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MINISTRY OF AVIATION

EXPLOSIVES RESEARCH & DEVELOPMENT ESTABLISHMENT

REPORT No. 26/R/62

The Stability of Colloidal Propellants: Part 6: Resorcinol as a Propellant Stabiliser

J.W. Grindlay
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with

REVIEW ON

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Appendix: The Determination of Resorcinol

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The Stability of Colloidal Propellants: Part 6:
Resorcinol as a Propellant Stabiliser

by J.W. Grindlay and G.J. Jeacocke

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Appendix: The Determination of Resorcinol

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1. SUMMARY

The fate of resorcinol in propellants of the normal and composite modified types on accelerated aging (as opposed to storage at ambient temperatures) has been investigated. The results have been correlated with those obtained from synthetic mixtures.

A study of the behaviour of nitrosated, nitrated, and some polynuclear, derivatives of resorcinol, on column chromatography, with an investigation into the variations in ultraviolet spectra of these derivatives when in hydroxylic solvents having different pH values, has permitted their quantitative recognition in propellants.

The behaviour of resorcinol with dinitrogen tetroxide has been investigated and, using synthetic mixtures, an unsuccessful attempt has been made to correlate the rate of loss of resorcinol with the known rate of decomposition of nitroglycerine.

Propellants containing resorcinol as part of mixed stabiliser systems have been examined, and relative rates of consumption determined.

2. INTRODUCTION

Resorcinol is used as a secondary stabiliser and burning-rate booster in composite modified propellants. A knowledge of the degradation products from a stabiliser permits conclusions to be drawn regarding the mechanism of the stabilisation reaction. This report describes work carried out in this connection.

3. EXPERIMENTAL

3.1 Examination of Resorcinol-containing Propellants after Heating

3.1.1 Appearance

All samples assume a red colour after a few days at 80°C; on more prolonged heating a dark red sublimate is produced.

3.1.2 Extraction Procedures

Dichloromethane is an effective solvent for resorcinol and its nitro and nitroso derivatives; it was therefore used for the first extraction of all samples examined. Part only of the red material is removed by this solvent, the non-extracted portion being firmly held by the nitrocellulose residue; it can be extracted by treatment with more powerfully hydroxylic solvents, ethanol, methanol, and water, in amounts increasing in this solvent order.

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In contrast to the residues obtained from propellants containing other stabilisers (carbamate, 2-nitrodiphenylamine) which are generally just "off white", the residues left after the vigorous extraction mentioned above were still highly coloured; this colour persisted even after the residues had been taken up in acetone and reprecipitated.

3.1.3 Column Chromatography

For a preliminary examination of adsorption characteristics, "disc chromatography" (Fig.1A) was used. This technique is useful since a complete chromatogram can be obtained with only a few drops of solution and information concerning developing agents is easily acquired. Further confirmation of the identity of the bands was obtained by the use of streak reagents.

After this, conventional column chromatographic techniques were adopted, using, either the dichloromethane extract, or a benzene or ethanol solution of the residue obtained by evaporation of the dichloromethane solution. Full details of the apparatus are given in Fig.1B.

When it was found that some components of the extract were present in very small amounts, the scale of the chromatography was increased. In this, tubes 2 inches in diameter and 18 inches long were used. These could deal with the extract from 50 g. of propellant, facilitating the setting up of mass balances for the stabiliser system. Table 1 shows some combinations of adsorbent, solvent and developer used.

TABLE 1

	Adsorbent	Solvent	Developer
A	Silicic acid: Celite = 2:1	Benzene or dichloromethane	Benzene/petroleum ether (40-60°), Petroleum ether/diethyl ether, Diethyl ether.
B	Activated alumina	Ethanol	Methanol with increasing proportions of water (2-25% vol/vol)

Silicic acid:celite is effective in separating the red components from the propellant extract, since they are very strongly adsorbed on this medium. Using activated alumina the more acidic nitroresorcinols are retained and the red components readily eluted. A convenient scheme of separation is thus available, especially as the nitroresorcinols can be "developed" by using methanol with increasing water content.

/3.1.4

3.1.4 Streak Reagents

To locate nitroglycerine on chromatographic columns after drying and extrusion, a solution of diphenylamine in concentrated sulphuric acid is used. A dark blue coloration indicates the position of the nitroglycerine band.

Similarly, a solution of ceric nitrate in 2 N nitric acid can be used to indicate the presence of resorcinol by the production of a reddish-brown colour.

3.1.5 Composite Modified Propellant containing both Resorcinol and 2-Nitrodiphenylamine

A preliminary investigation was carried out using a sample of the nominal composition:

Nitrocellulose	22.8	per cent
Nitroglycerine	26.2	" "
Triacetin	6.0	" "
Aluminium	17.0	" "
Ammonium perchlorate	25.6	" "
2-Nitrodiphenylamine	1.0	" "
Resorcinol	1.5	" "

Aliquots (approx. 2 g.) of the original material, and of the same material after 15-days heating at 80°C, were extracted with dichloromethane; this was subsequently removed by evaporation and the residues redissolved in benzene. The resulting solutions were chromatographed using procedure A (Table 1).

The chromatogram of the extract from the heated sample contained a narrow, reddish-coloured band of strongly adsorbed material. This was eluted with ethanol and, after removal of the solvent, appeared as a sticky red deposit which dissolved readily in water giving a red solution. This solution became purple on the addition of alkali. Examination of the u.v. spectrum of the aqueous solution confirmed the presence of resorcinol, and showed that the red colour was due to strong absorption at 570 mμ.

Owing to the presence of 2-nitrodiphenylamine, and possibly its degradation products, it was not possible to say whether any nitrated or nitrosated derivatives of resorcinol were present.

The stabiliser contents of samples of the heated propellant were determined, the results, together with those for the unheated material, being given below (p. 4).

/TABLE 2

TABLE 2

Sample	Resorcinol, %	2-Nitrodiphenylamine, %
Original	1.3	0.93
2 weeks at 80°C	0.52	0.92
3 weeks at 80°C	0.02	0.83

Similar results were also obtained with composite modified propellants having the same stabiliser combination but differing nominal compositions.

3.1.6 Composite Modified Propellant containing Resorcinol only

Since, as appears from the above results, resorcinol is almost entirely consumed before any attack on the 2-nitrodiphenylamine takes place, and as this latter material complicates the analytical procedures, it was decided to carry out a further investigation using a propellant containing resorcinol only. This had the nominal composition:

Nitrocellulose	22.1 per cent
Nitroglycerine	27.2 " "
Triacetin	6.6 " "
Aluminium	16.4 " "
Ammonium perchlorate	24.7 " "
Resorcinol	3.0 " "

Portions (approx. 60 g.) of this material were cut into small pellets, placed in loosely stoppered glass bottles and heated at 80°C for varying periods of time. After this a known amount (approx. 50 g.) was extracted with dichloromethane, the solvent removed, and the total weight of the extract obtained. This residue was then dissolved in benzene and chromatographed, using the larger columns, by procedure A. The following observations were made:

- (a) Development with benzene/petroleum ether: red band most strongly adsorbed, nitroglycerine, triacetin and a yellow band due to nitrated resorcinols held lower down the column.
- (b) Petroleum ether with increasing amounts of diethyl ether: incipient resolution of red band, other materials completely eluted.
- (c) Diethyl ether: red band resolved into two or three components depending on the history of the sample.

/By

By sectioning the extruded column and eluting the sections with ethanol, discrete fractions could be obtained. These however were again found to be heavily contaminated with resorcinol. Similarly the yellow fraction was found to contain nitroglycerine and triacetin which interfered with the u.v. spectra of the nitroresorcinols.

It was found possible to isolate the nitroresorcinols, either by dissolving the fraction in ethanol and chromatographing on alumina (procedure B, Section 3.1.3), or by extracting a solution of the fraction in chloroform with dilute aqueous alkali. Procedures for the identification and quantitative determination of these degradation products are described later.

The results from this exercise are collated in Table 3, named products being characterised qualitatively.

TABLE 3

Sample Heated at 80°C for:	Chromatographic Fractions from Methylene Chloride Extract	
	Composition of Yellow Band	Composition of Other Bands
2½ days and 1 week	N.G., triacetin, 4-nitro- resorcinol with some 2-nitro- resorcinol	Top: purplish-red band - aqueous solution red turning blue with alkali - not identified.
		2nd: orange-red band - aqueous solution red, turning bright red with orange fluorescence with alkali - identified as mainly resorcinol and resorufin.
2 weeks	ditto	Top: bluish-green band - aqueous solution red, alkaline colour similar to resorufin.
		2nd: purple band - aqueous solution red turning blue with alkali - not identified.
		3rd: orange-red band - identified as mainly resorcinol with some resorufin.
4 weeks and 5 weeks	ditto	Top: brown narrow band - not identified (not nitroso-resorcinol).
		2nd: red band - aqueous solution red turning blue with alkali - not identified.
		3rd: as 2nd.
		4th: orange-red - identified as resorcinol and resorufin.

/The

The possibility that the unidentified red and purple components, whose aqueous solutions turn blue with alkali, may contain resazurin can be eliminated, since the colour intensities, compared with that of pure resazurin (which has an extremely high molar extinction coefficient in alkaline solution), indicate the presence of a negligible amount. The bluish-green band from the "two weeks at 80°C" sample is interesting since it appeared also to be resorufin.

The resorcinol contents of the samples after heating, and that of the original material, were determined by the method given in the Appendix (p. 23). The results are given in Table 4.

TABLE 4

Sample	Resorcinol, %
Original	3.2
2½ days at 80°C	2.6
1 week at 80°C	2.0
2 weeks at 80°C	1.4
3 " " "	1.3
4 " " "	1.1
5 " " "	0.3

It was known that the fractions taken from the chromatographic columns ("red bands" Table 3) were heavily contaminated with resorcinol; nevertheless, even if they were assumed to be pure degradation products and a balance set up between total degradation products plus residual resorcinol, and original resorcinol, a serious discrepancy becomes apparent (residual resorcinol, 0.3; "red compounds", 1.5; nitroresorcinols, 0.1 per cent). The total is 1.9 per cent, against an original resorcinol content of 3.2 per cent.

A comparison between the amounts of material which can be extracted by dichloromethane from unheated and heated material is equally relevant. In the former case 35.1 per cent is extractable, while in the latter the value has dropped to 32.7 per cent. The residue from this type of extraction normally contains only nitrocellulose, aluminium, and ammonium perchlorate, the latter being extracted with ethanol; when the residues from the above extractions are so treated, an amount equal to 27.3 per cent of the original material is extracted from the unheated sample while from the heated sample 30.5 per cent is removed. Part of the original propellant is therefore being converted into dichloromethane insoluble, but ethanol soluble, material.

/3.1.7

3.1.7 Nitrocellulose-Resorcinol Mixtures

Nitrocellulose, with 4 per cent of its weight of resorcinol, was dissolved in acetone; aliquots of this solution were placed in wide-mouthed bottles and the solvent removed by heat and reduced pressure, leaving the nitrocellulose as a thin film. These samples were then heated at 80°C and the rate of fall of resorcinol content with time was determined.

With heating, a red coloration increased progressively while the resorcinol content fell at a rate comparable with that in the propellant (4.0 to 1.6 per cent in four weeks). 4-Nitroresorcinol, resorufin and a trace of 2-nitroresorcinol were identified.

The reaction mechanism in this simplified system appears therefore to be similar to that in the propellants.

3.2 Resorcinol, Nitrosoresorcinols and the Nitroresorcinols

3.2.1 Chromatographic Behaviour

Authentic samples of 4-nitroso, 2,4-dinitroso, 2- and 4-nitro, also 2,4- and 4,6-dinitro and 2,4,6-trinitroresorcinols were available, but, since the 4-nitroso, 2,4-dinitroso and 4,6-dinitro derivatives had not been detected in the preliminary work, they were not investigated here. The others were dissolved in benzene and their behaviour on silicic acid/celite investigated, using petroleum ether/diethyl ether 4/1 as the developer.

The 2,4-dinitro derivative was found to be most strongly adsorbed followed by the 2,4,6-trinitro, then resorcinol itself, after which came the 4, and then the 2-nitroresorcinol. Nitroglycerine and triacetin, however, interfere.

On activated alumina the acidic nitroresorcinols are strongly adsorbed, resisting development even by methanol containing 2 per cent of water; thus these can be separated from the easily eluted nitroglycerine, triacetin and polynuclear degradation products and subsequently developed using methanol with increasing proportions of water. It was found, particularly in the case of 2,4-dinitro resorcinol, that "double-zoning" sometimes occurred.

In non-polar solvents 2-nitroresorcinol produces a yellow band on both adsorbents; when using methanol as developer for alumina columns this changes to a characteristic purple colour. The same effect can be produced by extruding the silicic acid/celite on which this derivative is adsorbed and mixing a small portion intimately with alumina, when moistening with methanol produces the purple colour.

After development, drying, and extrusion, the columns were sectioned. Individual portions of the silicic acid/celite were extracted with ethanol, while water was used for the alumina.

3.2.2 Ultraviolet Spectrophotometry

Aqueous solutions of resorcinol and its derivatives were examined in the 220 to 450 mμ range. The curves are shown in Figs. 2, 3 and 4 and the wavelengths of the principal peaks given in Table 5 (p. 8).

/TABLE 5

TABLE 5

Compound	λ of Maximum, $m\mu$
Resorcinol	274
2-Nitroresorcinol	315
4-Nitroresorcinol	350
2,4-Dinitroresorcinol	392
4,6-Dinitroresorcinol	403
2,4,6-Trinitroresorcinol	393
4-Nitrosoresorcinol	297
2,4-Dinitrosoresorcinol	279

It has been mentioned that the nitroresorcinols are eluted from alumina columns with water. When 4-nitroresorcinol was chromatographed on, and eluted from, this adsorbent the resulting solution had a significantly different u.v. spectrum from that previously obtained. The principal peak was shifted from 350 to 406 $m\mu$.

Since the pH of distilled water which had been passed through a column of activated alumina was found to be approximately 10, this led to an investigation into the effect of the pH of the aqueous solution on the u.v. spectra of resorcinol and its derivatives. It was found that, in general, increase in pH caused a bathochromic shift of the principal peaks.

Table 6 (p. 9) shows the positions of the maxima in acidic and alkaline solutions, specimen absorption curves being given in Fig. 5.

Therefore, for positive identification, the pH of the solution must be carefully controlled. For example 2-nitro, 4-nitro and 2,4-dinitroresorcinol give completely unambiguous spectra at pH 4.5, a check at pH 7.5 confirms the 4-nitro derivative. Fig. 6, which shews "position of maxima versus pH" illustrates this point.

For quantitative work, the value C/D was determined at the appropriate pH value for each of the reference materials (C = concentration in mg/100 ml. and D = optical density at λ max); hence from the optical density (at λ max) of an "unknown", its concentration was found.

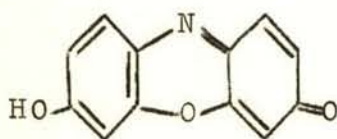
3.3 Resorufin and Resazurin

3.3.1 Preparation

Reference has already been made to the characteristic red colour assumed by heated propellants and nitrocellulose containing resorcinol. Resorufin and resazurin are reddish-purple dyestuffs which can be

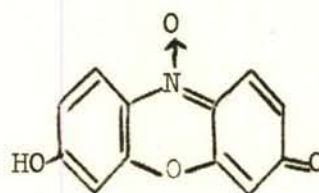
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produced under certain conditions by treating resorcinol with nitric and nitrous acids, and it was thought that these may be responsible for the colour changes mentioned above. These compounds are oxazones having the structures:



Resorufin

(7-hydroxyphenoxazine-3-one)



Resazurin

(7-hydroxyphenoxazine-3-one-10-oxide)

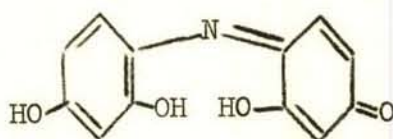
TABLE 6

Compound	λ max, m μ						
	pH 2	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8
2-Nitroresorcinol	315	315	315	315	317	327	330*
4-Nitroresorcinol	350	350	350	352	402	405	406
2,4-Dinitroresorcinol	344	391	395	395	395	398	400
2,4,6-Trinitroresorcinol	-	392	400	328 415	330 417	330 417	330 420
4-Nitrosoresorcinol	-	297	-	300	-	-	300
2,4-Dinitrosoresorcinol	-	273	275	280	281 332	282 333	334
Resorcinol	-	274	-	-	274	-	275

*At pH 10, the peak for 2-nitroresorcinol shifts to 390 m μ but the molecular absorption coefficient is much smaller.

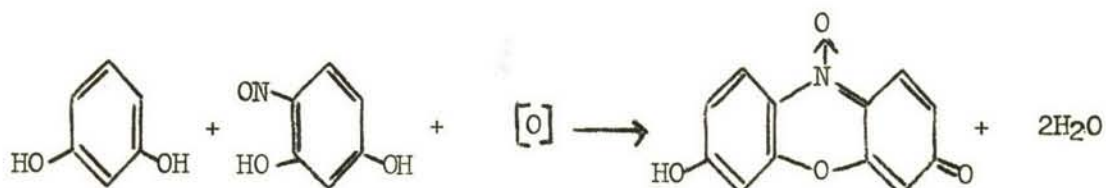
NOTE Where two values of λ max are given, two peaks of equal intensity are present.

In early preparation of resorufin (1) a cold ethereal solution of resorcinol was treated with nitric acid containing nitrous acid. Alternatively the indophenol of resorcinol can be produced (2) by treating an ice-cold, glacial acetic acid solution with sodium nitrite and sulphuric acid monohydrate:



/this

this has an intense blue colour and can be dehydrated by concentrated sulphuric acid at 70°C. More recently resazurin has been produced (3) by treating with manganese dioxide an equimolecular mixture of resorcinol and 4-nitrosoresorcinol dissolved in dilute sulphuric acid/acetone.



Since resazurin can be reduced by sulphuric acid, this preparation yields resorufin as a by-product.

Samples of these two materials were obtained from commercial sources, a brief summary of their properties being given in Table 7.

TABLE 7

	Resorufin	Resazurin
Source:	Eastman Kodak Co.	B.D.H. (indicator quality)
Appearance:	Purplish-black powder	Dark brown powder
Melting point:	Decomposes	Decomposes
Solubility of free acid in:		
(a) Water:	V. slight	Almost insol.
(b) Ether:	V. slight	V. slight
(c) Alcohol:	Slightly more soluble	Slightly more soluble
Solubility of sodium salt in water:	Approx. 5%	Approx. 1%
Colour of aqueous solutions:		
(a) acid:	Orange pink	Pale red
(b) alkali:	Intense red with orange fluorescence	Intense navy blue
Concentrated sulphuric acid:	Deep purplish blue	Orange-red

/Since

Since both of these commercial materials were found to be impure (resazurin is sold as the sodium salt and contains sodium carbonate), the compounds were synthesised, using the method of Oxley and Short (3), and their ultraviolet and infrared spectra determined. It was found that the purest resorufin could be produced by reducing resazurin in a Jones reductor.

3.3.2 Ultraviolet Characterisation

The principal absorption peaks of resorufin and resazurin in aqueous alkaline solution are shown in Fig. 7; the maxima are at 575 and 605 m μ . It was found that, if a solution of resorufin in methanol was passed through an alumina chromatographic column the subsequent ultraviolet spectrum had a much sharper peak carrying characteristic shoulders at 535 and 557 m μ (Fig. 8).

Under these conditions the value of C/D (as defined before) for resorufin was 0.38 and the molecular extinction coefficient (ϵ_{mol}) was found to be 56,200. Resorufin could thus be determined quantitatively.

3.3.3 Chromatographic Behaviour

A synthetic mixture of resorufin, resazurin, nitroglycerine and triacetin was added to a silicic acid/celite column and treated with developers of increasing strength. With petroleum ether: diethyl ether 1:1 two discrete bands were produced but they were still strongly adsorbed; only with pure diethyl ether were the bands slowly moved, the resazurin band becoming diffuse.

The same mixture on alumina can be developed slowly by using ethanol, more quickly by methanol, and rapidly eluted by methanol containing 2 per cent water.

3.4 Nitroglycerine/Resorcinol and Nitrocellulose/Resorcinol in Triacetin

In Section 3.1.7 it was shewn that mixtures of nitrocellulose and resorcinol could be used to simulate the behaviour of propellants on heating. Comparative experiments were therefore carried out using mixtures of the two main nitric esters with resorcinol. Nitroglycerine needs to be desensitised with triacetin but solutions of nitrocellulose of concentrations greater than 5 per cent in this solvent are impracticably viscous. Both series of solutions were therefore made with this concentration of nitric ester together with 2 per cent of resorcinol.

The samples were heated at 80°C and one of each series removed for examination each week. The original pale straw colour became progressively darker, and at 5 weeks the solutions were nearly black, becoming deep brownish-red on dilution with triacetin.

/Treatment

Treatment with benzene before chromatography precipitated a fine black powder from the nitroglycerine solution, and a black sludge of nitrocellulose from its solution.

Apart from an unknown bluish-purple component ($\lambda_{\max}$ 588 m μ in methanol/water) only 4-nitroresorcinol and resorufin were found, and these were in very small amounts as Table 8 shews.

TABLE 8

Ester	Weeks Heating	4-Nitroresorcinol, %	Resorufin, %
Nitrocellulose	1	0.021	0.002
"	5	0.067	0.016
Nitroglycerine	1	0.015	0.001
"	5	0.055	0.008

The rate of loss of resorcinol from heated propellants (Table 4, p. 6) would have led one to expect much greater amounts of degradation products, although the colour of the precipitated nitrocellulose and the production of a precipitate from the nitroglycerine solution indicated that the reaction was not straightforward. It was decided to investigate the rate of loss of resorcinol when it was heated in higher concentrations with nitroglycerine in triacetin, and to see if mass balances with respect to resorcinol and its reaction products could be obtained.

A bulk sample (triacetin 50 ml., nitroglycerine 50 ml. and resorcinol 10 g.) was made; this had a resorcinol content of 6.70 per cent. A solution containing no nitroglycerine (triacetin 100 ml. and resorcinol 10 g.) with a resorcinol content of 8.20 per cent was used as a "blank". Aliquots of these two mixtures were then heated at 80°C, and one of each series examined each week. The solutions containing nitroglycerine darkened rapidly and a black sludge was gradually deposited.

Using the technique already described, the residual resorcinol and degradation products were determined (Table 9, p. 13); the "blank" determination (Table 10, p. 13) confirmed that there was no direct reaction between resorcinol and triacetin.

/TABLE 9

TABLE 9

Sample	Resorcinol, %	Degradation Products		
		Resorufin, %	4-Nitro- resorcinol, %	2-Nitro- resorcinol, %
Original unheated	6.70	-	-	-
2 days at 80°C	6.65	0.009	0.045	-
1 week at 80°C	6.25	0.048	0.103	0.030
2 weeks at 80°C	5.05	0.081	0.100	-
3 weeks at 80°C	4.37	0.082	-	trace
4 weeks at 80°C	3.40	0.089	0.064	"
5 weeks at 80°C	1.98	0.070	0.042	"
6 weeks at 80°C	0.23	0.050	-	"
7 weeks at 80°C	0.005	0.050	0.035	"

TABLE 10

Sample	Resorcinol, %
Original unheated	8.20
2 days at 80°C	8.47
1 week " "	8.07
2 weeks " "	8.25
3 " " "	8.25
4 " " "	8.38
5 " " "	8.47
6 " " "	8.33
7 " " "	8.50

The slight fluctuation in the resorcinol content is probably due to variable loss of triacetin past the loose stoppers.

/The

The following observations were made:

- (i) Once again the bluish-purple product was formed; it was at a maximum after 4 weeks, then gradually diminished.
- (ii) The proportion of resorcinol which cannot be accounted for appears to increase with time of heating.
- (iii) The amount of insoluble sludge increases with heating time.
- (iv) There is no significant reaction between resorcinol and triacetin.

Since the sludge appears as the resorcinol disappears, its rate of formation was investigated and compared with the rate of loss of resorcinol. Aliquots of a mixture as before (nitroglycerine, resorcinol, triacetin) were heated at 80°C; when removed from the oven they were diluted with dichloromethane, in which the precipitate is virtually insoluble.

By transferring the mixture to an extraction thimble and giving the powder a final extraction with dichloromethane it was freed from nitroglycerine and triacetin. The amount of unreacted resorcinol was determined and the insoluble residue weighed; the results are presented in Table 11.

TABLE 11

Sample	Recovered Resorcinol, % (A)	"Brown Powder", % (B)	A + B
Original	7.04	Nil	7.04
2 weeks	5.13	1.59	6.72
3 "	4.30	2.21	6.51
4 "	3.44	2.92	6.36
5 "	2.49	3.51	6.00
6 "	0.77	5.75	6.52

As will be seen, the dichloromethane-insoluble material accounts very closely for the resorcinol missing from the system.

Examination of the Dichloromethane Insoluble Material

Preliminary tests indicated that this was fairly soluble in ethanol, and chromatography separated it into three bands. By combining all the material available and chromatographing it on alumina enough products were obtained for examination. They are insoluble in dichloromethane

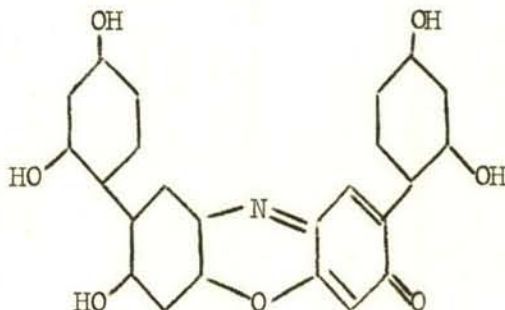
/and

and benzene, slightly soluble in diethyl ether and water, and very soluble in ethanol and basic solvents (pyridine, N,N-dimethyl formamide, tetrahydrofuran). The solubility in water can be increased by adding alkali; this also changes and enhances the colours (cf. resorufin and resazurin, p. 10).

Many attempts were made to carry out ultimate analyses on these fractions but it was found that after ignition an intractable residue remained. This was subsequently found to be alumina - obviously leached from the chromatographic column.

Since an examination of the infrared spectra of the three main fractions indicated that they were virtually identical, it was decided to attempt an ultimate analysis on the material "as prepared"; on ignition this material was found to leave no residue and afforded an analysis: C, 60.6; H, 3.8, N, 3.0, per cent. As it was thought that the material was hygroscopic and might have become damp during handling, determinations by the "Fischer" method were made. These gave values of 7.14 and 7.56 per cent. A check using the "water pistol" gave a result of 6.92 per cent, so that corrected values for the ultimate analysis are: C, 65.3; H, 3.8; N, 3.2, per cent. Attempts to determine the molecular weight of this material by the ebullioscopic method failed, since in the basic solvents needed to effect solution there was an apparent depression of the boiling point.

The colour changes undergone by solutions of this material, when made acid or alkaline, suggest that it is very similar to "lacmosol" which Musso et al. (4) claim to be 2,8-bis-(2,4-dihydroxyphenyl)-7-hydroxyphenoxazine-3-one, that is, resorufin made from 2 molecules of di-resorcinol:



$C_{24}H_{15}NO_7$ requires: C, 67.1; H, 3.49; N, 3.26, per cent, whereas the corrected ultimate analysis given earlier is represented by the formula $C_{23.6}H_{16.3}NO_{7.5}$. The small amount of resorufin present in the original material would tend to reduce the relative proportion of carbon, and thus make it possible that the compound produced is lacmosol or a polymer of similar empirical formula.

/Further

Further, a small amount of ammonia is liberated from this material on fusing with solid potassium hydroxide; this indicates that at least some of the nitrogen present is in the tertiary form, nitro or nitroso groups being unlikely to produce ammonia under these conditions.

Extraction of the aqueous solution produced by dilution of the melt affords large amounts of resorcinol and traces of acetic acid; these products would be expected from a constitution such as that postulated.

Of more importance from the point of view of propellant stabilisation is the observation that the "brown powder" when suspended in tetrachloromethane and treated with dinitrogen tetroxide in the same solvent undergoes no reaction in 6 hours at room temperature (cf. immediate reaction with resorcinol). At the end of this time the dinitrogen tetroxide can be recovered quantitatively.

3.5 Resorcinol and Dinitrogen Tetroxide

3.5.1 Equimolar Quantities under Anhydrous Conditions

In order to obtain information as to the derivatives and their approximate proportions to be expected in propellants, especially in the early stages, the reactions between resorcinol and dinitrogen tetroxide, both in anhydrous solvent, were studied. Since it is more convenient to work with fairly dilute solutions of dinitrogen tetroxide in tetrachloromethane, these were usually made about 0.05 molar and standardised by the method of Blay and Warren (5). The appropriate quantity of recrystallised, vacuum-dried resorcinol for an aliquot of the above solution is easily calculated, weighed and subsequently dissolved in anhydrous dichloromethane.

Attempts were made to prepare 4-nitrosoresorcinol by a method analogous to that used previously in the 4-nitro-N-methylaniline system



When the dinitrogen tetroxide solution is added to dichloromethane containing an equimolecular amount of resorcinol, the resulting solution becomes dark brown immediately. After a few minutes however the colour lightens and eventually becomes a clear yellow.

The addition of excess standard sodium hydroxide solution to the mixture, and subsequent back titration with standard sulphuric acid solution indicates that a very small proportion only of the expected nitric acid is present. Instead resorcinol is found to have been converted into a mixture of 4-nitro and 2,4-dinitroresorcinol.

In attempts to establish the nature of the first step in the reaction, various expedients were adopted with the object of removing the nitric acid which would be produced by the postulated mechanism. The above experiment was therefore repeated with the addition to the resorcinol solution of lithium or sodium fluoride (10 g. of pure, carefully-dried material) in attempts to adsorb the nitric acid and

/remove

remove it from the system (6). The suspension was stirred vigorously in order to disperse the solid phase as much as possible. The same colour changes were observed in the solutions as were noted in the absence of the co-ordinating agent, and on working up, the same products were found. A similar result was obtained when anhydrous sodium carbonate was used. These observations suggest either that the reaction by which 4-nitrosoresorcinol is converted to the nitro derivative is extremely rapid and fairly vigorous, or that the heterogeneous nature of the system prevents the rapid scavenging of the nitric acid.

3.5.2 Equimolar Amounts under Aqueous Conditions

Attempts were then made to produce 4-nitrosoresorcinol by an aqueous method; in this, resorcinol was dissolved in water to which three molecular equivalents of sodium hydroxide had been added; thus the resorcinol was present as the disodium salt (i.e. completely ionised) and there was sufficient sodium hydroxide to neutralize the nitric acid produced by the nitrosation reaction.

One molecular equivalent of dinitrogen tetroxide, dissolved in tetrachloromethane, was added slowly while the mixture was stirred vigorously; the aqueous layer, originally brown in colour, darkened considerably and the tetrachloromethane layer became colourless. Subsequently two molecular proportions of sulphuric acid were added in order to liberate the resorcinol derivatives and the resulting aqueous solution was examined for its adsorption in the u.v. region.

This indicated that the solution contained resorcinol and 2,4-dinitrosoresorcinol in approximately equal proportions and that 4-nitrosoresorcinol was not present. This result tends to confirm that the first step is nitrosation, since the speed of the reaction will be governed by the rate at which the dinitrogen tetroxide can be extracted from the tetrachloromethane; the presence of unchanged resorcinol with the 2,4-dinitrosoresorcinol shews that under the conditions obtaining here 4-nitrosoresorcinol is more easily nitrosated than is resorcinol itself.

3.5.3 Dinitrogen Tetroxide with Two Molecular Amounts of Resorcinol

If dinitrogen tetroxide is added to excess (two or more molecular equivalents) of resorcinol it should be possible to isolate nitrosated products, since there is an alternative "sink" for the nitric acid. Two molecular proportions of resorcinol were dissolved in dichloromethane and one molar equivalent of dinitrogen tetroxide dissolved in tetrachloromethane was added while the solution was being stirred vigorously.

The colour of the solution changed and became a fairly dark brown, similar to that found in the 1:1 experiments; however in the latter case, even after standing the brown colour persisted and did not give place to the yellow coloration observed in the former experiments.

/Chromatographic

Chromatographic separation of the products from this experiment, followed by determination of their u.v. absorptions, shewed that 4-nitro and 2,4-dinitroresorcinols had been produced, with a small amount of 2-nitroresorcinol, a fairly large amount of 4-nitrosoresorcinol, and some unreacted resorcinol remained. The presence of 2-nitroresorcinol was unexpected since, if the production of the nitroresorcinols proceeds through the nitrosoresorcinols, the formation of 2-nitrosoresorcinol must be inferred. However no mention of this compound could be found in the literature.

3.5.4 Resorcinol with Absolute Nitric Acid

In order to obtain a clearer idea of the mechanism of the production of the nitroresorcinols, resorcinol was reacted directly with nitric acid in the following way. To a small quantity of absolute nitric acid was added sufficient anhydrous tetrachloromethane to produce a homogenous solution (subsequent standardisation indicated that this was 0.03 normal).

To one molecular equivalent of resorcinol, dissolved in dichloromethane, was added two equivalents of the nitric acid solution. There was no visible change in the appearance of the solution for about one hour, after which it was possible to discern a very faint yellow colour which increased very slowly and was at a maximum in ten days.

The u.v. spectrum of the resulting solution (referred to the same mixed solvent) indicated that it contained a mixture of 2- and 4-nitroresorcinol; a portion was therefore chromatographed and the presence of these two derivatives confirmed. Since the solution still contained nitric acid the remainder was then heated (45°C) for five hours, after which the u.v. spectrum was again determined and found to be identical with that obtained before heating. Nitric acid was present even after this treatment, and chromatographic separation confirmed that only the 2- and 4-nitroresorcinols were present.

3.5.5 Miscellaneous Related Experiments

When resorcinol, dissolved in dichloromethane, was treated with two molecular proportions of dinitrogen tetroxide solution, and the resulting mixture allowed to stand at room temperature for 15 minutes, the products obtained were 4-nitro, 2,4-dinitro and a very small amount of 2,4,6-trinitroresorcinol.

2,4-Dinitroresorcinol when treated with either an equimolecular amount of dinitrogen tetroxide, or two equivalents of nitric acid, did not give any 2,4,6-trinitroresorcinol in 20 days at room temperature; the original material was recovered unchanged after the solution had been treated with alkali.

4-Nitrosoresorcinol when suspended in dichloromethane and treated with a solution of nitric acid in tetrachloromethane, slowly gave a bright yellow solution which, when subsequently examined, was found to contain a mixture of 4-nitro and 2,4-dinitroresorcinol.

/Resorcinol

Resorcinol was dissolved in 1,2-dichloroethane and dinitrogen tetroxide (1/10 equivalent) solution added; after this the vessel was sealed and placed in a thermostat bath at 75°C for two days. After this time a quantity of flocculent brown material had been deposited; this was filtered off and identified as 4-nitrosoresorcinol.

The solution was chromatographed on alumina - subsequent elution with methanol/water afforded a solution containing resorufin. The residual solution was then examined and found to contain a further quantity of 4-nitrosoresorcinol, some 4-nitroresorcinol, and a trace of 2-nitroresorcinol.

3.5.6 Summary of Results from Non-Aqueous Systems

These results suggest that the initial reaction between resorcinol and dinitrogen tetroxide in non-aqueous solvents is one of nitrosation:



The quantitative nature of this reaction cannot be established because of the ease with which the primary product (4-nitrosoresorcinol) is converted to 4-nitroresorcinol with formation of free nitrous acid. The latter then presumably nitrosates the 2-position, after which oxidation produces 2,4-dinitroresorcinol.

This is supported by the fact that a higher relative concentration of absolute nitric acid in the same solvent converts resorcinol only slowly into a mixture of 2- and 4-nitroresorcinols. 2,4-Dinitroresorcinol is not produced under these conditions. The formation of small amounts of 2,4,6-trinitroresorcinol when two molecular amounts of dinitrogen tetroxide were used is probably due to the higher concentration of nitrous acid present in this case.

3.6 Resorcinol and Nitroglycerine on Heating

The evolution of nitrogen dioxide from nitroglycerine heated at 80°C has been studied quantitatively (7), and this offers a useful means of observing the behaviour of a stabilising material. A known amount of resorcinol was dissolved in dibutyl phthalate to which a known volume of nitroglycerine had been added. This mixture was then heated at 80°C for such a period that, if the rate of decomposition was unchanged in the presence of solvent, 20 per cent of the resorcinol should have been converted to mononitroresorcinol if its behaviour in the system was similar to that in the resorcinol/dinitrogen tetroxide system.

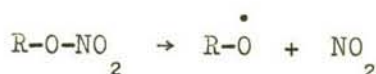
On examination of the mixture after the heating period 20 per cent of the resorcinol was found to have been converted to 4-nitroresorcinol and 1 per cent to 2-nitroresorcinol. However only 58 per cent of the resorcinol originally taken was present in the solution, thus even at the low concentrations used in this experiment resorcinol is being lost from the system at a greatly enhanced rate.

/4.

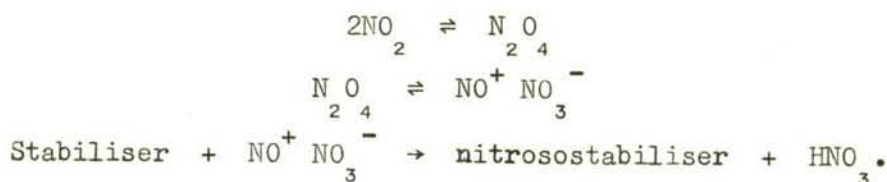
4. CONCLUSIONS

The conclusions to be drawn from this work relate to the general chemistry of resorcinol and to the stabilisation of propellants.

The first step in the decomposition of a nitric ester is (7):



The retention of NO₂ in the system results in an increase in concentration until the reaction becomes autocatalytic. It is the function of the stabiliser to remove the nitrogen dioxide, which it does by the general mechanism



This is known to obtain in the cases of N-methylaniline and diphenylamine and has been shown herein to apply to resorcinol.

It seems clear that resorcinol is an extremely efficient "scavenger" of dinitrogen tetroxide in propellants, reacting, for example, in preference to 2-nitrodiphenylamine. Not only does it remove the nitrosyl ion completely, but by subsequent reaction eliminates the nitric acid side product. The essence of a good stabiliser is that it should effect the complete removal of nitric acid.

(i) The very rapid nitrosation of resorcinol and conversion of the nitrosated products into nitro derivatives is, of course, in line with the well-known preparation of the nitroresorcinols from the nitrosoresorcinols. Interesting points to note are that the conversion of nitroso to nitroresorcinol takes place even at very low concentration in absolute nitric acid and that the reaction between absolute nitric acid and resorcinol is extremely slow.

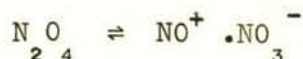
The role of nitric acid in the conversion of nitroso to nitroresorcinol has been said to be that of oxidising agent; however, it is only at fairly high water contents that nitric acid is an effective oxidising agent. In absolute nitric acid at ambient temperatures the equilibrium



/is

is almost entirely in favour of HNO_3 . This is confirmed by the slow rate of direct nitration of resorcinol.

It is suggested therefore that the most vigorous reagent for attack on the resorcinol molecule is the nitrosyl cation produced from dinitrogen tetroxide,



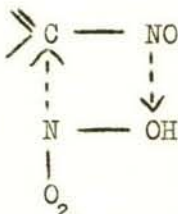
and that the next stage is the substitution of the 4-hydrogen by the nitrosyl ion, resulting in the production of an equimolecular quantity of nitric acid



followed by a rapid radical exchange



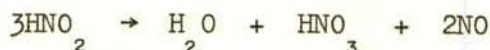
which could well be by a "four-centre" mechanism



and would produce a nitrocompound in the absence of nitronium ion, regenerating the nitrous acid for attack on the 2-hydrogen:



This cycle is modified to some extent by the reaction:



It has also been established that, when propellants containing resorcinol are subjected to accelerated storage, a different reaction mechanism obtains from that at ambient temperature - although the route by which the product is formed is not clear.

/Nitrosoresorcinol

Nitrosoresorcinol must be formed first and this together with another molecule of resorcinol produces the indophenol (p. 9), and since the resorufin content reaches a maximum early in the heating period it is possible that this is formed next. The explanation of the addition of further resorcinol molecules to the resorufin nucleus presents difficulties, since, although it may be possible to visualise condensations (known to occur) between molecules of resorcinol in the diketo form, these would be expected to be base catalysed, whereas a heated propellant tends to become acidic.

Nevertheless it is quite clear that under accelerated conditions resorcinol is removed from the system at an enhanced rate, which is very nearly directly proportional to the time of heating. This, since there is a considerable excess of nitric ester present in the systems, suggests that there is no direct attack on the nitric ester by the resorcinol. Although the precise temperature at which this reaction sets in was not determined in this work, it should be borne in mind that compositions containing resorcinol may be found to exhibit unusual behaviour after accelerated storage.

(ii) The changes in the u.v. spectra of aqueous solutions of the nitroresorcinols when the pH of the solutions is varied are seen to be explicable when the hydrogen-bonded nature of these compounds is considered, the nature of the "resorcinolate" ion being modified according to the presence of H^+ or OH^- ions in the solution. This shews that for positive identification of these derivatives it is necessary to set up the reference spectra at a fixed pH (or at two fixed values) and to determine the spectra of unknown material in solutions having similar pH.

5. BIBLIOGRAPHY

1. Nietzki, Dietze and Mackler, Berichte, 1889, 22, 3022.
2. Schoutissen, Recueil des Travaux Chimiques, 1921, 40, 754.
3. Oxley and Short, B.P.557, 136, 1943.
4. Musso, Seeger and Zahorszky, Angew. Chem., 1961, 12, 434.
5. Blay and Warren, E.R.D.E. Report No. 2/R/53.
6. B.P. 592, 240, 1947.
7. Phillips, Nature, 1947, 160, 753.

/ APPENDIX

APPENDIX:

THE DETERMINATION OF RESORCINOL

by J.W. Grindlay and (Miss) A.R. Howieson

A.1 INTRODUCTION

The method depends on the reaction of resorcinol with sodium nitrite and copper sulphate in dilute aqueous acetic acid solution. The dinitrosoresorcinol, initially formed, reacts with the copper ions to give a yellow complex, the colour intensity of which is proportional to resorcinol concentration.

A.2 REAGENTS

- (i) Methylene chloride - Judex (free from breakdown impurities).
- (ii) Chloroform (AR).
- (iii) Copper sulphate solution: 3% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water (wt/vol.).
- (iv) Acetic acid solution: 10% (vol/vol.).
- (v) Sodium nitrite solution: 2% (wt/vol.).

A.3 PROCEDURE

A.3.1 Propellants and NC Compositions

Weigh an appropriate quantity of the prepared sample (see Notes 1 and 2, Section A.3.4) into a Soxhlet thimble and extract for 10 hours with dichloromethane. Carefully evaporate off the solvent, redissolve the extracted residue in chloroform, and transfer the solution quantitatively to a small separatory funnel, the final solution volume being 15 to 20 ml. Extract the solution with 3 x 20 ml. portions of water and transfer the combined aqueous extracts to a standard flask (Note 2), filtering each extract through a cotton-wool plug, in order to retain any traces of chloroform. Dilute to the mark and mix.

Pipette 5 ml. (Note 3) into a 50 ml. standard flask and place 5 ml. water into a similar flask to serve as a blank. Add 1 ml. of 2 per cent sodium nitrite and 10 ml. of 10 per cent acetic acid to each and allow to stand for 5 minutes, then add 1 ml. of 3 per cent copper sulphate solution, dilute to the mark with water and mix.

Allow the solutions to stand for 15 to 20 minutes then measure their optical densities on a Spekker absorptiometer, using 1-cm. cells and Ilford 601 filters. From a calibration curve (previously prepared by using varying amounts of pure resorcinol from a standard solution) read off the amount of resorcinol in the 50-ml. sample solution, and hence calculate the percentage in the original sample.

/Calculation:

Calculation:

$$\% \text{ resorcinol} = \frac{M \times a}{w \times 10}$$

where: M = mg. resorcinol in the 50-ml. sample solution,
w = weight of sample taken,
a = dilution factor.

A.3.3 NG/Resorcinol/Triacetin Compositions

In this case, the sample is diluted sufficiently with dichloromethane, and the resultant insoluble matter re-extracted with the same solvent in a Soxhlet apparatus. The combined extracts are then treated as above.

A.3.3 2-Nitrodiphenylamine Present

When the 2-N.D.P.A. content is required in addition to that of resorcinol, the dichloromethane extracts are diluted to 50 ml. in a standard flask (after previous reduction by evaporation, if necessary) and 25 ml. removed with a clean dry pipette for the resorcinol determination. The remaining 25 ml. of solution is used for 2-N.D.P.A. determination as follows:

After evaporating off the solvent, the residue is dissolved in benzene, diluted to 50 ml. in a standard flask, with the same solvent, and a 5 ml. aliquot chromatographed on a silicic acid/celite column, the yellow 2-N.D.P.A. band being eluted through the column with petroleum ether/benzene (1:1), then made up to standard volume, and determined by measurement of the colour intensity, using a Spekker absorptiometer (Ilford 601 filters).

A.3.4 Notes

1. Composite modified type propellants should be cut into small thin slices about 1 cm. square and 1 - 2 mm. thick. They should not be ground, owing to possible segregation of aluminium.

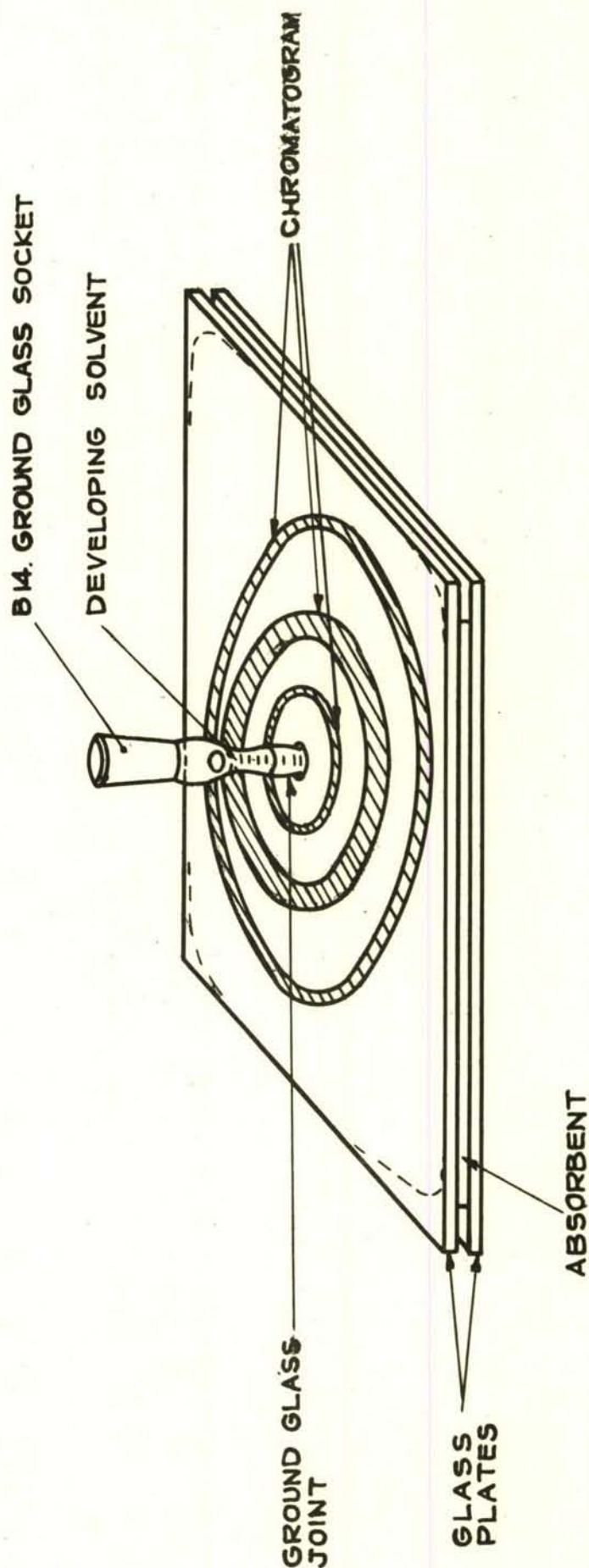
Ordinary double-base propellants, and similar compositions can, of course, be ground.

2. The amount of sample taken and the dilution of the aqueous extracts depend on the resorcinol content of the sample, e.g. for a resorcinol content of 3 per cent, 1 g. of sample is taken, and the aqueous extracts are diluted to 200 ml.; for, say, a resorcinol content of 1.4 per cent, the aqueous extracts would only be diluted to 100 ml.

3. For very small resorcinol contents, this aliquot can be increased to 10 ml.

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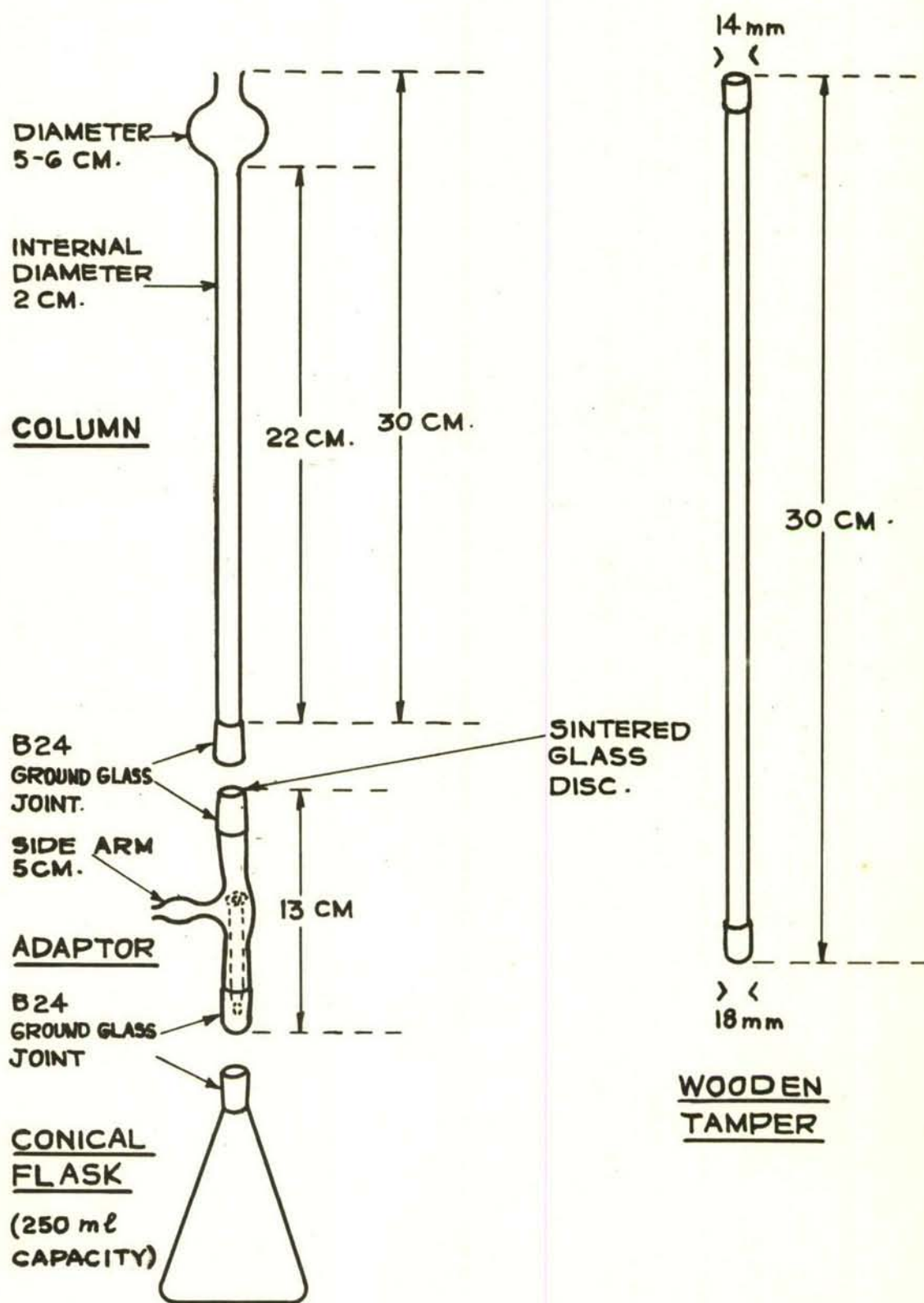


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FIG. 1A.

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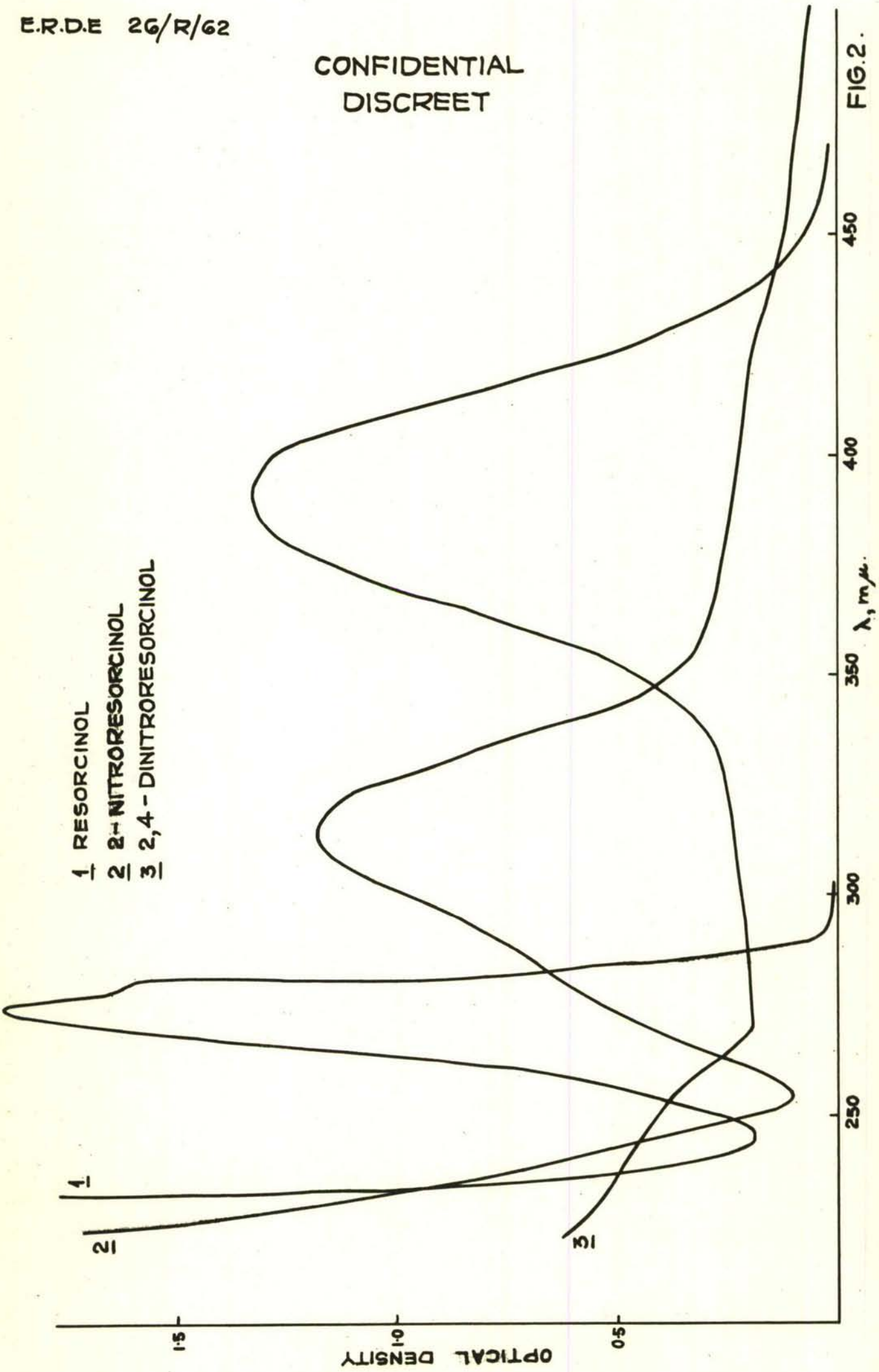
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FIG.1B.

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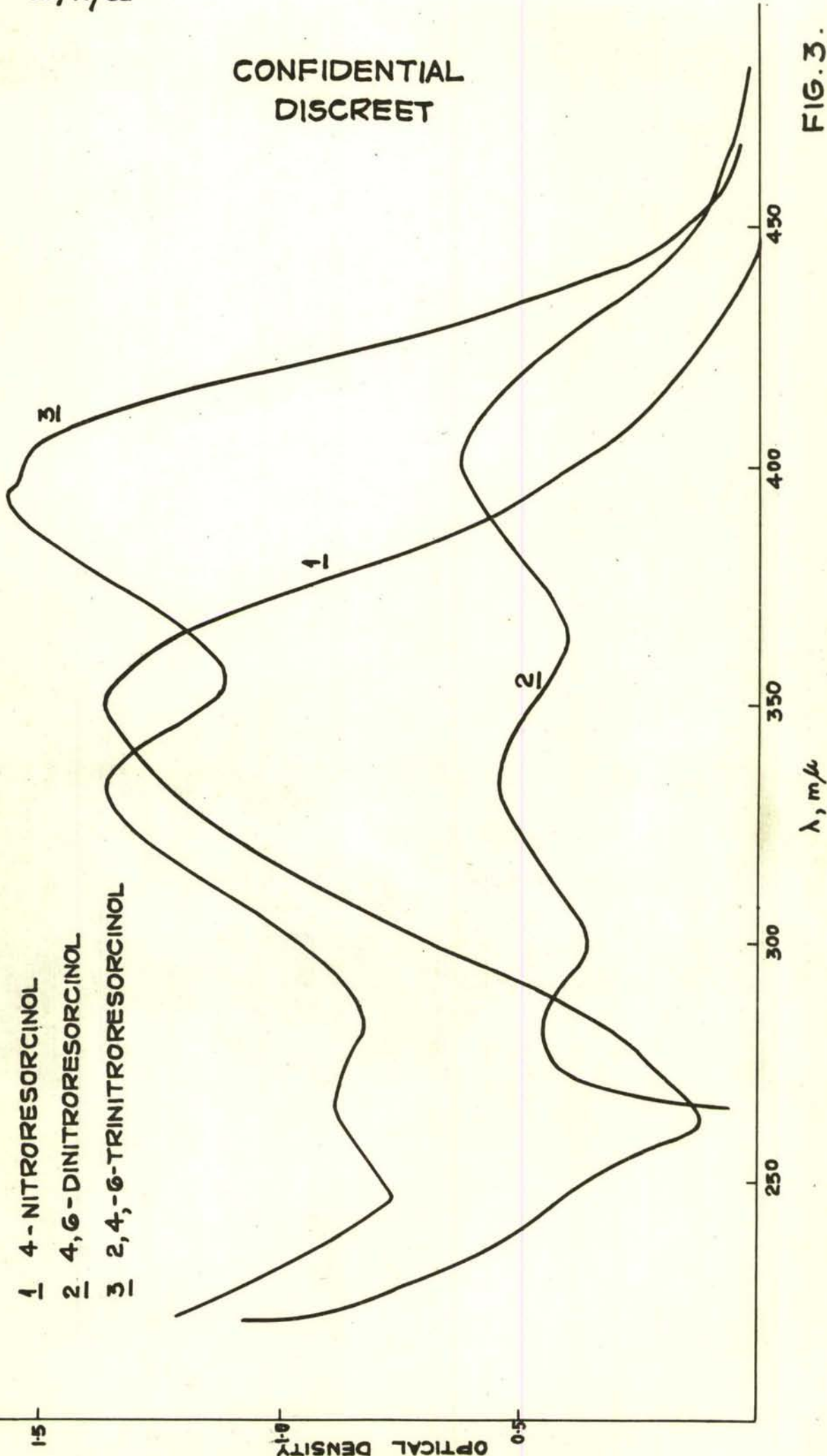


- 1 RESORCINOL
- 2 2-NITRORESORCINOL
- 3 2,4 - DINITRORESORCINOL

FIG.2.

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- 1 4-NITRORESORCINOL
- 2 4,6-DINITRORESORCINOL
- 3 2,4,6-TRINITRORESORCINOL

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FIG. 3.

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- 1 — 2,4-DINITRORESORCINOL
(ALCOHOL SOLUTION).
2 — 4-NITRORESORCINOL.

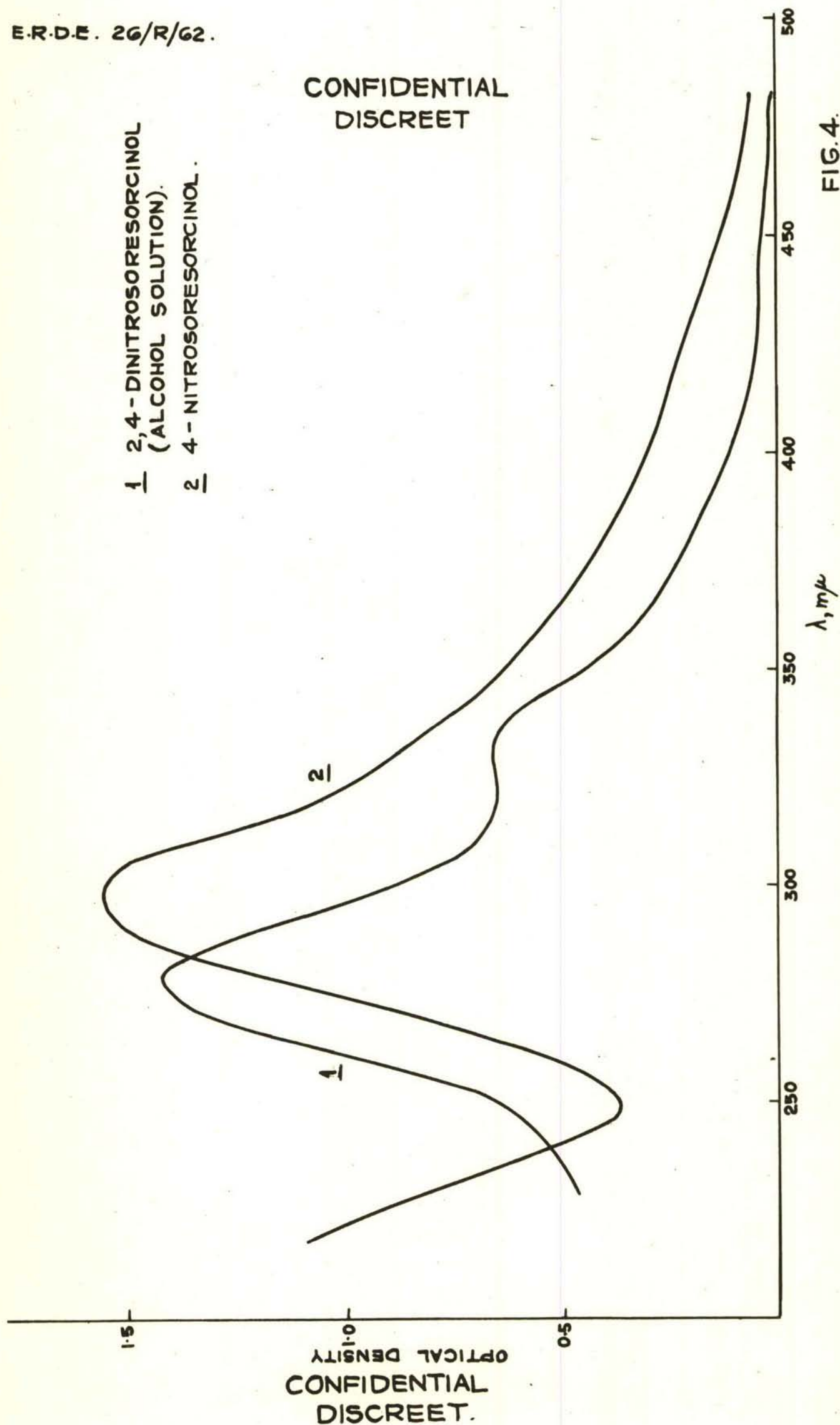
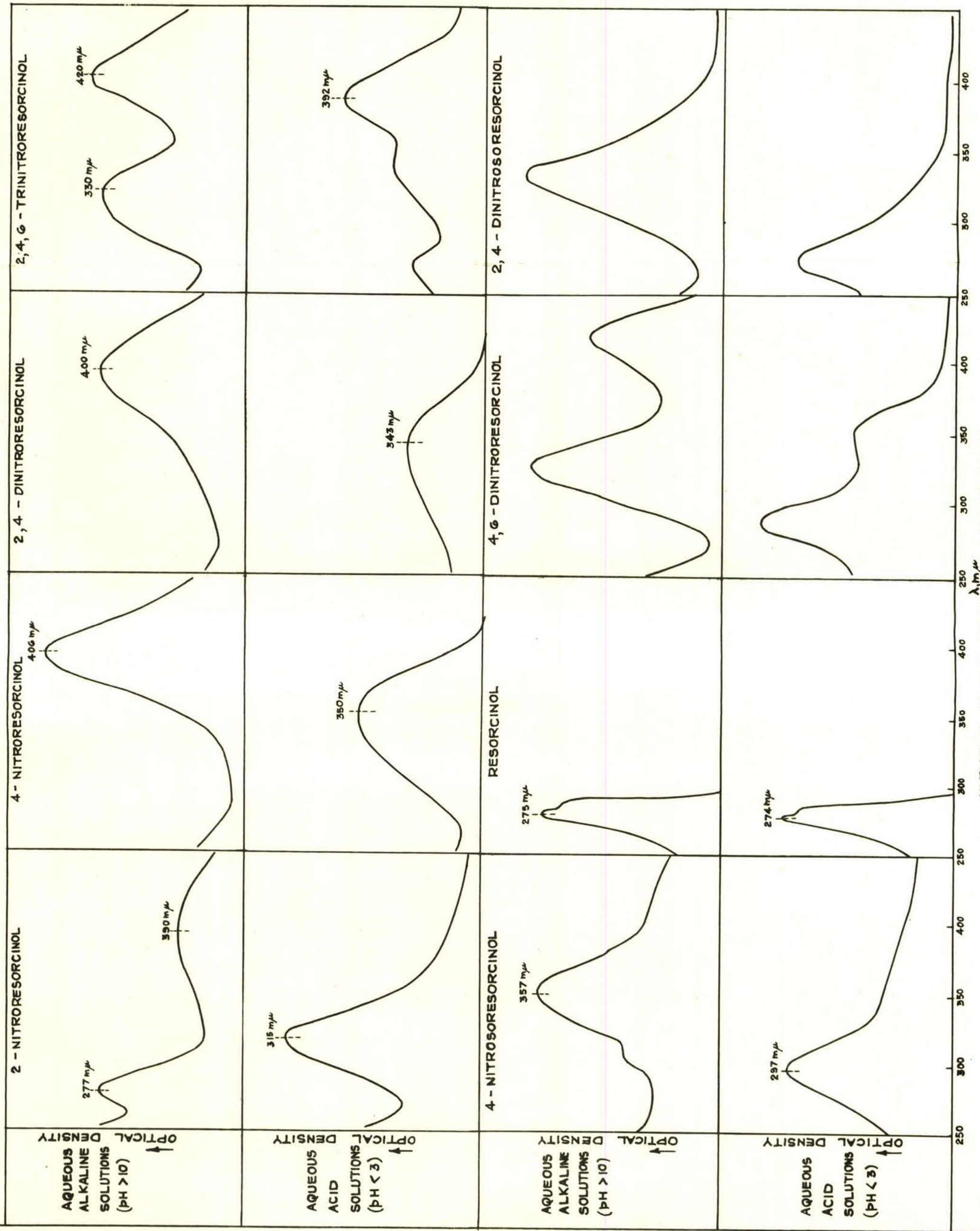


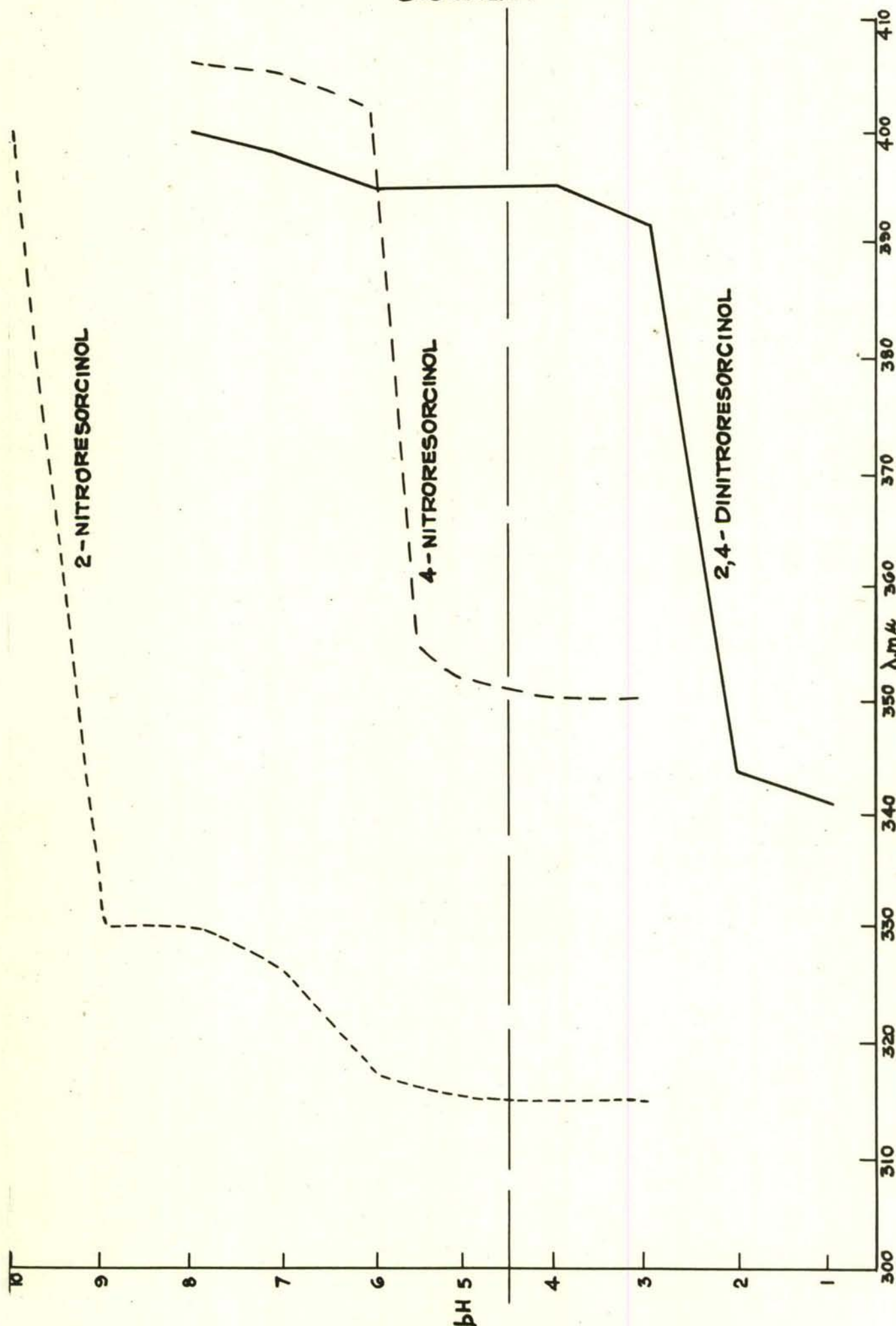
FIG. 4.

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VARIATION IN U.V. ABSORPTION WITH PH VALUE

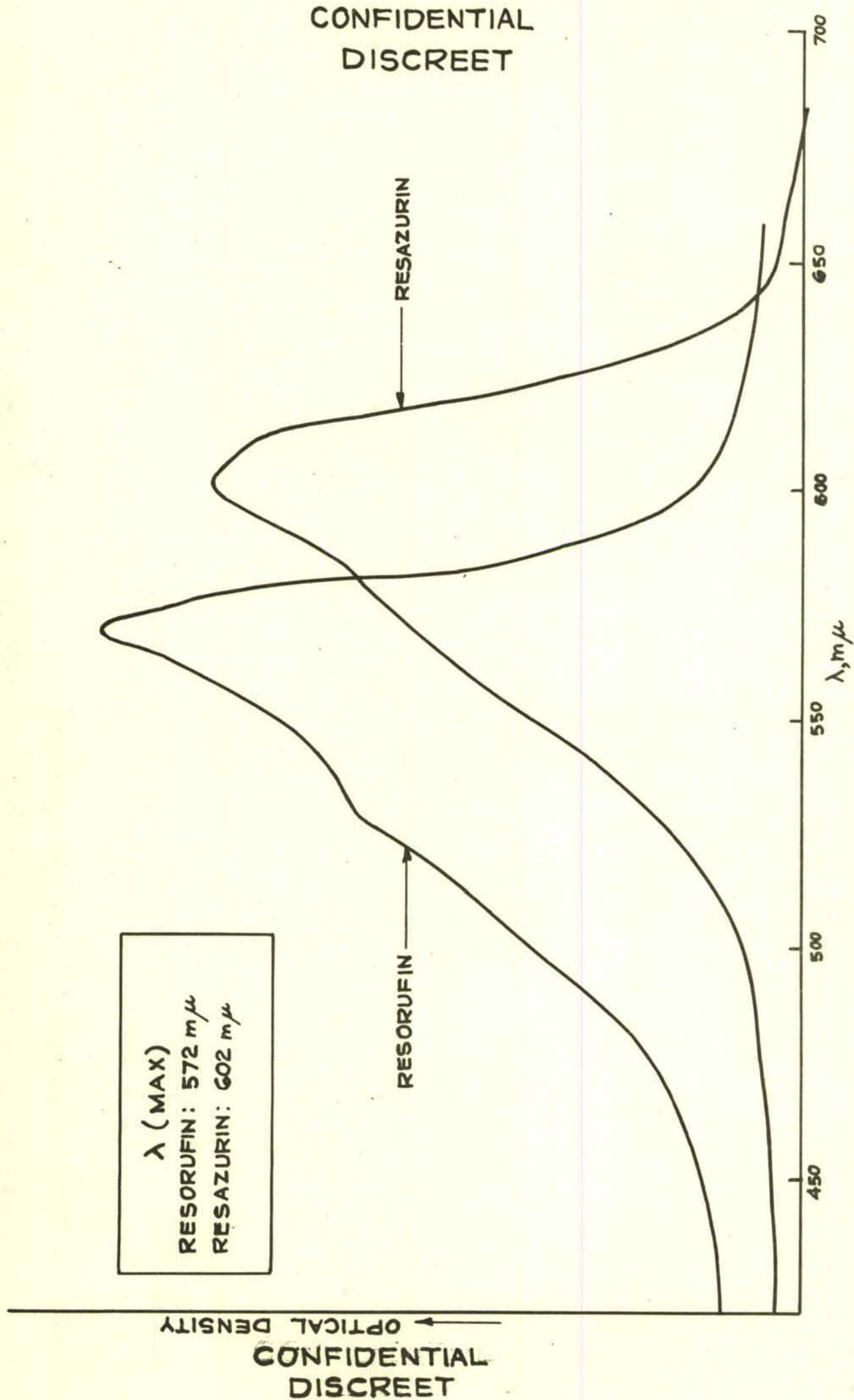
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VARIATION OF PRINCIPAL ABSORPTION PEAKS WITH pH VALUE

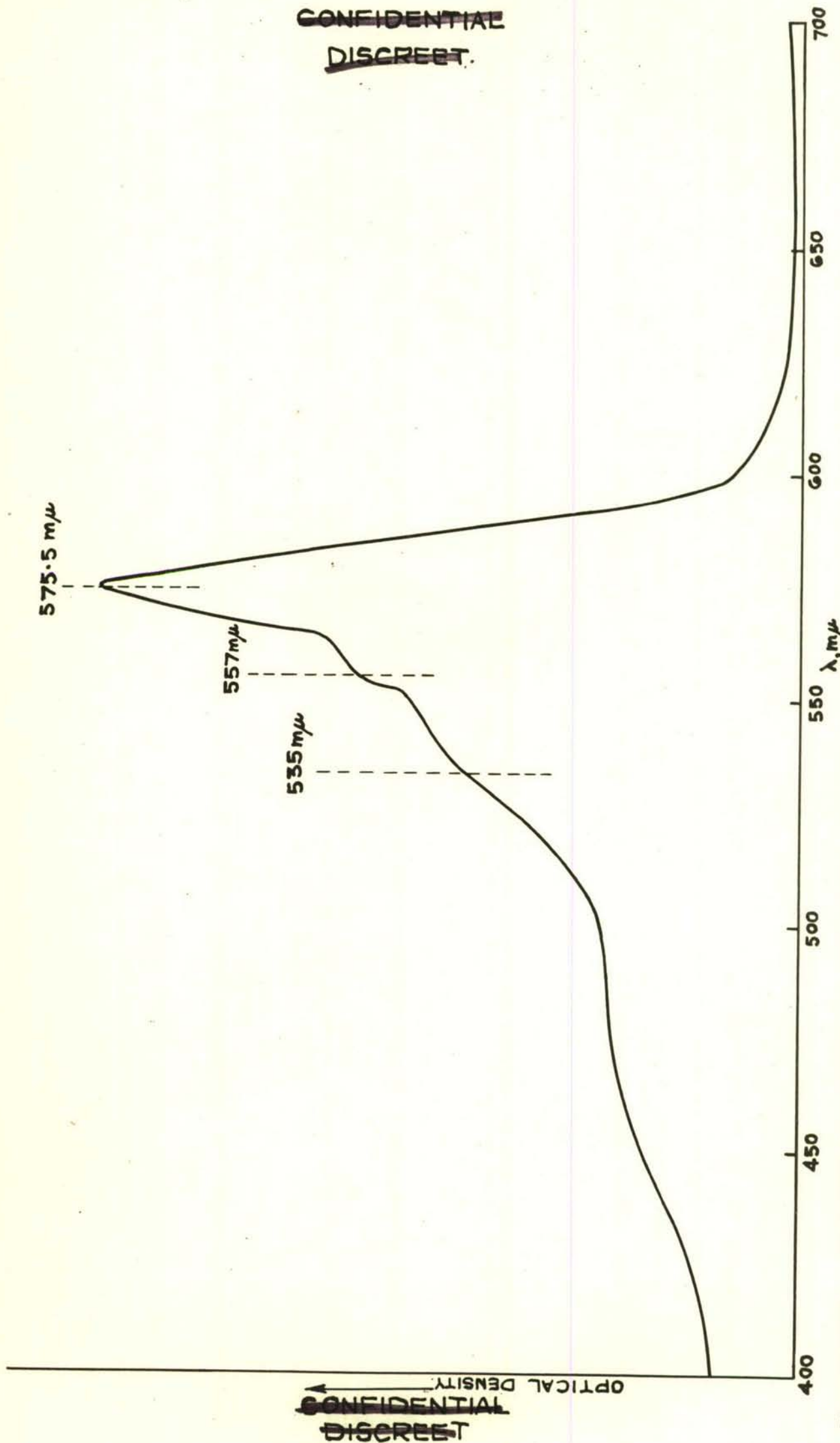
FIG. 6.

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RESORUFIN & RESAZURIN ABSORPTION SPECTRA (AQUEOUS ALKALINE SOLUTIONS) FIG. 7.

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RESORUFIN ABSORPTION PEAK OF METHANOL SOLUTION AFTER CONTACT WITH ACTIVATED ALUMINA. FIG. 8.

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E.R.D.E. Report
No. 26/R/62

The Stability of Colloidal Propellants: Part 6:
Resorcinol as a Propellant Stabiliser

J.W. Grindlay and G.J. Jeacocke

March, 1963

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J.W. Grindlay and (Miss) A.R. Howieson

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A study of the behaviour of nitrosated, nitrated, and some polynuclear, derivatives of resorcinol, on column chromatography, with an investigation into the variations in ultraviolet spectra of these derivatives when in hydroxylic solvents having different pH values, has permitted their quantitative recognition in propellants.

The behaviour of resorcinol with dinitrogen tetroxide has been investigated and, using synthetic mixtures, an unsuccessful attempt has been made to correlate the rate of loss of resorcinol with the known rate of decomposition of nitroglycerine.

Propellants containing resorcinol as part of mixed stabiliser systems have been examined, and relative rates of consumption determined.

24 pp., 8 fig., 11 tables

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J.W. Grindlay and (Miss) A.R. Howieson

A study of the behaviour of nitrosated, nitrated, and some polynuclear derivatives of resorcinol, on column chromatography, with an investigation

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into the variations in ultraviolet spectra of these derivatives when in hydroxylic solvents having different pH values, has permitted their quantitative recognition in propellants.

The behaviour of resorcinol with dinitrogen tetroxide has been investigated and, using synthetic mixtures, an unsuccessful attempt has been made to correlate the rate of loss of resorcinol with the known rate of decomposition of nitroglycerine.

Propellants containing resorcinol as part of mixed stabiliser systems have been examined, and relative rates of consumption determined.

24 pp., 8 fig., 11 tables

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