ORGANIC CHEMICALS DIVISION RESEARCH

St. Louis Research Report No. 2314

FINAL REPORT ON MINOR EXPLORATORY INVESTIGATIONS 1956-57

Job No. 2-02-750.01-3168

July 6, 1959

Written by: W. E. Koerner

Work done by: W. E. Koerner
O. B. Cecil

Monsanto

ST. LOUIS

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MONSANTO CHEMICAL COMPANY
ORGANIC CHEMICALS DIVISION
ST. LOUIS RESEARCH DEPARTMENT

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ON
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D I S T R I B U T I O N

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8. J. H. VanNess
9. Extra
10. Extra

DSW 621811

TABLE OF CONTENTS

INTRODUCTION

This report covers a variety of projects ranging from physical measurements made at the request of other divisions to original projects originating within our group. Because of this diversity, each section of this report will cover a separate project and will include all pertinent commentary.

LOW TEMPERATURE DIELECTRICS

The principle criteria for low temperature dielectric fluids are[1]:

1. The "cracking" (shattering due to strains in the cooled fluid) temperature must be -70°C. or below.

2. The dielectric constant at -55°C. must be no more than 28% below the +25°C. value for 60 ∿ and 1 kc.

3. The D. C. Resistivity at 100°C. must be greater than 500 X 10^9 ohm-cm.

Aroclor 1242 fails to meet criterion #1. Various additives, particularly TCB, have been mixed with Aroclor 1242 to give fluids which meet all requirements. Since these low viscosity mixes are "sensitive" to contamination, there was reason to believe that the addition of polymers would raise the viscosity and thereby "stabilize" the fluid.

Cracking temperature, viscosity, dielectric constant, power factor and D.C. resistivity measurements were made at various temperatures on mixtures of Aroclor 1242 with 5%, 10%, 15% and 30% of a mix containing 29% (Poly 85% 2-ethylhexyl + 15% ethylacrylate) in TCB. Similar measurements were made on a mixture of 90% Aroclor 1242 and 10% of the above polymer (without TCB). D.C. resistivity measurements were made on mixtures of Aroclor 1242, TCB and alkylated polystyrene. Since these values did not meet the criteria, no further measurements were made. Data for these measurements are shown in Table I and Graphs 1-4. All samples were cleaned with Attapulgus earth preceding electrical measurements. Paratone N was incompatible with Aroclor 1242.

Of the above mixes, only the 70% Aroclor 1242-30% mix of 29% (Poly. 85% 2-ethylhexyl + 15% ethylacrylate) in TCB fulfilled all criteria for low temperature dielectrics, but its D.C. resistivity was not as good as those of less viscous fluids already marketed. Tests designed to illustrate the sensitivity of this mix to added contamination yielded the data in Table II. Consideration of the conductivities, which would be additive, show the mix to be as sensitive to contamination as pure Aroclor 1242.

In general, the following observations may be made about fulfilling the criteria for low temperature dielectrics by the addition of polymers to Aroclor 1242:

1 Report 2912, Interim Report on Low Temperature Dielectrics, 12/2/53, R. J. Good.

TABLE I

Properties of Aroclor 1242 Mixes

Mixture	Cracking Temperature (°C.)	Viscosity (Saybolt Seconds) 25°C.	Viscosity (Saybolt Seconds) 50°C.	D.C. Resistivity (ohm cm X 10^8) 25°C.	D.C. Resistivity (ohm cm X 10^8) 100°C.
Aroclor 1242	-60°	198.8	57.08	4572	1398
95% Aroclor 1242 + 5% (1)*	-70°	473.4	122.6	1960	387
90% Aroclor 1242 + 10% (1)*	-70°	667.9	179.5	900	311
85% Aroclor 1242 + 15% (1)*	-75°	1102.1	317.9	1030	185
70% Aroclor 1242 + 30% (1)*	< -80°			1310	341
90% Aroclor 1242 + 10% (2)*	-70°			2140	429
75% Aroclor 1242 + 25% TCB	< -80°			4500	1580
71% Aroclor 1242 + 25% TCB + 4% (3)*				490	

(1)* - 29% (Poly 85% 2-ethylhexyl + 15% ethylacrylate) in TCB

(2)* - Poly 85% 2-ethylhexyl + 15% ethylacrylate

(3)* - alkylated polystyrene

DSW 621814

TABLE II

Sensitivity of Mixes to Contamination

Sample	D.C. Resistivity (ohm-cm X 10^9) 25°	D.C. Resistivity (ohm-cm X 10^9) 100°	Specific Conductance (ohm^{-1} cm^{-1} X 10^{-12}) 25°	Specific Conductance (ohm^{-1} cm^{-1} X 10^{-12}) 100°
Aroclor 1242	7070	1600	.1415	.625
Aroclor 1242 + 10% of saturated solution of tetrabutylammonium picrate in 1242	1740	360	.575	2.78
70% Aroclor 1242 + 30% (1)*	945	304	1.059	3.29
90% above blend + 10% of saturated solution of tetrabutylammonium picrate in 1242	290	137	3.45	7.30
Aroclor 1242	6080	922	.1645	1.085
Aroclor 1242 + 10% of saturated solution of HCl in 1242	58.1	6.65	17.2	.150
70% Aroclor 1242 + 30% (1)*	642	299	1.56	3.35
90% above blend + 10% of saturated solution of HCl in 1242	21.4	1.68	46.7	595

(1)* - 29% (Poly 85% 2-ethylhexyl + 15% ethylacrylate) in TCB.

TABLE III

Zone Refining of Impure Phenol

Fraction	UV Assay	Orthophenylphenol
Purest (Sample A)	102.6% (wt./vol.)	0.04% (wt./wt.)
Most impure (Sample D)	ca. 97-99*	3.83
Original Material	not run	0.98

* Unreliable assay due to interference of orthophenylphenol.

These results indicated that the purest sample was better than the ultraviolet standard. It should also be mentioned that the analysis for orthophenylphenol (OPP) was considered accurate only to 0.05% OPP. Each sample represented roughly 1/8 of the total tube contents.

1. Cracking Temperature

Although not completely proved, it seems likely that the lowering of the cracking temperature is relatively independent of the additive.

2. Dielectric Constant Lowering

The dielectric constant is much more selective. It is doubtful that this criteria could be met by a mix of only Aroclor and polymer.

3. D. C. Resistivity

Although the polymers increase the viscosity of the fluid, they apparently introduce electrical contamination.

ZONE REFINING

The successful use of zone refining in the preparation of extremely pure samples of semi-conductors led to an interest in applying this technique to the purification of organic solids and the concentration of impurities. A limited amount of work in the literature presented encouraging results in the purification of organic compounds.

An automatic "pulling" apparatus was constructed to enable a narrow heated zone to traverse a 12 inch length of organic material which was in a tube. The rate of pulling could be made either 0.8 inch/hr. or 1.7 inches/hr. The initial run, in which the organic material was impure phenol, was made in order to gain some experience with the apparatus and to determine whether or not the technique was suitable for very "impure" samples. Twenty-eight passes were made at a rate of 0.8 inch/hr. The results are shown below in Table III.

The results of further work on this project including a critical comparison of this technique with static crystallization will be presented in a forthcoming final report on Job No. 3531.

SURFACE AREA OF CYCLIZATION CATALYSTS

We were requested by Dr. Walter Knox of the Lion Oil Company Division to measure surface areas of three samples of an alumina based catalyst which had different past histories. The areas were determined by the method of Brunauer, Emmett and Teller. Calculations were made from nitrogen adsorption isotherms (-195°C.). The results are shown in Table IV.

The difference between the area of sample 366-162-1 and the other two is significant.

SANTOCEL SURFACE AREAS

DSW 621816

We were requested by Dr.Harry Teicher of the Inorganic Division to measure the surface area of two samples of silica gel as an aid in the development of a new Santocel. We determined the surface areas using the method of Brunauer, Emmett and Teller calculating the areas from nitrogen adsorption isotherms. The results are summarized in Table V.

TABLE IV

Catalyst Surface Areas

Sample	History	Surface Area (sq.m./gm.)
366-162-1	Used for 65 cycles	66
366-162-2	Fresh Catalyst	74
366-162-3	Used for 3 cycles	72

TABLE V

Santocel Surface Areas

Sample	Surface Area (sq. meters/gm.)
Santocel C, Batch 051020	134
Santocel FR, Pilot Run	231
Santocel FR, Batch 136924	370
Santocel FR, Batch 136925	345
Santocel FR, Batch 136926	351
Synton 200, Pilot Plant Lot 4	164
Synton 200, Interim Production	173

CARBOXYLATION OF BENZOIC ACID TO PHTHALIC ACID

A few exploratory experiments were made attempting to carboxylate benzoic acid to phthalic acid using the old Dept. 18 catalyst (phthalic acid decarboxylation) to see if the equilibrium concentration of phthalic acid was high enough to make this an attractive route to phthalic acid. No phthalic acid was recovered from these experiments. The effectiveness of the catalyst was proved by decarboxylating phthalic acid to benzoic acid.

Estimations by Dr. Kern Sears predicted a very unfavorable equilibrium constant for the reaction:

$$\text{benzoic acid}(s) + CO_2(g) \rightleftarrows \text{phthalic acid}(s)$$

Subsequent discussion with Prof. G. B. Kistiakowsky brought out the observation that the carboxylation of benzoic acid to phthalic acid should not be greatly different than the carboxylation of benzene to benzoic acid. Highly precise thermochemical data are available for these compounds and they predict a very unfavorable equilibrium from the point of view of benzoic formation.

In considering these conclusions it must be borne in mind that an unfavorable equilibrium for carboxylation with CO_2 to yield the free acid does not rule out the possibility of discovering economically attractive coupled carboxylations in which the carboxylating agent might be a carbonate salt and the final product might be a salt of phthalic acid.

SPECIFIC HEAT OF DI(2-BUTOXYETHYL)ADIPATE

The specific heat of di(2-butoxyethyl)adipate was estimated, using the method of Johnson and Huang (Can. J. Tech. 33,421(1955), to be 0.44 at 20°C. From a brief survey of similar organic liquids a temperature coefficient of + 0.001/°C. was estimated.

THERMAL STABILITY OF POLYMERIC OIL ADDITIVES

A sample of ethylene maleic anhydride copolymer octadecyl imide (40% in oil) supplied by Dr. Fred Lippmann (Dayton NBP 368521) and a sample of ethylene maleic anhydride copolymer-Aldol 14 ester-dimethylaminopropyl imide (66/34) from the Organic Division Engine Laboratory were subjected to differential thermal analysis to see if deterioration of these products could be identified with an observable exothermic or endothermic reaction. No endothermic or exothermic reaction was observed where the samples were heated to 300°C.

ELECTRICAL RESISTANCE OF MERSIZE 70R

Dr. E. Reaville requested a value for the value of the dielectric constant of Mersize 70R to answer a request from an instrument company Attempts to measure the dielectric constant were unsuccessful and the resistance measurements shown in Table VI suggest that Mersize 70R should be considered a poor conductor rather than a dielectric.

TABLE VI

Specific Resistivity of Mersize 70R
(December 1956 Production)

Temperature	Specific Resistivity (ohm-cm)
25°C.	3×10^6
95°C.	0.3×10^6

PHOSPHOROUS AMIDE REACTION MECHANISM

Dr. T. Reetz has found that the following reaction will take place at 80°C.

$$P[N(CH_3)_2]_3 + 3ROH \longrightarrow P(OR)_3 + 3(CH_3)_2NH$$

He has postulated that the reaction will proceed through the following intermediate:

$$(ROP[N(CH_3)_2]_3)^- \quad H^+$$

This leads to the prediction that mixtures of an alcohol and $P[N(CH_3)_2]_3$ should show electrical resistivities lower than either of the components due to the presence of the ionic reaction intermediate. Such measurements were made using ethanol (absolute with 0.5% benzene as denaturant) and are summarized in Table VII.

TABLE VII

Specific Resistivities at 25°C.

Sample	Specific Resistivity (ohm-cm.)
$P[N(CH_3)_2]_3$	3.4×10^8
Ethanol	9.8×10^6
Equimolar Mixture of alcohol and amide	
2 minutes after mixing	5.0×10^6
8 " " "	4.5×10^6
40 " " "	5.0×10^6
73 " " "	5.5×10^6
98 " " "	5.9×10^6
192 " " "	6.4×10^6

DSW 621819

Qualitatively the data support Dr. Reetz's postulate, but the possibility of trace ionizable impurities being present in the amide and ionizing to a greater extent in ethanol solution is not ruled out of consideration by these data.

NOTEBOOK PAGE NUMBERS

Low Temperature Dielectrics A 83255-70
Zone Refining A 107428
Catalyst Surface Areas A 87542-4
Santocel Surface Areas A 77583-6, A 87505-7, A 87509, A 87511-2
Carboxylation of benzoic acid to phthalic acid A 87503-4, A 87508, A 87510, A 87519-20
Specific Heat of Di(2-butoxyethyl)adipate A 96169
Oil Additive Thermal Stability A 41709
Electrical Resistance of Mersize 70R A 94032-3
Phosphorous Amide Reaction Mechanism A 105111-2

W. E. Koerner

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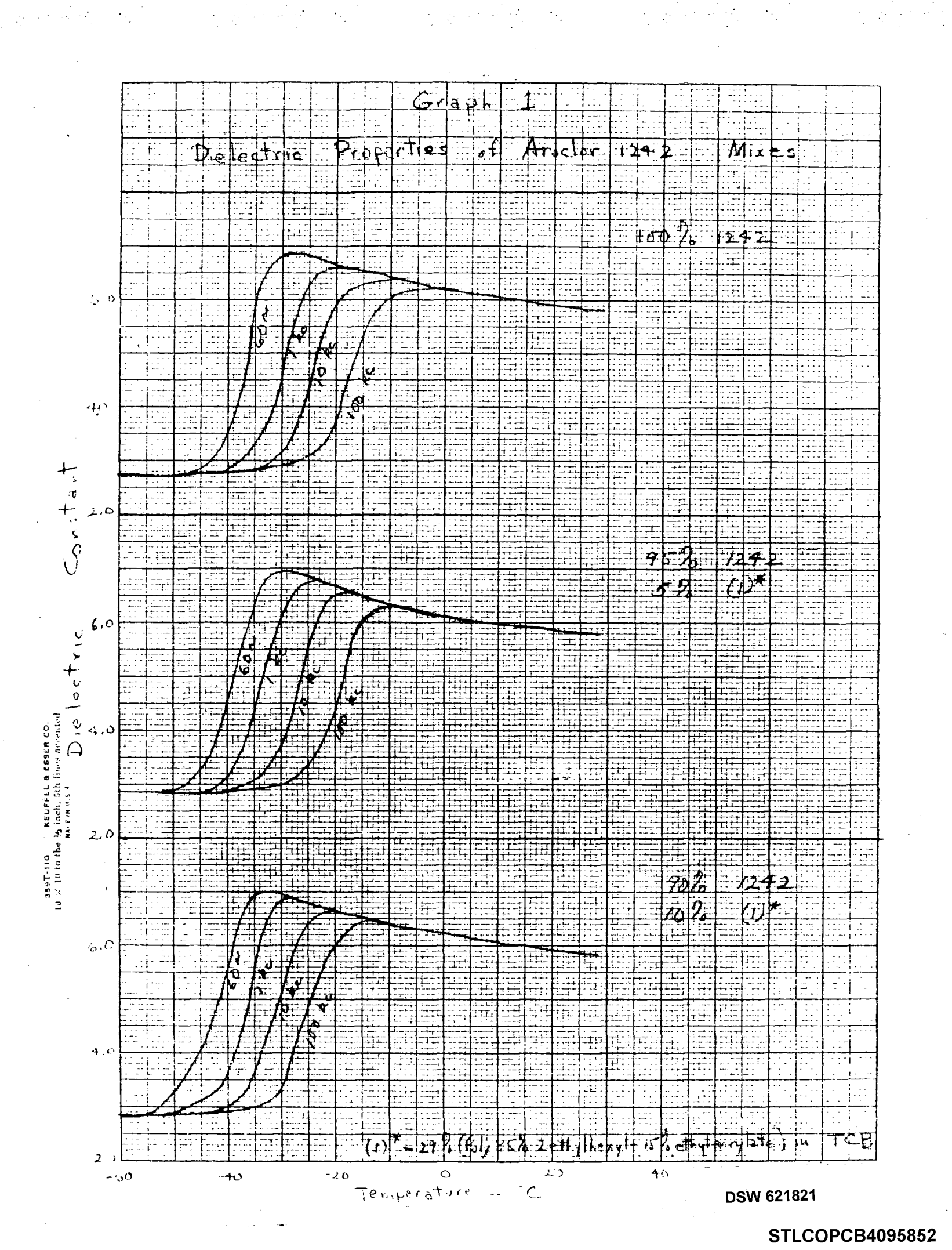
DSW 621820


Graph 1
Dielectric Properties of Aroclor 1242 Mixes
100% 1242
95% 1242
5% (1)*
90% 1242
10% (1)*
60 ~
25°
10°
-10°
Dielectric Constant
6.0
4.0
2.0
-30
-40
-20
0
20
40
Temperature — °C
(1)* = 27% (Poly 25% 2 ethylhexyl 15% ethylene) in TCB
KEUFFEL & ESSER CO.
DSW 621821
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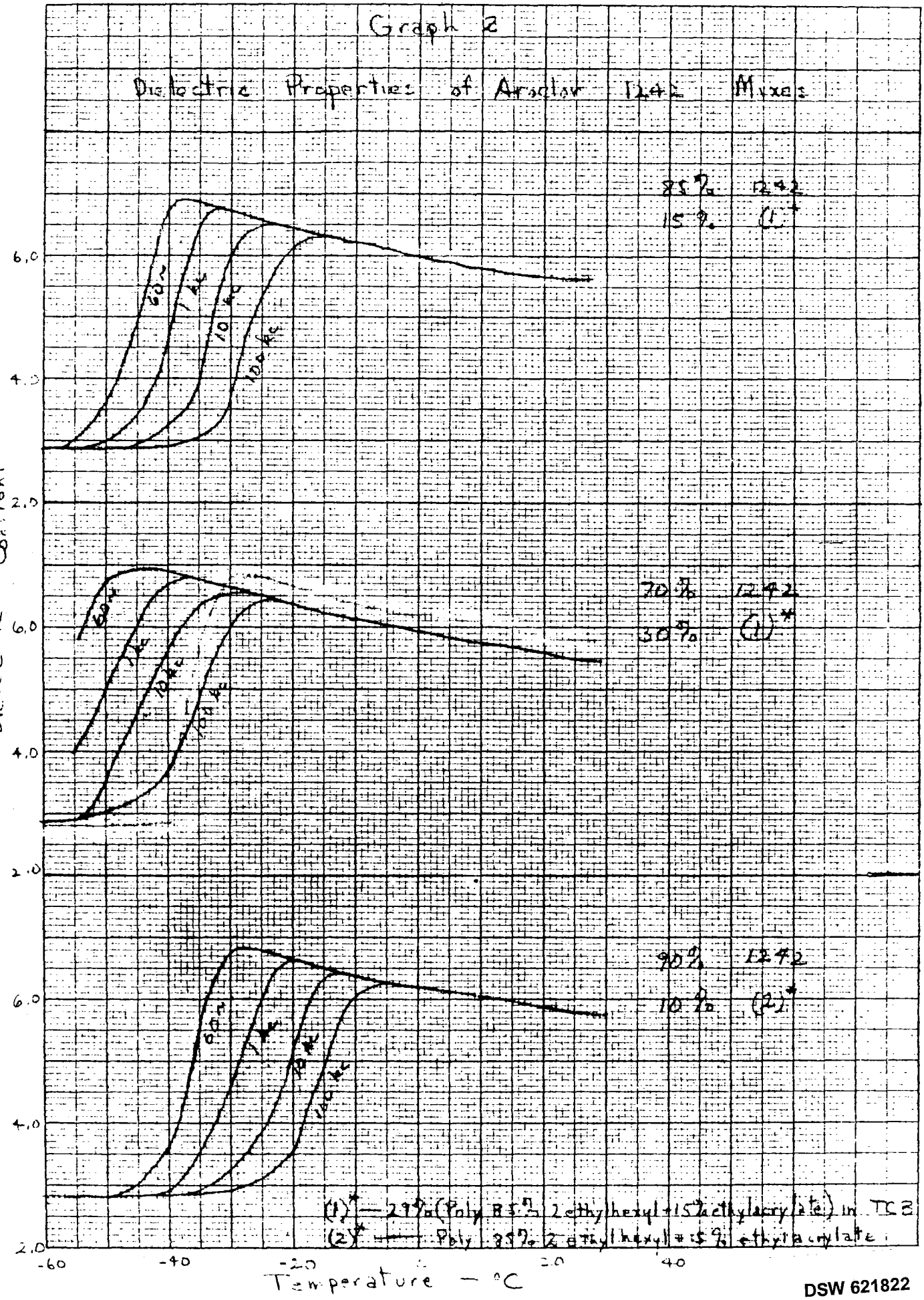

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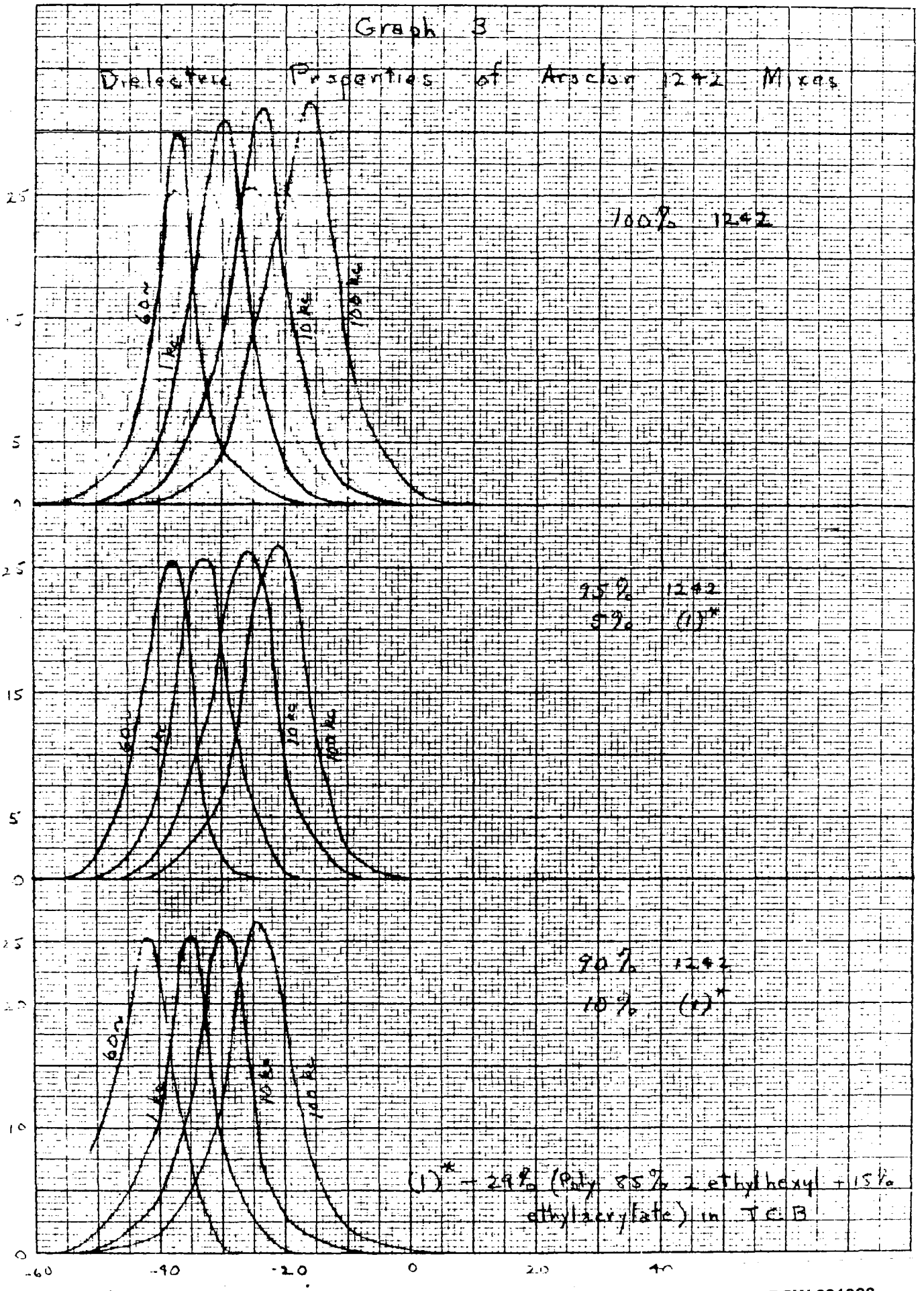
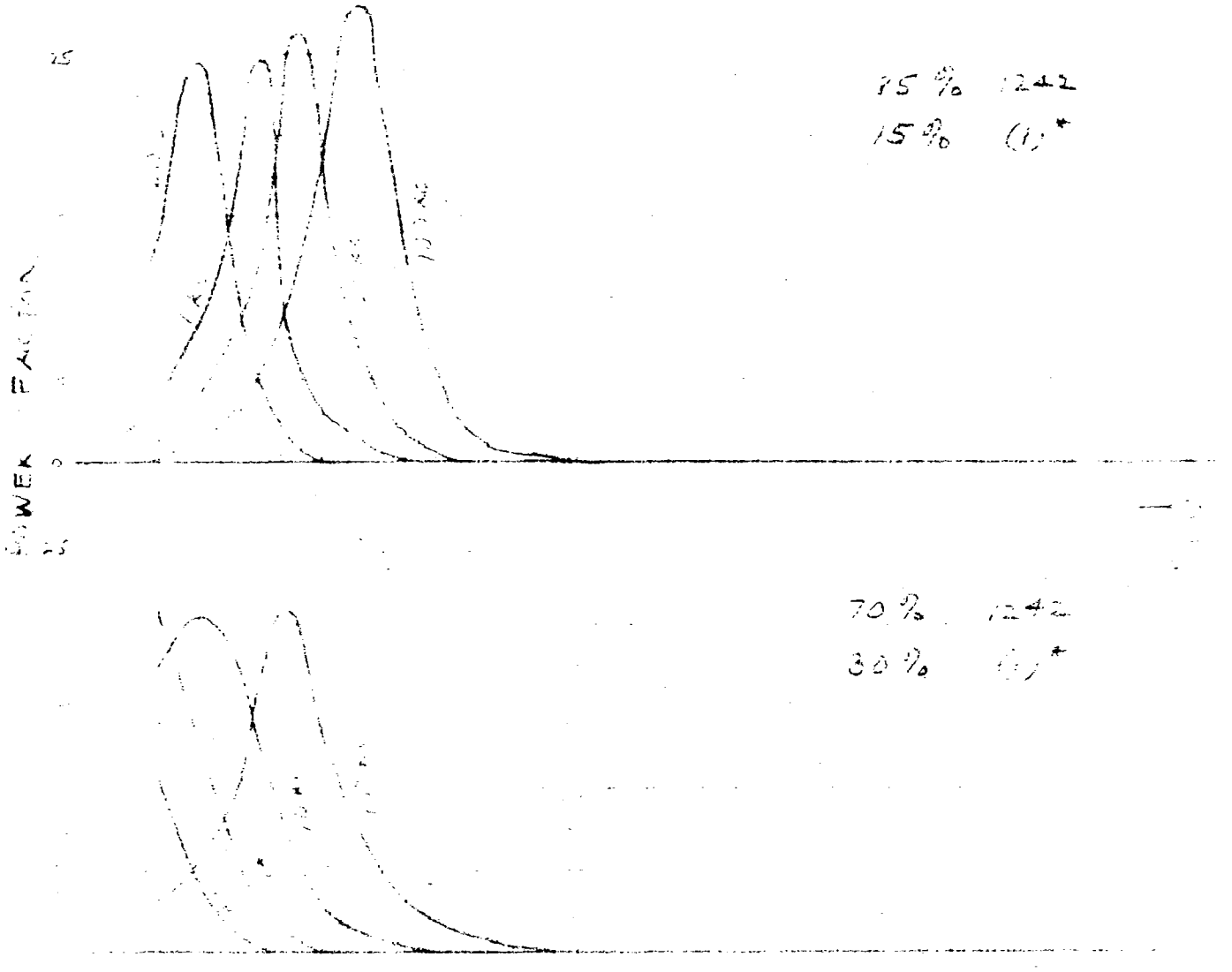


Graph 4

Dielectric Properties of Aroclor 1242 Mixes



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