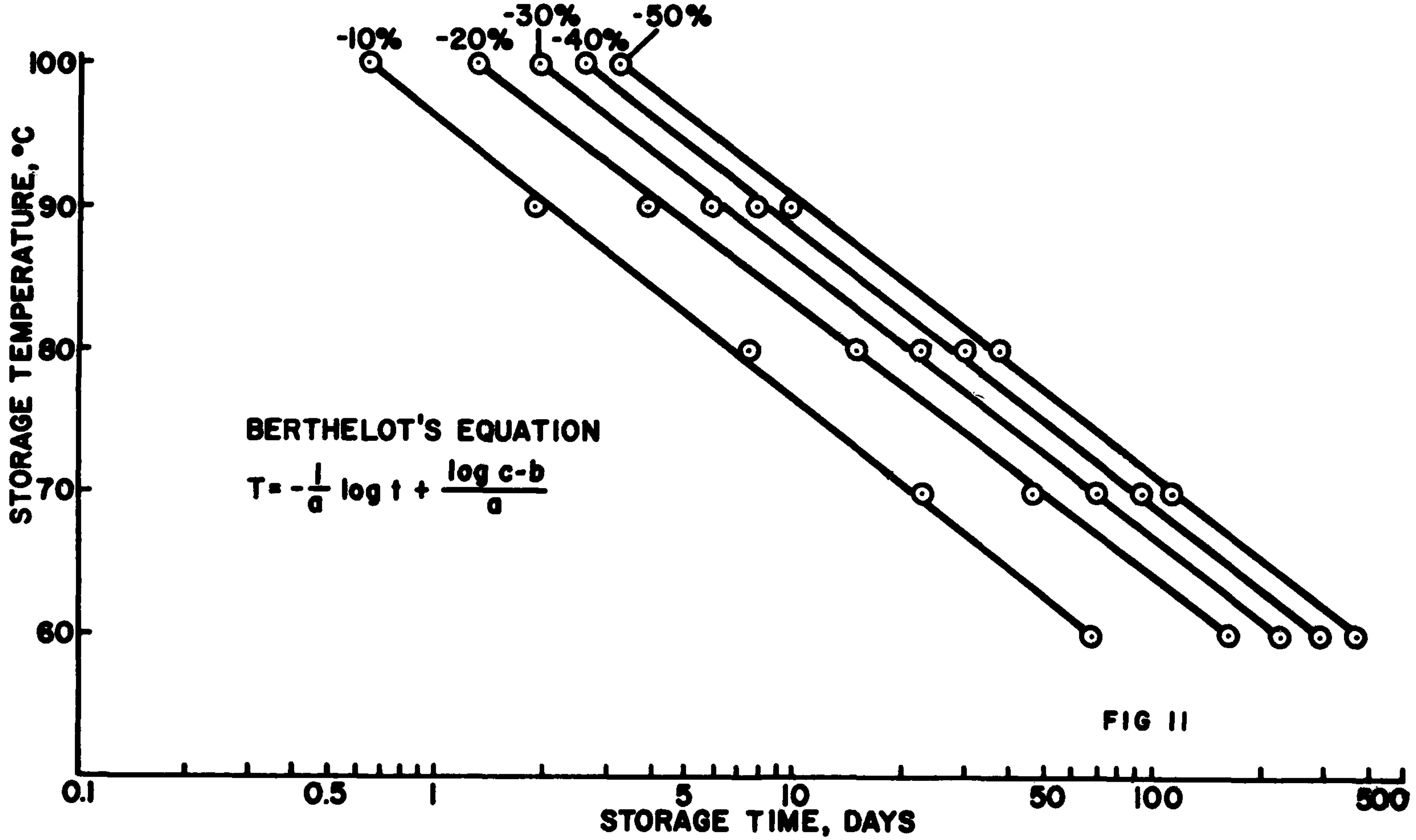
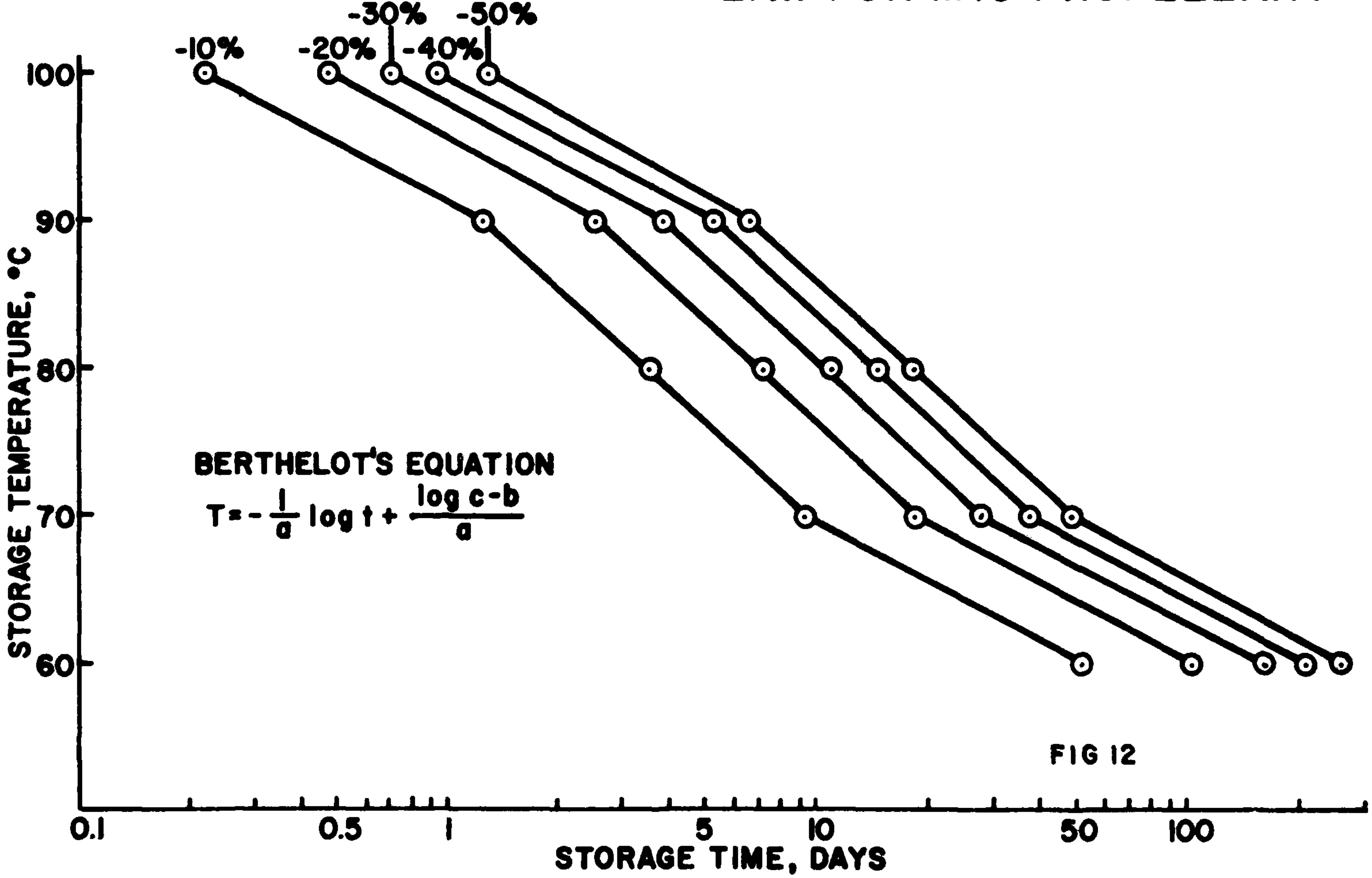


FIG 11

DETERIORATION PHENOMENA EXPRESSED BY BERTHELOT'S LAW FOR M10 PROPELLANT



BERTHELOT'S EQUATION

$$T = -\frac{1}{a}\log t + \frac{\log c - b}{a}$$

FIG 12

COMPARING DATA FROM ARRHENIUS VS BERTHELOT'S EQUATIONS

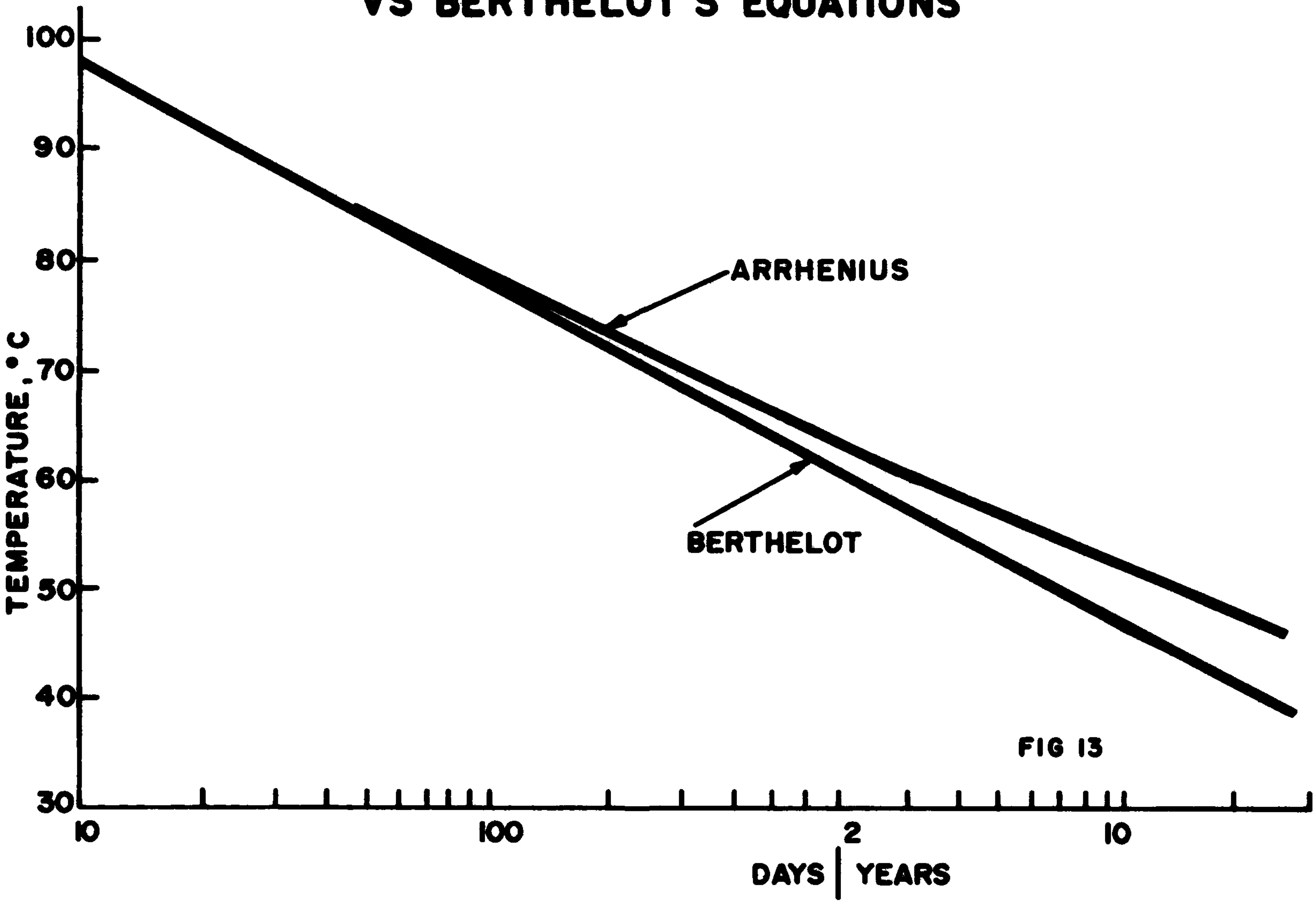


FIG 13