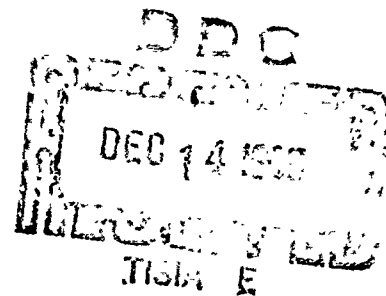


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THE PRODUCTION OF VISIBLE LIGHT BY
THE THORIA-CERIA MANTLE; PHYSICAL
CHARACTERISTICS AND A PROPOSED
THEORY OF THE OCCURRING MECHANISMS
AND PROCESSES

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ABSTRACT

An explanation of the production of visible light by a thoria-ceria mantle is presented. It is proposed that the thoria acts as a chemical catalyst and localizes the exothermic reaction within the mantle structure.

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BACKGROUND

The development of long burning flares for visual signal or marker purposes has long been desired for in-service applications. Efforts in this field have produced colored flares which burn at the rate of one minute per inch¹ and phosphorus flares which burn approximately two minutes per inch.

However, to produce a signal which would burn continuously for four hours or more with these compositions, the design problems and volume requirements of the associated hardware are prohibitive for an in-service use.

Electrical systems have been attempted. Some of the associated problems with this method of visual output quickly eliminated its use. The bulb filaments were too fragile to withstand the service applications and the candlepower output of these devices was too low for effective signal or marker use.

A system, which seems to meet the necessary requirements of long burning time and satisfactory visual output, may be available by adapting the Welsbach mantle for signal purposes. An initial investigation indicated that a two-pound tank of propane is capable of producing a 100 candlepower source for 10 hours. By changing the size of the mantle, it seems feasible to produce a signal of 250

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candlepower for a duration of four hours.

Further study of this system was deemed necessary.

LITERATURE SEARCH

The Welsbach mantle consists of a mixture of approximately 1% cerium dioxide and 99% thorium dioxide. Frequently, these materials are referred to as ceria and thoria. Normally, a hydrocarbon-air mixture is used as the flame source for these mantles. The exact mechanisms involved in the production of visible energy are not known, however, many explanations have been made.

"The extraordinary luminosity of thorium oxide impregnated with a little cerium oxide is attributed to the fact that thorium oxide radiates but little heat, and so is heated to a high temperature in the Bunsen flame, whereas the admixed cerium oxide has the property of omitting a very intense light at high temperatures. Pure cerium oxide luminesces but little when introduced into the Bunsen flame, for the reason that it has the property of radiating not only much light, but also much heat simultaneously; as the emission of light increases strongly with temperature, and pure cerium oxide does not attain a very high temperature in the Bunsen flame because of its strong radiation of heat, its high emissivity for light can only come into play when the cerium oxide is embedded, in relatively small amount in

thorium oxide, with its low emissivity for light and heat. Only in this way can it attain the high temperature necessary for strong luminosity in the Bunsen flame. In general, a mixture of 99% thorium oxide with 1% cerium oxide has shown itself to be the most satisfactory. For a mantle prepared with this mixture, the maximum emission lies in the short-wave length part of the spectrum. For this reason, the incandescent gas light has a white color, tending towards greenish, as contrasted with the more reddish light of other incandescent bodies." ²

Another reference claims that the excitation of the mantle is the effect of catalytic recombination of radicals and hydrogen atoms at the interface of the flame and mantle.³

To sum up the work of other investigations in this area, "in all -- investigations -- on the Welsbach mantle, the doubts and controversies over the existence of luminescence seem to hinge on (the) uncertainty of the determination of the solid (mantle) temperature. Without knowing this temperature, it is not possible to determine whether Kirchhoff's law is violated." ⁴

Another reference indicated "the mantle is not an effect of ⁵ ordinary emissivity:"

1. The surface shows a fatigue effect.
2. The radiance violates Kirchoff's law by a factor of several hundred.
3. There are upper and lower temperature limits.
4. There is a brief afterglow.
5. Activators are very effective - the same ones as for ultraviolet and cathode-ray excitation.

It is now apparent, after conducting a basic literature search, that there exists vast differences of opinions and theories as to the phenomenon of the production of visible energy by the thoria-ceria mantle. Most of the differences appear to originate because of the assumption that the mantle is no higher in temperature than the maximum flame temperature. The lack of knowledge, as to what the mantle temperature actually is, has prompted the generation of theories and explanations where it became necessary to coin terms such as cold light, chemiluminescence and candoluminescence in order to explain this phenomenon.

PHYSICAL CHARACTERISTICS OF A THORIA-CERIA MANTLE

Using a Perkin-Elmer Rapid Scan Monochromator, Model 108, the relative intensity distribution of the visible portion of the spectra from a commercial thoria-ceria mantle was obtained* using a propane-air mixture as the flame source. This distribution is shown in Figure 4. The statistical fitting of this data by the least squares method indicated a temperature of 2960°K, with a constant emissivity in the region of the spectra investigated.** Measurements of the color temperature at 650 mμ was taken using an optical pyrometer manufactured by the Pyrometer Instrument Company and a temperature of 1713°K was indicated. The calculation of the emissivity of the mantle based on the two temperature measurements of 650 mμ indicates an emissivity of 0.0043.

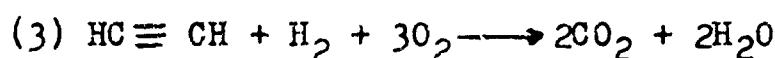
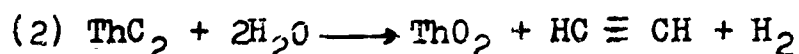
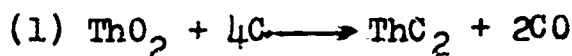
Since the mantle is completely opaque in the region of the wave lengths under consideration, this would indicate a reflectivity of 0.9937.

* See Appendix A

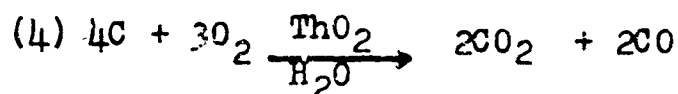
** See Appendix B

PROPOSED THEORY OF THE MECHANISMS AND PROCESSES OCCURRING
IN A THORIA-CERIA MANTLE

It is proposed that the thoria (thorium dioxide) serves as a catalyst in the formation of acetylene, olefins and hydrogen in the mantle via a thorium carbide intermediate and subsequent hydrolysis of this intermediate. Oxidation of these products then occur either within the mantle or on the exterior surface of the mantle. The proposed reaction mechanism is demonstrated below:



The overall reaction would be



By the proposed catalytic mechanism, two requirements of the fuel should be that both free carbon and water must be present for the mechanism to occur as proposed. The water actually would serve as a catalyst in this reaction also, for it enters and leaves the reaction zone at exactly the same rate and is in the same chemical form before and after the reaction.

This proposed mechanism would suggest that acetylene and hydrogen would be oxidized in the very immediate area of the mantle. If the oxidation process occurs within the mantle, the heat generated would be absorbed by the mantle for the most part, with subsequent radiant release of energy by the mantle. If the oxidation process occurs on the exterior surface of the mantle, some of the heat released would be absorbed by the mantle and released radiantly.

The thoria's chief purpose then would appear to be that it acts to localize the principal exothermic reaction within the mantle, thus allowing a locally higher temperature to exist than is normally possible in the propane-air flame.

The ceria's (cerium dioxide) chief purpose is to emit the energy gained by the mantle from the exothermic reaction in a manner that is more conducive to the production of white light.

INFORMATION SUPPORTING THE PROPOSED THEORY

The catalytic properties of thoria have been demonstrated in many different reactions.⁶ In the majority of the reactions, carbon-hydrogen-oxygen compounds are passed over heated thoria and the normal products are olefins, carbon monoxide, carbon dioxide and water.

In the Fischer-Tropsch process of converting coal or coke to gasoline or petroleum-like products, a cobalt-thorium dioxide catalyst has successfully been used.⁷

Thorium carbide, the proposed intermediate, is formed by heating thorium dioxide with carbon.⁸ This compound, upon hydrolysis, yields principally acetylene, ethylene, methane and hydrogen, and is believed to contain $(:C:::C:)^{-2}$ groups, which accounts for the primary products of acetylene and hydrogen.^{9,10}

If thorium carbide is a main constituent of the mantle during the combustion processes, then the maximum temperature of the mantle should approach the melting point of the thorium carbide as a limit due to the heat of fusion of the carbide.¹¹ The melting point of thorium carbide is 3046°K .¹² The measured temperature of a thoriaceria mantle was only 86°K lower than this temperature.

Another temperature limitation, that would be imposed on the proposed mechanisms and processes, is the theoretical

maximum temperature possible for an acetylene-oxygen reaction, since this is the proposed main product oxidized within or upon the exterior of the mantle. Dean lists this temperature as being 3323°K ¹³ for the acetylene-oxygen maximum temperature.

Since the theoretical maximum temperature for the propane-air flame is 2198°K ¹⁴, the fact that a significantly higher mantle temperature exists (2960°K) can be explained by the proposed theory. Likewise, it is not necessary to account for the white light radiated by the mantle as some strange phenomenon which must be titled "candoluminescence" or "chemiluminescence." It can readily be explained by the normal electromagnetic radiation laws as simply thermal radiation.

CONCLUSIONS AND RECOMMENDATIONS

It is the conclusion of the author, that the proposed theory of the mechanisms and processes that occur in the thoria-ceria mantle are quite feasible. The theory does not rely on any process or mechanism that has not been observed individually.

If this theory is correct, it is possible to generate a red or green light by preparing a mantle of thoria and strontium oxide or barium oxide, respectively, assuming that the vapor pressure of these alkaline earth oxides, at the temperatures prevalent, would be low enough to have a stable mantle. Both of these oxides have rather specific band emissions in the visible and should afford a method of producing a long burning signal producing colored light.

It is recommended that:

- a. Mantles be prepared and investigated that consist of thoria and barium or strontium oxides and,
- b. Emission studies in the ultraviolet region of the spectra of the propane-air flame and of the mantle be initiated for comparison of the amounts of olefinic and acetylenic compounds present, with and without the mantle.

APPENDIX A

METHOD OF OBTAINING THE RELATIVE INTENSITY DISTRIBUTION
OF THE THORIA-CERIA MANTLE

Using a Perkin-Elmer Rapid Scan Monochromator, Model 108, with an IP 27 photomultiplier, the spectra of the thoria-ceria mantle and a standard Illuminant A bulb was obtained. (See Figures 1 and 2.)

Knowing the actual energy distribution of Illuminant A¹⁵ (see Figure 3) it was possible to determine a response for the total system. Applying this response to the recorded distribution for the thoria-ceria mantle, a relative energy curve for the emitted light of the mantle was obtained (see Figure 4).

APPENDIX B

THE DETERMINATION OF THE TEMPERATURE AND EMISSIVITY
OF THE THORIA-CERIA MANTLE

From Planck's equation,

$$(5) \quad I = \epsilon C_1 \lambda^{-5} (e^{\frac{C_2}{\lambda T}} - 1)^{-1}$$

where - $e^{\frac{C_2}{\lambda T}} \gg 1$, the following form of the equation is obtained:

$$(6) \quad \ln I + 5 \ln \lambda + \frac{C_2}{\lambda T} = \ln \epsilon + \ln C_1$$

When the emissivity of the source is constant within the wave length region considered, the right side of the equation, $\ln \epsilon + \ln C_1$, is constant. Therefore,

$$(7) \quad \ln I_1 + 5 \ln \lambda_1 + \frac{C_2}{\lambda_1 T} = \ln I_2 + 5 \ln \lambda_2 + \frac{C_2}{\lambda_2 T}$$

Solving for T,

$$(8) \quad T = C_2 (\lambda_2 - \lambda_1) \left(\frac{1}{5 \ln \frac{\lambda_1}{\lambda_2} + \ln \frac{I_1}{I_2}} \right)$$

As the equation indicates, only the ratio of the intensities of the two wave lengths is required. Therefore, although the actual intensity is not known, the relative intensity of each wave length is known, and the calculation of the temperature of the emitting source is obtainable.

The determination of the emissivity was made by measuring the black body temperature of the mantle by

use of an optical pyrometer and using this temperature, T_B , and the emissivity, $\epsilon_B = 1.00$, in equation (9).

$$(9) \ln \epsilon_M = \left(\frac{C_2}{\lambda} \right) \left(\frac{T_B - T_M}{T_B T_M} \right) + \ln \epsilon_B$$

Equation (9) was derived from equation (6) in the following manner:

$$(10) \ln I + 5 \ln \lambda - \ln C_1 = \ln \epsilon - \frac{C_2}{\lambda T}$$

Since I , the intensity, λ , the wave length, and C_1 , are constant, a relationship for determining the emissivity, ϵ_M , is derived by letting

$$(11) \ln \epsilon_B - \frac{C_2}{\lambda T_B} = \ln \epsilon_M - \frac{C_2}{\lambda T_M}$$

where λ , the wave length, is the wave length of light observed in the optical pyrometer. Rearranging equation (11) yields equation (9).

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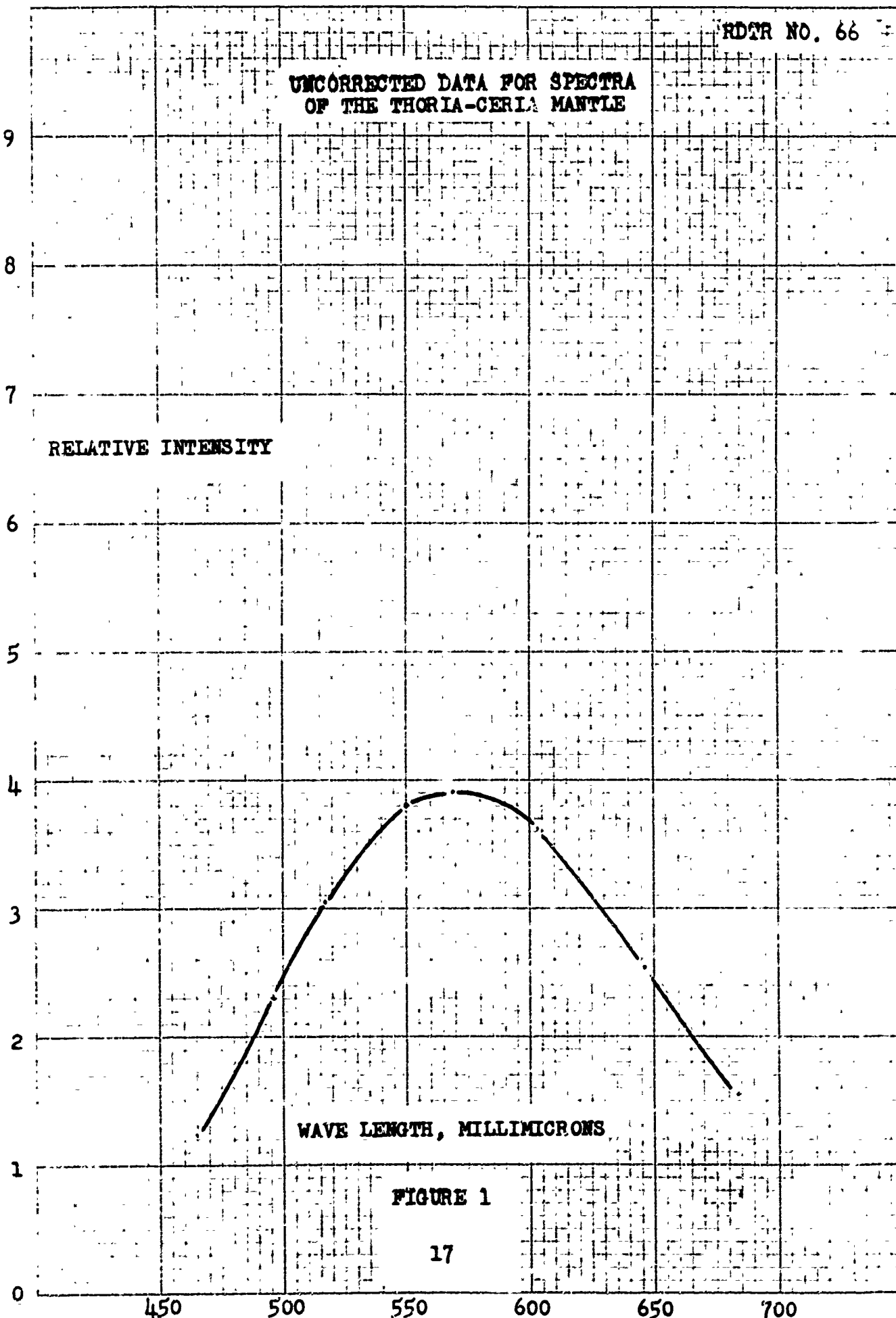
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UNCORRECTED DATA FOR SPECTRA
OF THE THORIA-CERIA MANTLE

RELATIVE INTENSITY

WAVE LENGTH, MILLIMICRONS

FIGURE 1



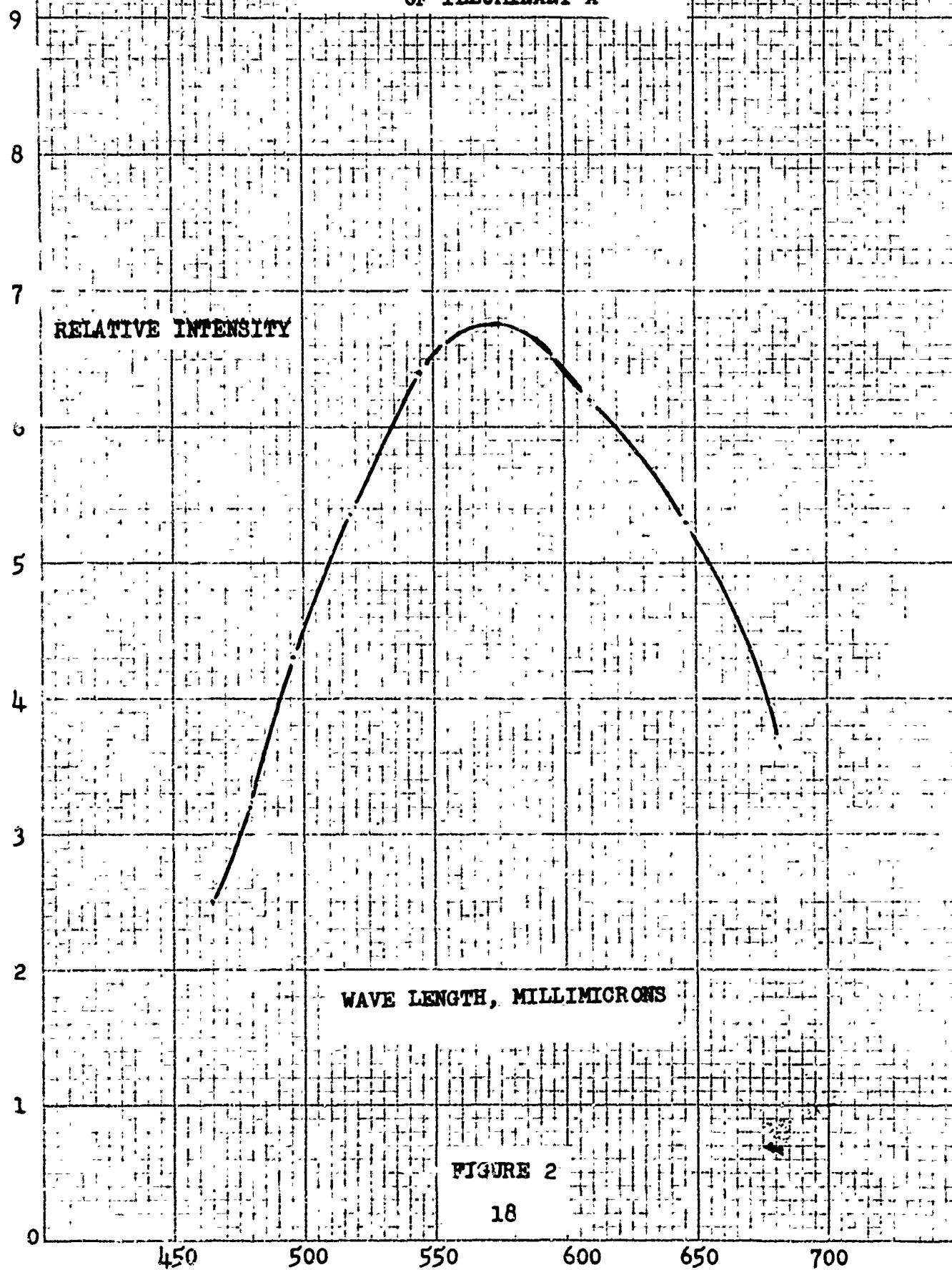
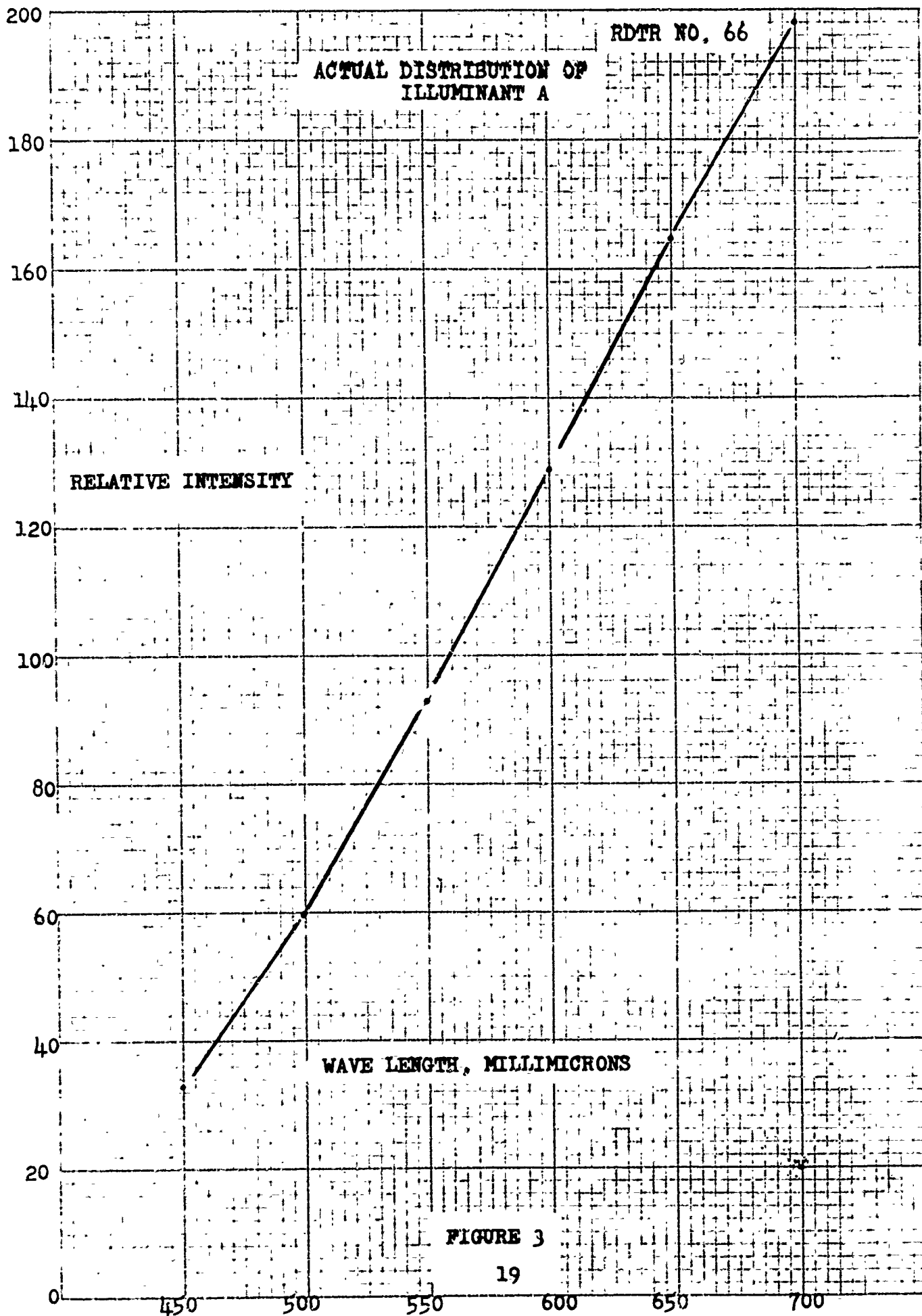


FIGURE 2

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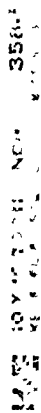


FIGURE 4

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