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NEW RARE EARTH ANTIKNOCK ADDITIVES THAT
ARE POTENTIAL SUBSTITUTES FOR TETRAETHYL LEAD

AEROSPACE RESEARCH LABORATORIES

DECEMBER 1974

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Work accomplished at the USAF Aerospace Research Laboratories has demonstrated that certain lanthanide beta-diketonate chelates can function as antiknock agents in gasoline. Many lanthanide beta-diketonate chelate compounds were screened using ASTM knock-rating procedures. Antiknock effectiveness was observed to be a function not only of the particular lanthanide and ligand involved but also highly dependent upon test procedure and fuel type. Tetrakis (2,2,6,6-tetramethyl-3,5-heptanedionato)cerium(IV), Ce(thd) ₄ , was found to be superior in performance to tetraethyl lead as an antiknock agent for gasoline		

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when tested by the Supercharge Method (ASTM D909-67). The significance of this result, compared to the inferior performance of Ce(thd)₄ relative to tetraethyl lead observed in all other tests, is examined. A synergistic increase in octane number was observed when certain organic compounds were added to fuel containing Ce(thd)₄. The compound was tested additionally in independent studies which included single cylinder and on-the-road V-8 engine tests. Addition of 0.5 gram of Ce per gallon produced an increase of 2 road octane numbers in a V-8 engine. Other important properties were also evaluated. Unseparated rare earth chelates derived from an inexpensive ore exhibited antiknock effectiveness approximately equivalent to Ce(thd)₄ in motor octane number tests. Use of these novel rare earth additives in place of lead alkyls would result in reduced environmental pollution by lead and possibly other noxious emissions. The results of these investigations are presented and assessed. Topics requiring study or further development are identified.

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PREFACE

This interim technical report, "New Rare Earth Antiknock Additives That Are Potential Substitutes For Tetraethyl Lead", presents an application of pertinent portions of the research on metal chelates and combustion chemistry accomplished by scientists of the U.S. Air Force Aerospace Research Laboratories under Project 7023, during the period from October 1964 to October 1974. Appendices C, D, E, and F contain the reports of other organizations which participated to limited extents during various stages of the testing. The test results reported by Ethyl Corporation (Appendix E) and Sun Oil Company (Appendix F) were performed under "no-cost" agreements with the U.S. Government.

The authors would like to thank the following persons for their contributions: Mr. W.E. Bettoney, Petroleum Laboratory, E.I. DuPont De Nemours and Co., Inc., Wilmington, Del. and Dr. Walter L. Borkowski, Sun Oil Company, Marcus Hook, Pa. for their continued interest and helpful discussions; Capt. S.G. Hill, USAF Aero Propulsion Laboratory and Mr. T.J. O'Shaughnessy, USAF Aerospace Fuels Laboratory who arranged for testing at the Aerospace Fuels Laboratory at Wright-Patterson Air Force Base; Dr. H. El-Bisi and Mr. H. Ammlung, U.S. Army Materials Command, who arranged for testing at the U.S. Army Fuels and Lubricants Research Laboratory; Dr. Daryl Pocker, NRC Postdoctoral Fellow at ARL, for obtaining scanning electron micrographs; Dr. J. Stara and Dr. D. Moore of the EPA Environmental Toxicology Laboratory, Cincinnati, Ohio, for making the preliminary results of their toxicological studies on $Ce(thd)_4$ available to us; Dr. David W. Young, Consultant to the Federal Energy Administration, Chicago, Illinois for providing information on the synergistic effect on road octane numbers obtained by using organic co-additives with $Ce(thd)_4$; Mr. John N. Bowden of the U.S. Army Fuels and Lubricants Research Laboratory for his comments on the draft manuscript.

TABLE OF CONTENTS

SECTION		PAGE
I	INTRODUCTION	1
II	PERFORMANCE TESTING	2
III	SYNTHESES AND PROPERTIES	24
	1. TETRAKIS (2,2,6,6-TETRAMETHYL-3,5- HEPTANEDIONATO)CERIUM(IV)	24
	2. TRIS(2,2,6,6-TETRAMETHYL-3,5- HEPTANEDIONATO) LANTHANIDE(III)	24
	3. MIXED TRIS, TETRAKIS(2,2,6,6-TETRAMETHYL- 3,5-HEPTANEDIONATO) LANTHANIDE(III), (IV)	24
	4. TETRAKIS(1,1,1-TRIFLUORO-5,5-DIMETHYL- 2,4-HEXANEDIONATO)CERIUM(IV)	25
	5. TETRAKIS{1,3,DI(2-NAPHTHYL)-1,3- PROPANEDIONATO}CERIUM(IV)	26
	6. BIS(DIISOBUTYRILMETHANATO) HYDROXOPRASEODYMIUM(III)	26
	7. OTHER CERIUM AND PRASEODYMIUM CHELATES	27
	8. CEROUS NAPHTHENATE	28
	9. CEROUS OCTOATE	28
	10. CERIC OXIDE	28
	11. 2,2,6,6-TETRAMETHYL-3,5-HEPTANEDIONE	28
	12. METHYLCYCLOPENTADIENYLMANGANESE TRICARBONYL	28
IV	SOLUBILITY	29
V	STABILITY	31
	1. CHARACTERIZING THE SEDIMENT	31
	2. THE EFFECT OF WATER	32
	3. THE EFFECT OF GLASS	32

Table of Contents (Cont'd)

SECTION	PAGE
4. THE EFFECT OF LIGHT	32
5. THE EFFECT OF AIR	32
6. THE EFFECT OF H(THD)	35
7. ACCELERATED AGING TESTS	36
8. THE EFFECT OF ANTIOXIDANT	36
9. COMPATIBILITY	37
VI TOXICITY	38
VII PRODUCTS OF COMBUSTION	41
VIII RAW MATERIALS	42
IX ALTERNATE METHODS OF ADDITIVE INTRODUCTION	45
X DISCUSSION	46
1. PERFORMANCE	46
2. STABILITY	51
3. EXHAUST EMISSIONS	51
4. CONCLUSIONS	52
REFERENCES	54
APPENDIX A: DEFINITIONS, PHYSICAL PARAMETER VALUES, ETC. EMPLOYED	57
APPENDIX B: LIST OF ABBREVIATIONS	59
APPENDIX C. REPORT ON TESTING CONDUCTED BY U.S. ARMY FUELS AND LUBRICANTS RESEARCH LABORATORY	60
APPENDIX D: FINAL REPORT ON TESTING CONDUCTED BY U.S. ARMY FUELS AND LUBRICANTS RESEARCH LABORATORY . . .	68
APPENDIX E. REPORT ON TESTING CONDUCTED BY ETHYL CORPORATION	87

Table of Contents (Cont'd)

SECTION	PAGE
APPENDIX F: REPORT ON TESTING CONDUCTED BY SUN OIL COMPANY	103

LIST OF TABLES

TABLE		PAGE
I	SUMMARY OF TEST RESULTS ASTM ISOCTANE PRF	4
II	SUMMARY OF TEST RESULTS COMMERCIAL Pb-FREE AMOCO, PREMIUM GRADE	5
III	SUMMARY OF TEST RESULTS MOBIL RE 145 A	6
IV	SUMMARY OF TEST RESULTS ASTM 80 OCTANE PRF	7
V	SUMMARY OF TEST RESULTS RMFD-254-72	10
VI	SUMMARY OF TEST RESULTS 50/50 ISOCTANE/n-HEPTANE	15
VII	SUMMARY OF TEST RESULTS O-XYLENE	16
VIII	INSPECTION DATA MOBIL BLEND RE 145 A	19

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	ANTIKNOCK EFFECTIVENESS AS A FUNCTION OF ADDITIVE CONCENTRATION FOR $\text{Ce}(\text{thd})_4$ AND TEL IN ISOCTANE PRIMARY REFERENCE FUEL BY THE SUPERCHARGE METHOD, ASTM D 909-67	18
2	ANTIKNOCK EFFECTIVENESS AS A FUNCTION OF ADDITIVE CONCENTRATION FOR $\text{Ce}(\text{thd})_4$ AND TEL IN COMMERCIAL, Pb-FREE AMOCO PREMIUM-GRADE GASOLINE BY THE SUPERCHARGE METHOD, ASTM D 909-67	21
3	TRANSMISSIVITY VS. WAVELENGTH FOR A DILUTE SOLUTION OF $\text{Ce}(\text{thd})_4$ IN ISOCTANE	34
4	COMPARISON OF MOTOR OCTANE NUMBER WITH SPECIAL MOTOR OCTANE NUMBER FOR ARL-56 AND TEL IN RMFD-254-72 FUEL BLEND	47
5	COMPARISON OF RESEARCH OCTANE NUMBER WITH SPECIAL MOTOR OCTANE NUMBER FOR $\text{Ce}(\text{thd})_4$ IN RMFD-254-72 FUEL BLEND	49

SECTION I

INTRODUCTION

Emissions from internal combustion engines are significant contributors to environmental pollution. Increasing concern for the decrease in environmental quality observed in recent years, particularly in urban areas, has led to increased efforts to reduce these emissions. As is well-known, these efforts have included engine intake modifications, fuel composition changes, and exhaust products treatment. Gasolines containing Pb antiknock compounds are incompatible with the current catalytic exhaust converters, poisoning the noble metal catalysts which are the active elements. Furthermore, the United States government has imposed regulations which require the drastic reduction and eventual elimination of Pb in gasolines.

It has been estimated [1] that removal of lead alkyls from gasoline will reduce by about 6% the recoverable gasoline from each barrel of crude oil. Discovery of an acceptable substitute could effectively restore this loss to our dwindling reserves. Several Pb-free candidate antiknock additives have been proposed in the past, but most of these have not been found to function as viable replacements for tetraethyl and/or tetramethyl lead. The need for a Pb-free antiknock additive which will provide the necessary octane improvement for present-day gasoline stocks is especially critical now in this period of enhanced environmental concern, limited sources of supply, and increased costs for both raw material and processing.

This report describes the results of work accomplished at the U.S. Air Force Aerospace Research Laboratories [2], pursued initially for entirely different purposes, which have led to the evaluation of numerous compounds as potential replacement antiknock additives for the lead alkyls. Several classes of compounds containing the lanthanide elements which show varying amounts of antiknock activity are described. The compound of cerium referred to as ARL-56 or $\text{Ce}(\text{thd})_4$ was found to be superior in performance to tetraethyl lead as an antiknock agent for aviation grade gasoline when tested on a mole equivalent basis by the Supercharge Method (ASTM D 909-67). This compound also exhibited significant antiknock activity when tested in automobile engines. Factors in addition to the results of performance tests which must be considered in evaluating a new antiknock additive are discussed.

SECTION II

PERFORMANCE TESTING

The antiknock effectiveness of various additives was measured using ASTM procedures. Testing was conducted at the Aerospace Fuels Laboratory (SFQLA) on approved equipment by an experienced operator. This laboratory participates on a regular basis in the ASTM National Aviation Fuel Exchange Group.

In initial testing neat isooctane was used as the fuel. This standard reference fuel was readily available and would enable verification under all foreseeable conditions. As the work progressed, the positive results obtained led to an interest in testing firstly in a practical aviation-grade Pb-free gasoline and subsequently in fuels more nearly representative of automotive gasoline.

Despite efforts to do so, we were never able to secure a sample of practical aviation-grade Pb-free gasoline. Accordingly, tests were conducted with commercially obtained Amoco Pb-free premium grade gasoline. This had the highest octane rating of any obtainable practical fuel of which we were aware.

As for the automotive grade fuels, a 55-gallon drum of Pb-free gasoline was made available to us by Mobil Research and Development Corporation (Mr. W. D. Myers). We also tested with ASTM 80 Octane Primary Reference Fuel (ASTM 80 PRF) purchased from Phillips Petroleum Company.

The U.S. Army Fuels and Lubricants Research Laboratory (AFLRL) tested one additive, $\text{Ce}(\text{thd})_4$, in five full boiling range gasolines. These were selected to vary widely in research and motor octane numbers and in hydrocarbon type composition. ASTM 80 PRF, 50% isooctane-50% n-pentane, 77% toluene-23% n-heptane, and an alkylate feed stock were used in tests by AFLRL.

Based on these tests, we procured a drum of a full boiling range reference fuel RMFD-254-72 from Phillips Petroleum Company. This fuel is used by the CRC Road Octane Group for evaluation of road octane requirements of automobiles. A few tests were made in o-xylene and in a blend of 50% isooctane 50% n-heptane.

Samples were prepared at the Aerospace Research Laboratories (ARL) and conveyed to the SFQLA test site. The samples were usually prepared in one-gallon glass containers. Because of an enounced concern for safety during transportation, there was a period when one-gallon plastic containers were used.

Military aviation gasolines are governed by specification MIL-G-5572E. This allows the introduction of materials as antioxidants. Some of the solutions displayed stability problems. Efforts were made to correct this by addition of the ligand used in preparation of the additive. The addition of an antioxidant material was also tried. These aspects are discussed in more detail in a subsequent section of this report.

Ethyl Corporation and Sun Oil Company tested one additive, Ce(thd)₄, under no-cost contracts with the U.S. Air Force. In the Ethyl Corporation work, five test fuels were used: ASTM 80 PRF, 90% isooctane-10% n-heptane, and commercial Pb-free regular grade Sohio, Amoco, and Marathon gasolines. Additional tests included water contact, observation of combustion system deposits, existent gum, oxidation induction period, and copper corrosion test.

Sun Oil Corporation tested the additive in two 1973-model cars by the Modified Uniontown Method for road octane number for comparison with Motor Octane Number response and with TEL response. The two additives were also compared for emissions using the 1971 Federal Test Procedure Hot Start Cycle in a 1973 400 CID Ford. It should be noted that no attempt was made to tune the engines for the new additive being tested.

The results of these engine tests are contained in Tables I, II, III, IV, V, VI, and VII for the work done at WPAFB and in Appendices C, D, E, and F, which contain the reports received from the other organizations. It will be noted that the additive concentrations in the tables are given both in grams of metal added per gallon and in millimoles additive added per gallon. The work was conducted on a molar basis since this has significance from a chemical point of view. However, since the industry prefers to cite and compare results on the basis of grams metal per gallon, the weight concentrations are provided as well.

For those readers unfamiliar with the import of the various octane number measurements, a short description of each follows:

Research Octane Number (RON) is obtained from test ASTM D 2699-70. This test covers the determination of knock characteristics of motor gasolines intended for use in spark-ignition engines under low-speed, low temperature conditions, and is an indicator of antiknock quality for engines operating at full throttle and low engine speed.

Motor Octane Number (MON) is obtained from test ASTM D 2700-70. This test covers the determination of knock characteristics of motor and aviation type gasolines, intended for use in spark-ignition engines, under high speed, high temperature conditions and is an indicator of anti-knock quality for engines operating at full throttle, high engine speed and part throttle, low and high engine speed.

Supercharge Performance Number (SPN) is obtained from test ASTM D 909-67. This test covers the determination of the knock-limited power of fuels for use in spark-ignition aircraft engines, under supercharge rich-mixture conditions, such as might correspond to take-off and climb-out.

Road Octane Number (RdON) is obtained by determining the knock characteristics of motor gasolines in spark-ignition engines during use, on the road and is usually intermediate between the research and motor numbers.

TABLE I
SUMMARY OF TEST RESULTS
ASTM ISOCTANE PRF

Additive	Grams Additive U.S. Gallon	Grams Metal U.S. Gallon	Millimoles Additive U.S. Gallon	Research Octane Number	Motor Octane Number	Supercharge Performance Number
Ce(thd) ₄	0.568	0.0911	0.65	101.6	101.3	111.1, 112.2
	0.334		2.38		102.4	115.8, 123.1
	0.494		3.53			131.3
	5.73	0.920	6.56		103.5	136.1, 137.0
	12.5	2.00	14.3		105.3	145.0, 145.7
Pr(thd) ₃	0.447	0.0916	0.65	100.7		106.1
Nd(thd) ₃	0.451	0.0938	0.65	100.7		106.1
Yb(thd) ₃	0.470	0.112	0.65	100.9		106.8
TEL		0.135	0.65	101.6		104.9
Isooctane	-	-	-	100	100	100

TABLE II
SUMMARY OF TEST RESULTS
COMMERCIAL Pb-FREE AMOCO, PREMIUM GRADE

Additive	Grams Additive U.S. Gallon	Grams Metal U.S. Gallon	Millimoles Additive U.S. Gallon	Research Octane Number	Motor Octane Number	Supercharge Performance Number
-	-	-	-	99.7, 99.0 100.0	91, 91.0 91.1, 91.0	
Ce(thd) ₄	0.568	0.0911	0.65			112.7*
		0.159	1.13	100.0	91.1	
		0.332	2.37	100.0	91.5	
	2.08	0.334	2.38			115.2*
		0.491	3.50	100.0	91.6	
	3.08	0.494	3.53			130.0*
		0.913	6.52	101.1	91.6	
	5.73	0.920	6.56			136.3*
		1.98	14.2	101.7		
	12.5	2.00	14.3			157, 151.1, 155.0*
TEL		0.135	0.652			112.7
		0.730	3.52			115.2
		1.36	6.55			143.2
		2.95	14.2			152.5

*Always read at the peak of the indicated mean effective pressure (IMEP) vs fuel/air (F/A) curve. Peaks seemed to come at F/A of 0.122 while the usual position is at F/A = 0.113.

TABLE III

SUMMARY OF TEST RESULTS

MOBIL RE 145 A*

Additive	Grams Additive		Grams Metal		Millimoles Additive		Research		Motor	
	U.S. Gallon		U.S. Gallon		U.S. Gallon		Octane Number		Octane Number	
							88.0**		79.0,80.0	
Ce(thd) ₄			0.420		3.0		90.3		79.5,80.5	
Ce(acac) ₄					3.0				80.0	
TEL			0.622		3.0				80.5	
			0.947		4.57				79.5	
			1.01		4.87		92.4		83.5,83.3	
			1.04		5.02		92.0		83.2	
			1.06		5.09				82.8	
			1.06		5.10				82.8	
			1.08		5.21		92.9		84.5	
			1.09		5.26		91.5		80.1	

*Sample of lead-free blend supplied by:

**See Table VIII

W.D. Myers, Manager
 Fuels Service Group
 Research Department
 Mobil Research and Development Corp.
 Paulsboro, New Jersey 08066

TABLE IV
SUMMARY OF TEST RESULTS
ASTM 80 OCTANE PRF

Additive	Grams Additive		Millimoles Additive		Research Octane Number	Motor Octane Number
	U.S. Gallon	U.S. Gallon	U.S. Gallon	U.S. Gallon		
Ce(thd) ₄		0.0907	0.647		83.4, 82.8	84.8
		0.332	2.37		86.4	
	2.62	0.420	3.00			86.5, 86.4
						86.4, 86.4
						87.8* ∇
		0.491	3.50		88.1	
	5.24	0.841	6.00			86.6* π
		0.913	6.52		87.7	
	13.1	2.10	15.0			~87.5*+
Ce(tdh) ₄	2.76	0.420	3.00			87.2
Ce(hen) ₃	1.76	0.420	3.00			81.6
Ce(acac) ₄	1.61	0.420	3.00			81.3
R.E.(thd) ₃	0.510	0.153	0.65			82.6
		0.705	3.00			85.3
R.E.(thd) ₃ ⁺ DXE70	2.35	0.705	3.00			85.3
	0.0044	-	0.02			85.3

* The mixture heater was turned off during this evaluation.

+ Operator noted that the longer this concentration was run, the better the performance seemed to become.
 π Last test of this series with the mixture heater off. Operator noted there appeared to be some spark plug trouble at this point in time.

Engine may not have been cleaned out completely from previous Ce(thd)₄ test.

∇ Not completely stable - if run over 30 min. the pressure continues to drop-possible build-up of cerium.

TABLE IV (Cont.)

SUMMARY OF TEST RESULTS

ASTM 80 OCTANE PRF

Additive	Grams Additive U.S. Gallon	Grams Metal U.S. Gallon	Millimoles Additive U.S. Gallon	Research Octane Number	Motor Octane Number
Ce(thd) ₄ ⁺ DX570	0.565	0.0906	0.647	82.8	84.8
	0.0009	-	0.004		
H(thd)	1.78	-	9.68	81.7#	81.7#
	2.21	-	12.0		
Ce(thd) ₄ ⁺ H(thd)	0.568	0.0911	0.65	83.8	86.4
	0.0965	-	0.52		
	2.62	0.420	3.00		
	0.446	-	2.42		
	2.62	0.420	3.00		
	0.553	-	3.00		
	6.11	0.981	7.00		
	1.04	-	5.64		
	13.1	2.10	15.0	90.0	90.0
	2.23	-	12.1		
(CH ₃ C ₅ H ₅)Mn(CO) ₃	0.688	0.172	3.14	84.9	
Ce(thd) ₄ ⁺ TEL		0.420	3.00		87.4
		0.499	2.41		

TABLE IV (Cont.)
SUMMARY OF TEST RESULTS
ASTM 80 OCTANE PRF

Additive	Grams Additive U.S. Gallon	Grams Metal U.S. Gallon	Millimoles Additive U.S. Gallon	Research Octane Number	Motor Octane Number
TEL		0.317	1.53		85.9
		0.620	2.99		89.7, 89.7*
		0.622	3.00	87.2	89.7, 89.3
					89.9
		1.06	5.09		93.0
		1.58	7.64		96.0
		2.11	10.2		98.0
	3.16		15.3		100.0, 101

TABLE V
SUMMARY OF TEST RESULTS

RMFD-254-72

Additive	Grams Additive U.S. Gallon	Gram Metal U.S. Gallon	Millimoles Additive U.S. Gallon	Motor Octane Number
-	-	-	-	75.0, 74.4 75.0, 81.2*
Ce(thd) ₄	2.62	0.420	3.00	76.6, 76.8 84.5* 85.3* 86.6* 76.3 86.9*
	5.24	0.841	6.00	
	8.73	1.40	10.0	
	12.5	2.00	14.3	
	13.1	2.10	15.0	

* The mixture heater was turned off during this evaluation.

■ Air @ venturi inlet @ 40°C (104°F) venturi outlet @ <25°C (<77°F). Barometric pressure 29.18"Hg.
 Fuel sample flow rate on side gauge changed from 1.5 to 1.2
 Fuel reference flow rate on side gauge changed from 1.2 to 0.9
 Micrometer settings from a normal of 0.625 to 0.525 because of lowered temperature.

Thus we have increased the compression ratio.

Operator noted that engine

† Attempted to run suspension

π Amount of additive measured out; solution saturated @ <<3 millimole/gallon.

◇ Very impure. Only about one-half of measured amount dissolved.
 ⊗ Very impure. Never crystallized. Product was an oil. Used entire sample from 0.2 gram prep-exact amount not known.

TABLE V (Cont.)
SUMMARY OF TEST RESULTS

RMFD-254-72

Additive	Grams Additive U.S. Gallon	Grams Metal U.S. Gallon	Millimoles Additive U.S. Gallon	Motor Octane Number
Ce(thd) ₄ ⁺ (ClCH ₂) ₂	2.62	0.420	3.00	77.5
	0.568	-	5.74	
	2.62	0.420	3.00	76.8
	2.27	-	23.0	
	7.86	1.26	9.00	77.7
	1.70	-	17.2	
Ce(thd) ₄ ⁺ C ₅ H ₁₀ Br ₂	2.62	0.420	3.00	77.9
	0.805	-	3.5	
(ClCH ₂) ₂	0.568	-	5.74	75.0
Ce(acac) ₄		0.420	3.00	75.0
Ce(fod) ₄	3.96	0.420	3.00	75.5, 77
	9.91	1.05	7.50	86.2*
	13.2	1.40	10.0	76.2#, 81
Ce(tfa) ₄	2.26	0.420	3.00	75.4
CeO ₂		0.420	3.00	75.5†
Ce(tdh) ₄	13.1	2.00	14.3	76.8

TABLE V (Cont.)

SUMMARY OF TEST RESULTS

RMFD-254-72

Additive	Grams Additive U.S. Gallon	Grams Metal U.S. Gallon	Millimoles Additive U.S. Gallon	Motor Octane Number
Ce(dibm) ₄	2.28	0.420	3.00	75.2
Ce(dnp) ₄	4.30 π	0.420 π	3.00 π	74.4
Ce(facam) ₄	3.24	0.422	3.01	77.9
Ce(mhd) ₄	2.11	0.420	3.00	75.5
Ce(hfa) ₄	2.89 $\diamond$	0.419 $\diamond$	2.99 $\diamond$	76.2
Ce(hfa) ₃	2.28	0.420	3.00	75
Ce(naphthenate) ₃	1.69	0.420	3.00	76.0
Ce(octoate) ₃	1.71	0.420	3.00	75.6
Ce(4-6 nonane- diene) ₄	$\bullet$	$\bullet$	$\bullet$	76
Ce(thd) ₄ ⁺ TCP	2.62 1.10	0.420 -	3.00 3.00	77.0

TABLE V (Cont.)

SUMMARY OF TEST RESULTS

RMFD-254-72

Additive	Grams Additive U.S. Gallon	Grams Metal U.S. Gallon	Millimoles Additive U.S. Gallon	Motor Octane Number
Pr(thd) ₃ ⁺ TCP	0.691 0.368	0.141 -	1.00 1.00	75.0
Pr(facam) ₃	2.54	0.426	3.01	75.5
Pr(OH)(dibm) ₂	1.41	0.423	3.00	75.5
Pr(thd) ₃	0.691	0.141	1.00	75.0
Nd(thd) ₃	2.08	0.433	3.00	75.2
La(thd) ₃	2.07	0.417	3.00	75.0
Sm(thd) ₃	0.700	0.150	1.00	75.6
Tb(thd) ₃	2.13	0.477	3.00	76.0
Er(thd) ₃	2.15	0.502	3.00	75.0
Ho(thd) ₃	2.14	0.495	3.00	76.0

TABLE V (Cont.)
SUMMARY OF TEST RESULTS
RMFD-254-72

Additive	Grams Additive U.S. Gallon	Grams Metal U.S. Gallon	Millimoles Additive U.S. Gallon	Motor Octane Number
TEL	0.103	0.50		76.3
	0.207	1.00		77.4
	0.616	2.97		79
	0.620	2.99		79.3
	0.622	3.00		87.8*
	1.24	5.99		83.0, 87.9*
	2.07	9.98		85.0, 88.2*
	3.10	15.0		85.7, 88.0*
(CH ₃ C ₅ H ₅)Mn(CO) ₃		3.00		77.2
R.E. (thd) 3,4		3.00		76.8

TABLE VI
SUMMARY OF TEST RESULTS
50/50 Isooctane/n-Heptane

Additive	Grams Additive U.S. Gallon	Grams Metal U.S. Gallon	Millimoles Additive U.S. Gallon	Motor Octane Number
Ce(thd) ₄	2.62	0.420	3.00	61.0
		2.00	14.3	69.8
TEL		0.616	2.97	65.2

TABLE VI
SUMMARY OF TEST RESULTS
o-Xylene

Additive	Grams Additive U.S. Gallon	Grams Metal U.S. Gallon	Millimoles Additive U.S. Gallon	Motor Octane Number
-	-	-	-	101.9
Ce(thd) ₄	2.62	0.420	3.00	101.9
TEL				102.2*

* Concentration not precisely defined (greater than 5 millimoles/Gal)

The ultimate test for any fuel-additive combination is the actual performance observed in routine use. Insofar as the ASTM methods give results which do correlate with observed behavior, they are useful standardized rating procedures.

As it turned out, for the class of additives with which we are dealing, the SPN appears to be the better indicator of the performance of the additive per se. Unfortunately, for various reasons this information was obtained only near the end of our testing period. As a result the bulk of the data on the effect of ligand structure was gathered on the much less responsive Motor Method. Nevertheless, the ability of the additives to function in ASTM 80 PRF provides much valuable information. The efficacy of the mixed rare earths, tested as RE(thd)_{3,4}, was demonstrated.

The metal most frequently tested was cerium. From the hypotheses that led to this work it was concluded that cerium was the most likely practical candidate element. Solubility and volatility being important considerations, Ce(thd)₄ was the first compound selected for testing. Not only did it prove superior to the Pr(thd)₃, Nd(thd)₃, and Yb(thd)₃ tested at the same time, it has remained the apparent material of choice to this date.

It is an interesting and puzzling fact that the rare earth chelate additives did not function nearly as well, in terms of Δ RON and Δ MON, in gasolines as they did in the paraffin hydrocarbon materials. The disparate results influenced the course of this investigation significantly. The initial tests were conducted in isooctane using the Supercharge Method. When they proved successful (see Figure 1) the testing was extended to the Motor and Research Methods.

In an effort to get data on a representative gasoline, we tested Amoco Pb-free premium. Our early data on Amoco were the discouraging RON and MON numbers. Several factors then caused us to change the thrust of our efforts.

When TEL was tested in Amoco, the response was about the same as for Ce(thd)₄. The FIA analysis of the Amoco fuel showed 40.0% aromatic and 1.5% olefinic material. Since aromatic compounds decrease the effectiveness of TEL as an antiknock, perhaps by acting as stabilizers for the decomposition [3], it was thought that a similar effect might be occurring with the Ce(thd)₄.

This was thought to be reinforced by subsequent tests, which showed Ce(thd)₄ performed reasonably well in ASTM 80 PRF but not well in the Mobil fuel, which had a high aromatic content (Table VIII). However, later review of the results listed in Table III indicated that this may have been from not using high enough concentrations of additive.

AFLRL, based on results in fuels having a wide variation of compositions, reached the same tentative conclusion: "aromatics may be the major ARL-56 inhibitor."

With this in mind, one fuel, RMFD-254-72, was selected for further tests involving gasolines. Data on ASTM 80 PRF continued to be accumulated until this gasoline was received. Upon receipt, all further tests were conducted in

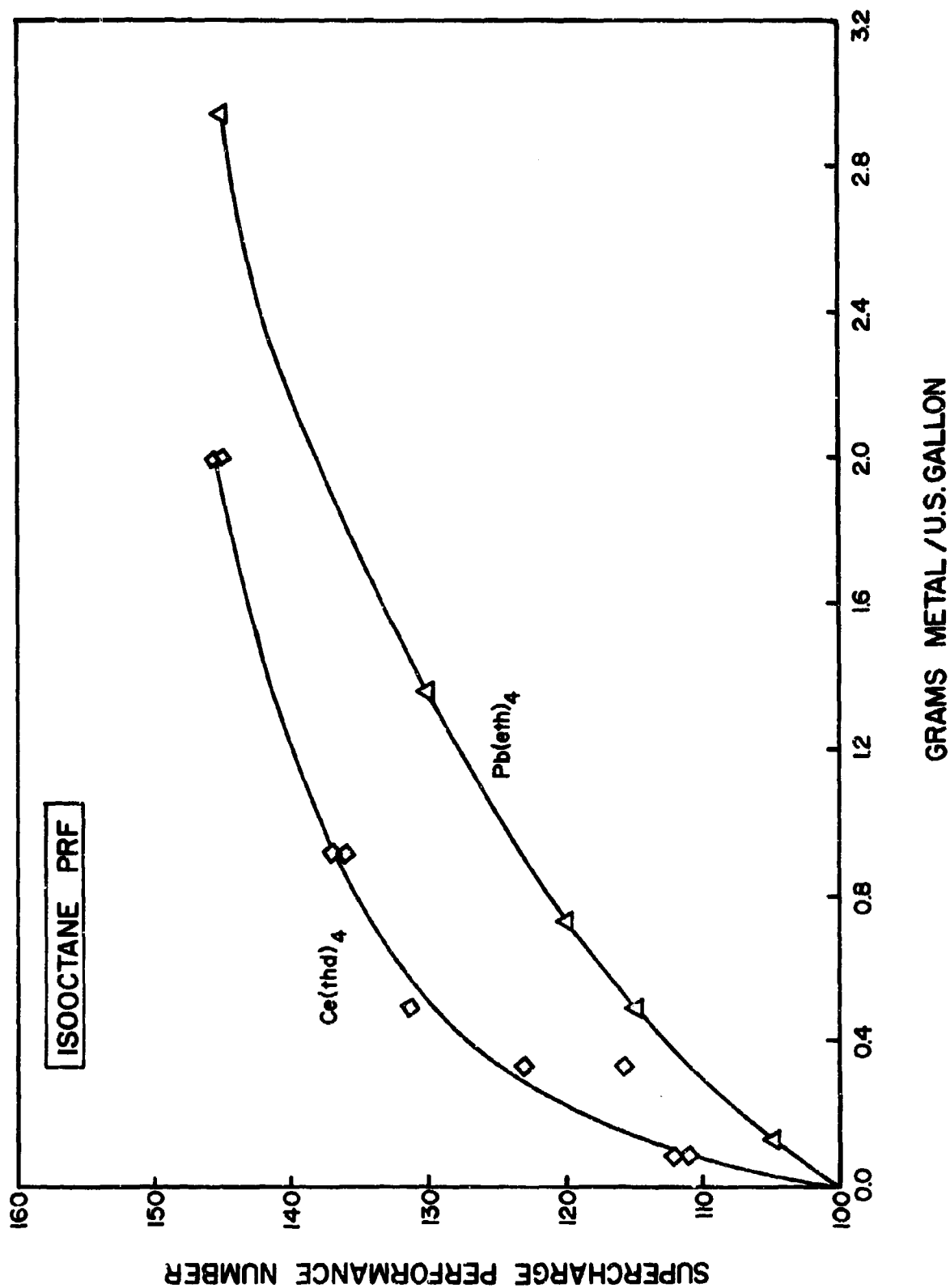


Figure 1. Antiknock Effectiveness as a Function of Additive Concentration for $Ce(thd)_4$ and TEL in Isooctane
Primary Reference Fuel by the Supercharge Method, ASTM D 909-67.

TABLE VIII

INSPECTION DATA MOBIL BLEND RE 145 A

Research ON	88.0
Motor ON	80.0
Gravity, °API	57.8
RVP, psi	8.3
ASTM Distillation, °F	
IBP	86
5%	113
10%	126
20%	147
30%	169
40%	193
50%	221
60%	250
70%	280
80%	309
90%	345
EP	402
% Rec.	98
% Res.	1
% Loss	1
FIA, % Aromatics	34.0
FIA, % Olefins	9.9
Fia, % Saturates	56.1
Sulfur, Wt. %	0.063
Lead ppm	2.2

RMFD-254-72. Since the additives would have to function in gasolines, the rationale was that the testing should be done in this practical fuel. Only at the very end were the SPN results with Amoco obtained, for completeness.

The Amoco SPN results (see Figure 2) completely changed the thinking. It then became clear that the composition of the fuel was not the problem in this instance. Rather, that the variation in response had to be tied in some way to differences in the test methods themselves and their interaction with the fuel.

In comparing the various test methods it was noted that the method of charging the combustible mixture is different in all three. In the Supercharge Method, D 909-67, the fuel is injected as a spray into the preheated air stream and directed onto the intake valve stem. In the Research and Motor Methods the fuel is introduced via carburetion and then ducted to the intake valve. Moreover, in the Motor Method, D 2700-70, the fuel-air mixture is heated in the intake ducting by an immersion blade heater to a temperature of 149°C (300°F).

The effect of the mixture heating, as well as the geometrical effect of the heater blade, was investigated by operating the engine with the heater blade electrical power turned off. With ASTM 80 PRF, the results (Table IV) are inconclusive with regard to the temperature effect, but do show a possible effect due to obstruction of the flow.

On the other hand, when using the RMFD-254-72 fuel (Table V) heating the mixture charge produces a demonstrable effect. This is true for the clear fuel as well as the Ce(thd)₄, Ce(fod)₄, and TEL compositions. No inference regarding the effect of a flow obstacle is possible in this case, since RON data were not taken.

This, then, led us to consider the conditions prevailing in the various intake systems. Fuel injection is used in the Supercharge Method, as discussed earlier. The fuel is injected through a nozzle at high pressures (1200 or 1450 psi), forming a conical spray pattern. This finely divided mist is centered in the inlet elbow so that the core of the spray impinges on the intake valve stem. Thus, air and fuel are delivered well-mixed directly to the cylinder inlet.

In the Research and Motor Methods the fuel is mixed with air using a carburetor. The carburetor is fitted with a curved inlet pipe connecting with the inlet surge pipe. A 90 degree elbow and vertical pipe may be used instead. On the Research engine the carburetor is mounted directly onto the cylinder.

An intake manifold is located between the carburetor and cylinder in the Motor Method. An electric immersion mixture heater, centrally located with respect to the manifold walls, is installed with the opening between the two prongs of the heater directly opposite the carburetor inlet. The prongs are straight and parallel to each other.

From the above description one can see that the path of the fuel-air mixture from the time of mixing until it reaches the intake valve becomes progressively more tortuous in going from Supercharge to Research to Motor Method. In the Supercharge Method the fuel is introduced as a fine mist

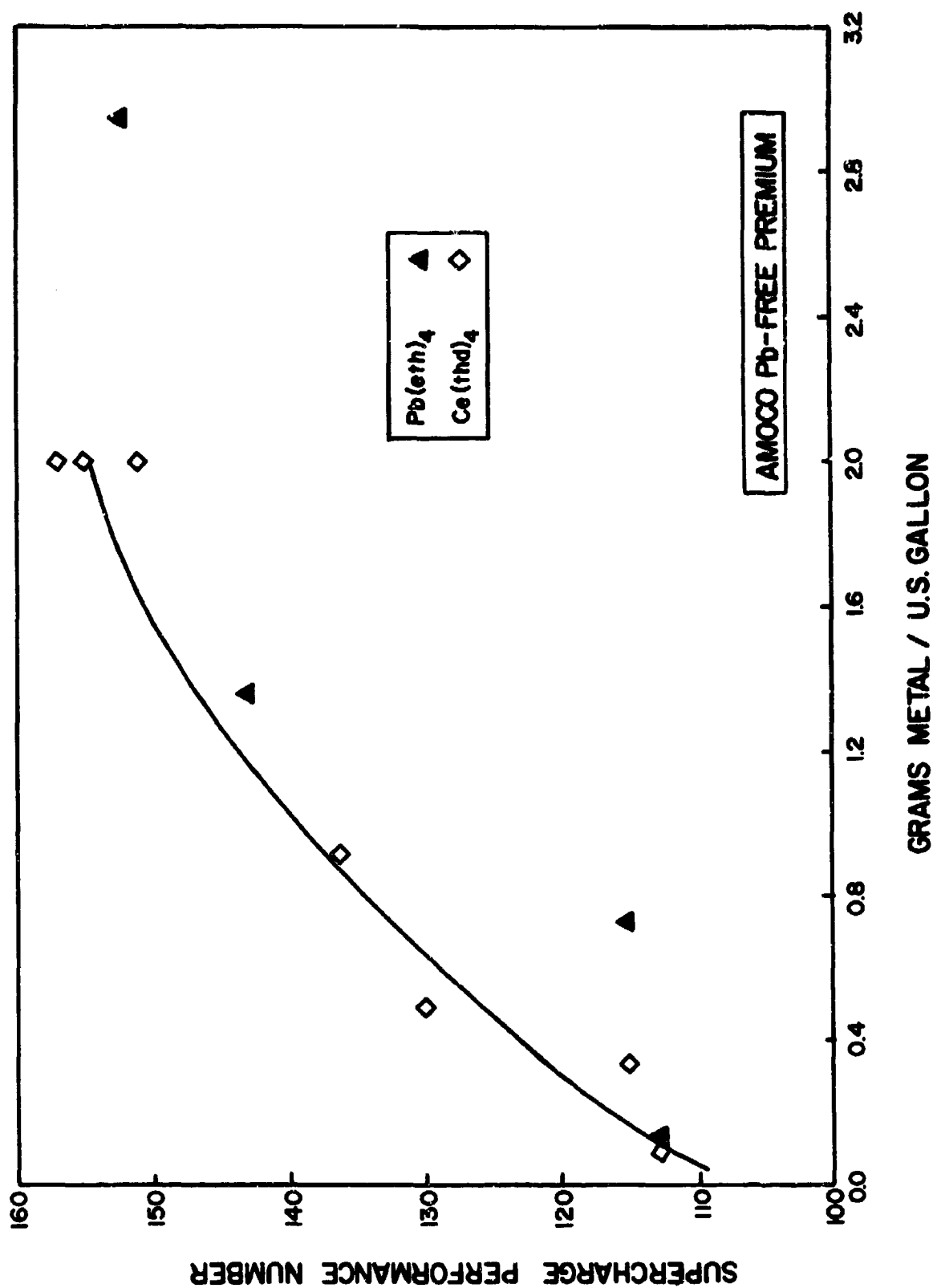


Figure 2. Antiknock Effectiveness as a Function of Additive Concentration for Ce(thd)₄ and TEL in Commercial, Pb-Free AMOCO Premium-Grade Gasoline by the Supercharge Method, ASTM D 909-67.

metered in under pressure. In the other two methods the fuel is aspirated in through the metering devices of the carburetor.

As the fuel enters the region of low pressure, flashing occurs. The vigor of this process may be expected to shatter some of the fuel droplets formed during carburetion, producing smaller mist-like droplets. The degree to which this occurs may be expected to depend upon the properties of the particular fuel being used. A mixture of vaporized fuel and fine mist of un-vaporized fuel, together with the larger parent droplets, then exists.

As this mixture wends its way through the inlet system, some coalescence occurs. Impingement on the internal surfaces also occurs; this fuel must be vaporized from the surface in order to be transported. In the presence of the immersion heater, not only is the path longer and the internal surface area much greater, but the heating also introduces additional complications resulting generally in poorer knock performance.

The rare earth beta-diketonates possess remarkable thermal stability in the pure state, being stable to several hundreds of degrees. Their stability under intake conditions, mixed with fuel and air, is not known. However, long times required to attain complete equilibrium in engine tests (in some cases, two to three hours) have been observed. Conversely, the engines also exhibited long times for clean-out when operated on clear fuel.

This led to the hypothesis that during induction a portion of the additive deposited along the intake system. Because of the vapor pressure-temperature relationships of the additives, together with their thermal stability, these deposits were subsequently removed during flushing. The Ethyl Corporation results (Appendix E) show just this behavior. The alkyl fuels laid down their deposits at an earlier stage in the process.

Tetraethyl lead has a vapor pressure of 2 torr at 50°C. The vapor pressures of the rare earth-thd compounds are much lower; a temperature of 175 to 225°C is required to attain a similar value. Dissolved in small concentrations in the fuel, the chelates would be expected to have very low partial pressures. Therefore, during the vaporization of the fuel the additives would be expected to remain predominantly with the liquid phase. The complete evaporation of very small mist droplets could produce some additive in very finely divided form.

After impinging upon the surfaces, the fuel component subsequently distills away but only very little of the additive. With the lapse of time the concentration of the additive in the liquid phase on the wall increases. During this period the amount of additive distilling into the intake stream is increasing. And so it goes until an equilibrium is attained, perhaps by saturation, after which no more change is observed. Later, when running on clear fuel the reverse process occurs and the additive deposits are removed. This again accords with the observations of Ethyl Corporation in Appendix E.

All n-heptane/isooctane fuels have boiling points of 99°C. These gave higher octane number increases than the full-boiling gasolines. O-xylene, with a boiling point of 144°C (291°F), corresponds to the heavy end of the

full-boiling gasolines. The greater tendency for repeated flashing, forming fine mist, is seen as the reason the alkyl fuels gave a deposit closer to the carburetor (see Appendix E) than the gasolines and also why the $\text{Ce}(\text{thd})_4$ performed better in those fuels. The greater the percentage of the fuel transformed into a fine mist and the finer the mist, the better the probability of delivering the additive to the cylinder would seem to be.

Therefore, we recommend that these aspects be investigated further. In particular, the use of fuel injection should be studied since this seems to work quite well and gives performance superior to TEL. However, we must caution that other factors, such as fuel-air ratio to mention just one, may be important reasons why we observed performance superior to TEL in the Supercharge engine tests.

Should tests on automobiles equipped with fuel injection engines prove successful, especially should these additives outperform or at least compete with TEL, the conversion to fuel injection systems in future designs should be considered.

The following quote [4] succinctly summarizes the advantage of fuel injection:

"Fuel injection overcomes several disadvantages of carburetors. A carburetor mixes air and fuel. Heat from the engine vaporizes this mixture to make it burn properly. The expansion of the heated air reduces the amount of air going to the cylinders. The cylinders get differing amounts of the vapor, depending on their distance from the carburetor. Some of the gasoline often fails to burn because of improper vaporization. The engine may flood (get too much gasoline), or ice up in winter and vapor lock in summer.

"Fuel injection divides the carburetion process into two systems. One controls the air flow; the other the fuel. Electronic or mechanical controls link the two systems, thus insuring that each cylinder gets the same amount of fuel. The cylinders also get only the amount of fuel that will burn in the amount of air that enters them. The nozzles break the fuel into a fine spray so that it all burns. The cylinders get more air, because the air does not have to be heated. This increases power and does not waste unburned fuel. Cold engines start quickly and run smoothly. The throttle controls only the air flow. Therefore, the engine cannot be flooded."

By minimizing the quantity of pollutants produced, particularly during cold starts, this system would ease the load on the clean-up devices. It should also help effect improved fuel economy. The increased cost should be offset, in some measure at least, by the savings in intake system treatment devices.

SECTION III

SYNTHESES AND PROPERTIES

1. tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato) cerium(IV); Ce(thd)₄

Ce(thd)₄ can be prepared from Ce(NO₃)₃·6H₂O by air-oxidation as we described previously [2] or can be prepared from other ceric salts, e.g., (NH₄)₂Ce(NO₃)₆ as reported below:

Ten millimoles of (NH₄)₂Ce(NO₃)₆, 5.48 g., was dissolved in the minimum amount of distilled water. Forty millimoles 2,2,6,6-tetramethyl-3,5-heptanedione, 7.37 g., was dissolved in 50 ml. of 95% ethanol. To the ethanol solution of the ligand was added forty millimoles reagent NaOH, 1.6 g., which had been previously dissolved in the minimum amount of distilled water. The solution of Na(thd) thus formed was stirred for approximately fifteen minutes (the solution is a light yellow color). Next the (NH₄)₂Ce(NO₃)₆ solution was added to the Na(thd) solution dropwise with stirring. The color of the resulting solution immediately turned dark red-brown, and a small amount of Ce(thd)₄ precipitated at this point. Additional distilled water was added to precipitate the remaining Ce(thd)₄. The crude Ce(thd)₄ was collected by filtration, dried, and recrystallized from methylcyclohexane or toluene. The density of Ce(thd)₄ is 1.138 g/cc.[5] While no attempt was made to optimize yields using this procedure, yields in the range of 80-90% were obtained. Thermal gravimetric analysis of Ce(thd)₄ in a helium atmosphere shows the compound to be volatile with sublimation occurring in the range of 190°C to 290°C. The temperature at which half the sample had sublimed was ca. 267°C.

Elemental Analysis for Ce(thd)₄

	Calculated (%)	Found (%)
Carbon	60.52	60.36
Hydrogen	8.77	8.55
Cerium	16.05	16.44

2. tris(2,2,6,6-tetramethyl-3,5-heptanedionato) lanthanide(III); Ln(thd)₃

"Lanthanide" in this instance stands for each of the tris lanthanides individually (i.e., lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, or lutetium). A general method which has been reported previously [6-11] was used to prepare the individual tris lanthanide-thd chelates. This method is capable of producing the individual chelates in ca. 90-97% yields.

3. Mixed tris, tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato) lanthanide(III), (IV); Ln(thd)_{3,4}

A quantity of 94.25 grams of mixed "Rare Earth Oxide" (Lindsay Chemical Co., code 330) containing approximately 48% CeO₂, 24% La₂O₃, 17% Nd₂O₃, 5% Pr₆O₁₁, 3% Sm₂O₃, 2% Gd₂O₃, 0.2% Y₂O₃, and 0.8% other rare earth oxides was placed in a Teflon beaker to which was carefully added concentrated reagent hydrochloric

acid. The mixture was heated on a hot plate in the hood until all the "Rare Earth Oxide" had reacted. Approximately 500 c.c. concentrated HCl was required. The solution was taken to dryness, and 65.1 grams of the hydrated mixed rare earth chlorides thus produced was dissolved in approximately 50 c.c. of distilled H₂O. With constant stirring, the mixed rare earth chloride solution was added to a solution containing 600 millimoles 2,2,6,6-tetramethyl-3,5-heptanedione, 124 c.c., which had been diluted previously with approximately 400 c.c. of 95% ethanol and to which had been added subsequently a solution of 600 millimoles, 24 grams, of reagent NaOH dissolved in ca. 50 c.c. distilled H₂O. A quantity of mixed Ln(thd)_{3,4} precipitated from solution initially. Approximately 500 c.c. distilled water was added and the solution was allowed to stir overnight. The crude red-brown colored product was collected by suction filtration through a medium porosity sintered glass funnel and was air dried for 3 hours. The product obtained was not recrystallized, but was used as such. Percent yield, based on supplier's analysis of starting material, is 96%.

Elemental Analysis Found	%
Cerium	13.29
Lanthanum	4.22
Neodymium	5.13
Praseodymium	1.33
Samarium	0.62
Gadolinium	0.74
Yttrium	0.39
Carbon	53.40
Hydrogen	7.60

Molecular Weight (benzene) 758

4. tetrakis(1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato)-cerium (IV); Ce(tdh)₄

Two hundred millimoles of 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione (Eastman Organic Chemicals), 39.2 grams, was added to 100 c.c. 95% ethanol. To this solution was added 200 millimoles of reagent NaOH, 8.0 grams, dissolved in 50 c.c. distilled water. The solution was stirred and fifty millimoles of (NH₄)₂Ce(NO₃)₆ (Matheson, Coleman, and Bell), 27.4 grams, dissolved in 75 c.c. distilled water was added. A red-brown color was immediately present upon addition of the ceric salt. This color is indicative of the formation of the ceric β-diketonate. Five hundred c.c. of distilled H₂O was added and the red-brown Ce(tdh)₄ precipitated from the solution. The crude Ce(tdh)₄ precipitate was collected via suction filtration through a medium porosity sintered glass funnel and was air dried. The dried Ce(tdh)₄ was dissolved in boiling methylcyclohexane and filtered while hot. The filtered solution was allowed to cool and pure Ce(tdh)₄ crystallized. The crystallized Ce(tdh)₄ was collected by suction filtration and was air dried; m.p., 138-139°C. Thermogravimetric analysis showed the Ce(tdh)₄ to be volatile, with sublimation commencing at approximately 125°C, and the temperature at which one-half of the sample had sublimed was ca. 199°C.

Elemental Analysis for $\text{Ce}(\text{tdh})_4$

	Calculated (%)	Found (%)
Carbon	41.74	41.57
Hydrogen	4.38	4.13
Fluorine	24.76	24.98
Cerium	15.22	15.71
Molecular Weight	920.77	880 in CHCl_3

5. tetrakis[1,3-di(2-naphthyl)-1,3-propanedionato] cerium (IV); $\text{Ce}(\text{dnp})_4$

Thirty millimoles of 1,3-di(2-naphthyl)-1,3-propanedione (Eastman Organic Chemicals), 9.73 grams, was dissolved in reagent grade benzene. To this solution was added 30 millimoles of reagent NaOH, 1.2 grams, dissolved in absolute ethanol. Next 7.5 millimoles $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (Matheson, Coleman, and Bell), 4.13 grams, dissolved in absolute ethanol was added to the continuously stirred solution. A dark brown color appeared in the solution upon the addition of the ceric solution. The solvent was removed by evaporation. The crude brown solid was redissolved in boiling benzene. The solution was filtered while hot with all benzene-insoluble material being removed and discarded. The $\text{Ce}(\text{dnp})_4$ was allowed to crystallize from cold benzene. The crystals were collected by suction filtration and were air dried; m.p., 147-150°C with decomposition. Thermogravimetric analysis indicated that $\text{Ce}(\text{dnp})_4$ sublimes in the range of 300-400°C, but decomposed prior to complete volatilization with increasing temperature in an inert atmosphere. Differential thermal analysis in air, however, shows an exotherm ca. 204°C., indicative of partial decomposition as reflected by the M.P. observation.

Elemental Analysis for $\text{Ce}(\text{dnp})_4$

	Calculated (%)	Found (%)
Carbon	77.08	77.86
Hydrogen	4.22	4.52
Cerium	9.77	9.41
Molecular Weight	1433.62	1100; 1130 (benzene)

6. bis(diisobutyryl)methanato)hydroxopraseodymium (III); $\text{Pr}(\text{OH})(\text{dibm})_2$

This compound was prepared in a manner similar to that which has been reported (12) for the analogous erbium complex.

Elemental Analysis for $\text{Pr}(\text{OH})(\text{dibm})_2$

	Calculated (%)	Found (%)
Carbon	46.16	33.84, 33.86
Hydrogen	6.67	4.90, 5.11
Oxygen	17.08	23.62, 23.13
Praseodymium	30.09	37.69, 37.90

7. Other Cerium and Praseodymium Chelates

All other reported cerium compounds were prepared by the procedure reported for $\text{Ce}(\text{thd})_4$ using $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, and the respective ligands were used instead of 2,2,6,6-tetramethyl-3,5-heptanedione.

Elemental Analysis for $\text{Ce}(\text{fod})_4$

	<u>Calculated (%)</u>	<u>Found (%)</u>
Carbon	36.37	36.60
Hydrogen	3.05	3.28
Fluorine	40.27	38.83
Cerium	10.61	11.19, 11.05

Elemental Analysis for $\text{Ce}(\text{tfa})_4$

	<u>Calculated (%)</u>	<u>Found (%)</u>
Carbon	31.93	31.38
Hydrogen	2.14	2.35
Fluorine	30.30	25.55
Cerium	18.62	20.05

Elemental Analysis for $\text{Ce}(\text{mhd})_4$

	<u>Calculated (%)</u>	<u>Found (%)</u>
Carbon	54.53	55.33
Hydrogen	8.16	7.73
Cerium	19.88	20.79

Elemental Analysis for $\text{Ce}(\text{dibm})_4$

	<u>Calculated (%)</u>	<u>Found (%)</u>
Carbon	56.82	57.69
Hydrogen	7.95	8.21
Cerium	18.41	18.63

Elemental Analysis for $\text{Ce}(\text{facam})_4$

	<u>Calculated (%)</u>	<u>Found (%)</u>
Carbon	48.89	50.79
Hydrogen	5.22	5.34
Fluorine	21.09	25.01
Cerium	12.96	12.24

Elemental Analysis for $\text{Pr}(\text{facam})_3$

	<u>Calculated (%)</u>	<u>Found (%)</u>
Carbon	46.82	49.11
Hydrogen	5.00	4.80
Fluorine	20.20	20.30
Praseodymium	16.64	16.32

8. Cerous Naphthenate

Cerous naphthenate was obtained from Research Organic/Inorganic Chemical Corp., Cat. No. CE204, and was used as received.

9. Cerous Octoate

Cerous octoate was obtained from Research Organic/Inorganic Chemical Corp., Cat No. CE205, and was used as received.

10. Ceric Oxide; CeO_2

Ceric oxide was obtained from American Potash and Chemical Corp., Code 217, and was tested as received.

11. 2,2,6,6-tetramethyl-3,
5-heptanedione; H(thd)

H(thd) was obtained from either Peninsular Chemresearch or Pierce Chemical Company, and was used as received.

12. Methylcyclopentadienyl
manganese tricarbonyl

Methylcyclopentadienyl manganese tricarbonyl was obtained from Research Organic/Inorganic Chemical Corp. and was used as received.

SECTION IV

SOLUBILITY

The solubility of $\text{Ce}(\text{thd})_4$ in isooctane was measured at 22°C and found to be 50.9 grams per liter (193 grams per U.S. gallon). This is 431 times the solubility of $\text{Pr}(\text{thd})_3$ under the same conditions, the value determined for $\text{Pr}(\text{thd})_3$ being 0.118 grams per liter (0.447 grams per U.S. gallon).

The solubility of $\text{Pr}(\text{thd})_3$ in isooctane is marginal. Modifying ligand structure may effect some change in this and related cases. Another possibility, employing adducting agents to increase the solubility, was studied briefly with $\text{Pr}(\text{thd})_3$. Adducts may form when all the available coordination sites have not been filled, which is certainly true in this case.

The initial tests were made by adding tricresylphosphate (TCP) to isooctane solutions of $\text{Pr}(\text{thd})_3$ and $\text{Ce}(\text{thd})_4$, respectively. There was no immediate dissolution at room temperature, but both chelates dissolved upon heating. The resulting solutions were stable to dry ice temperature, with no oil or solid material separating from solution.

In the next test, 20-ml saturated solutions of $\text{Pr}(\text{thd})_3$ were prepared using isooctane and Pb-free Amoco premium gasoline. A quantity of $\text{Pr}(\text{thd})_3$ equal to that required to form the respective saturated solutions was then added to each. Upon the addition of 1 ml TCP to each solution, the additional $\text{Pr}(\text{thd})_3$ dissolved. After evaporation of the volatile fuel component, in each case a solution of $\text{Pr}(\text{thd})_3$ in TCP remained. Based upon this evidence, it is concluded that the addition of TCP will increase solubility of $\text{Pr}(\text{thd})_3$ in isooctane by a factor of two (from 0.65 to 1.30 millimoles per U.S. gallon).

It would be desirable to increase the solubility to a much greater extent. The use of adducting agents free from phosphorus or sulfur is indicated by other existent conditions. Accordingly, the addition of methanol was tried - up to 6 moles per mole $\text{Pr}(\text{thd})_3$ - but this did not change the solubility of $\text{Pr}(\text{thd})_3$ in isooctane.

The addition of $\text{Ce}(\text{thd})_4$ to isooctane produces color changes from light yellow through orange, through red, to a very opaque solution as the concentration is increased. This additive dissolved extremely well in the Pb-free Amoco premium and Mobil RE 145A fuels, even the largest amount added dissolved without stirring in less than one-half hour. Dissolution in isooctane was somewhat slower.

The low temperature solubility of $\text{Ce}(\text{thd})_4$ in isooctane was examined at dry ice temperature. Isooctane has a melting point of -107.4°C, well below the -78°C temperature at which the test was conducted. A sample of 0.12 gram $\text{Ce}(\text{thd})_4$ was dissolved into 35 ml of isooctane. This corresponds to 15 millimoles additive per gallon or 2.1 grams cerium per gallon. The sample flask was placed in dry ice. The solution was intact after overnight exposure with no visible change or solid phase present. Based on this evidence, it is

concluded that $\text{Ce}(\text{thd})_4$ is sufficiently soluble at -78°C that all anticipated practical additive concentration levels in gasoline can endure extremely cold weather storage.

SECTION V

STABILITY

Early in the testing program it became apparent that some solutions in isooctane were undergoing decomposition upon standing. In all cases this became evident because of the formation of a sediment. In the case of the $\text{Ce}(\text{thd})_4$, decomposition was also accompanied by a color change which made the process appear more striking.

Since long-term storage of the solutions without decomposition is clearly desirable, efforts were made to determine the cause(s) and find a remedy. $\text{Ce}(\text{thd})_4$, having a strong color in its solutions as well as being a promising candidate compound, was selected for study. While the tests conducted were not quantitative, they do provide information on the effects of various common interacting agents encountered in practice as well as the observed results of some possible remedies.

1. Characterizing the Sediment

One of the first things done when it became apparent there was a problem was to collect a sediment sample. The solution in which the decomposition was first observed was prepared at a concentration level of 0.65 millimoles of $\text{Ce}(\text{thd})_4$ per gallon of isooctane. Originally a clear orange color, part of it was consumed during the original test on the D 909-67 engine. The balance, stored in a clear glass gallon bottle in dim light, showed no observed evidence of change for at least four weeks. Some decomposition was noticed on the forty first day. Solutions of $\text{Pr}(\text{thd})_3$, $\text{Nd}(\text{thd})_3$, and $\text{Yb}(\text{thd})_3$ in isooctane prepared at the same time in the same molar concentration exhibited no apparent change at this time. These solutions were clear and colorless.

The sediment consisted of very fine particles, so fine that, upon shaking, the individual particles were no longer visible to the naked eye. The particulate material was so fine that, subsequently, these suspensions were tested for their own effectiveness as antiknock additives, without any apparent effect on the test equipment.

Filtering of the suspension produced a yellowish material on the filter frit which was so fine that the frit had to be scraped to obtain a sample for analysis. The sample was washed with distilled, demineralized water, then with neat isooctane before being dried by pulling air through the filter for several hours. The sample was analyzed for cerium, hydrogen, and carbon by duplicate analysis with the following results:

Cerium	73.36%, 73.61%
Hydrogen	1.05%, 1.08%
Carbon	7.31%, 7.35%

A second sample of sediment was prepared by adding neat isooctane to dilute the supernatant liquid phase, mixing, allowing to settle, decanting and evaporating to dryness with an air line. The resulting dry dusty powder was

pelleted with KBr and an IR spectrum was obtained. This spectrum was similar to but not identical with the spectrum of pure CeO_2 pelleted with KBr.

2. The Effect of Water

A 6-ml sample of $\text{Ce}(\text{thd})_4$ in isooctane was split into two portions. To one portion was added a small amount (5 μl) of water; the other portion served as a control. No apparent change in either sample was observed in 2 1/2 weeks. Since this appeared to confirm expectations that water would not affect the additive material, the test was terminated at this point. This experiment, together with later experiments by Ethyl Corp., indicates that $\text{Ce}(\text{thd})_4$ is stable to hydrolysis. $\text{Ce}(\text{thd})_4$ is insoluble in water and loss from gasoline is not expected when gasoline solutions are contacted with water.

3. The Effect of Glass

A test was conducted to determine whether the particular glass in the bottles in which the sediment had formed was a contributing agent. Pieces of the handle were cleaned by a standard procedure (i.e., cleaning in Chromerge followed by water, acetone, and isooctane rinses). They were then immersed into 3 ml of a $\text{Ce}(\text{thd})_4$ - isooctane solution. No apparent change in the solution, color, or sediment-formation was observed in the time the test was conducted and the test was terminated.

4. The Effect of Light

A 12-ml solution of $\text{Ce}(\text{thd})_4$ in isooctane was prepared and divided into two clear glass sample bottles. One bottle was wrapped in aluminum foil to exclude all visible radiation. Both bottles were placed in a corner of the laboratory away from sunlight. No effect was observed in 119 days. The solution in the foil-free bottle was diluted by one half and split into two clear glass bottles. Seventy five days later, or 194 days after the solution was initially prepared, it was observed that some residue had formed on the bottom of these two foil-free containers. They were then moved out of the corner of the laboratory; one was placed in a north window and the second was placed directly in front of the tube of an adjustable desk-type fluorescent lamp (Sylvania FC8TD-CW). Twelve days later this initial test was concluded. When emptied, the solution in the bottle kept wrapped in aluminum foil appeared unchanged (total elapsed time, 178 days) but the other two solutions had a precipitate on the bottom and the walls of their containers where the solutions were in contact. The solution placed under the fluorescent light had the most precipitate. The precipitate dissolved quickly in HCl, forming a light yellow solution.

The bottles were cleaned and new tests were begun using the concentration of 2.38 millimoles $\text{Ce}(\text{thd})_4$ per gallon isooctane. The color of the solution was much lighter than in the previous test. (The previous solutions were highly concentrated; the addition of $\text{Ce}(\text{thd})_4$ to isooctane produces color change from light yellow through orange and red to a very opaque fluid as the concentration is increased.) One sample bottle was wrapped in aluminum foil to serve as a control. A second test is discussed under the section on the effect of air. A third sample was placed directly before a fluorescent lamp bulb

(Sylvania FC8TD-CW-RS). Within three days this latter sample showed indications of decomposition. Within five and one half days the liquid phase was clear and water white and a light yellow precipitate was on the bottom.

Next, two 60-ml samples of 1.188 millimoles $\text{Ce}(\text{thd})_4$ per gallon is octane were placed into square sided sample bottles wrapped in aluminum foil to keep out all light except that admitted by a window area. The window area in one case was left clear and in the other case was covered with a Corning color specification C.S. 2-64 sharp cutoff filter specified to have a transmittance of less than 0.5% at all wavelengths shorter than 620 nm. This filter was chosen on the basis of the transmission curve referred to in the section on the effect of air. The two bottles were placed side by side directly in front of a fluorescent lamp tube (Sylvania FC8T9-CW-RS) with their windows facing the tube. Nineteen and one half days later the solution in the bottle with the clear window appeared to be a faint yellow when viewed through the window. However, when the aluminum foil was removed, it was quite apparent the liquid phase was water white and a yellow sediment covered the bottom. When the foil was removed from the bottle with the Corning C.S. 2-64 filter, the solution still retained its original color, was clear, and showed no traces of precipitate apparent anywhere. It appears that $\text{Ce}(\text{thd})_4$, like tetraethyl lead, is light-sensitive.

5. The Effect of Air

A sample of 2.38 millimoles $\text{Ce}(\text{thd})_4$ in isooctane in a clear glass bottle was placed in a hood, and air was bubbled through it intermittently. Make-up isooctane was added periodically. Some exposure to light due to its position in the hood occurred. After six days of this treatment no effect was apparent. This sample was subsequently diluted with isooctane to a sufficient degree to permit a transmission curve to be obtained in the visible region with a Beckman IR-4 spectrometer in a 1 cm deep cell, double beam mode. This diluted solution was a clear, light yellow color. The transmission curve is shown in Fig 3.

Three hundred ml of solution containing 14.3 millimoles $\text{Ce}(\text{thd})_4$ per gallon isooctane were prepared and divided into six aliquots. In two of these solutions (I, II) dissolved air was removed by bubbling argon (99.999%, gold label), previously saturated with isooctane, through them for 1/2 hour. Although the flow rate was carefully adjusted to minimize entrainment, some isooctane was observed to form condensation droplets on the Tygon connecting hoses. One of the argon-purged samples (I) and one of the as-prepared samples (III) were placed side by side directly before a fluorescent lamp bulb (Sylvania FC8T9-CW-RS); their twins (II, IV) were wrapped in aluminum foil and placed in a dark corner of the hood. Of the remaining two samples one (V) was placed in the hood and air, saturated with isooctane, was then continuously bubbled through it. The last sample (VI) stood next to it as a control. All the sample bottles were closed by rubber stoppers. Glass stopcocks were used in the bubbling experiments.

Within four days all of these solutions showed the first signs of decomposition, a light colored turbidity just below the surface upon tilting the bottles. As it turned out, the air bubbling rate was not quite correct and the sample (V)

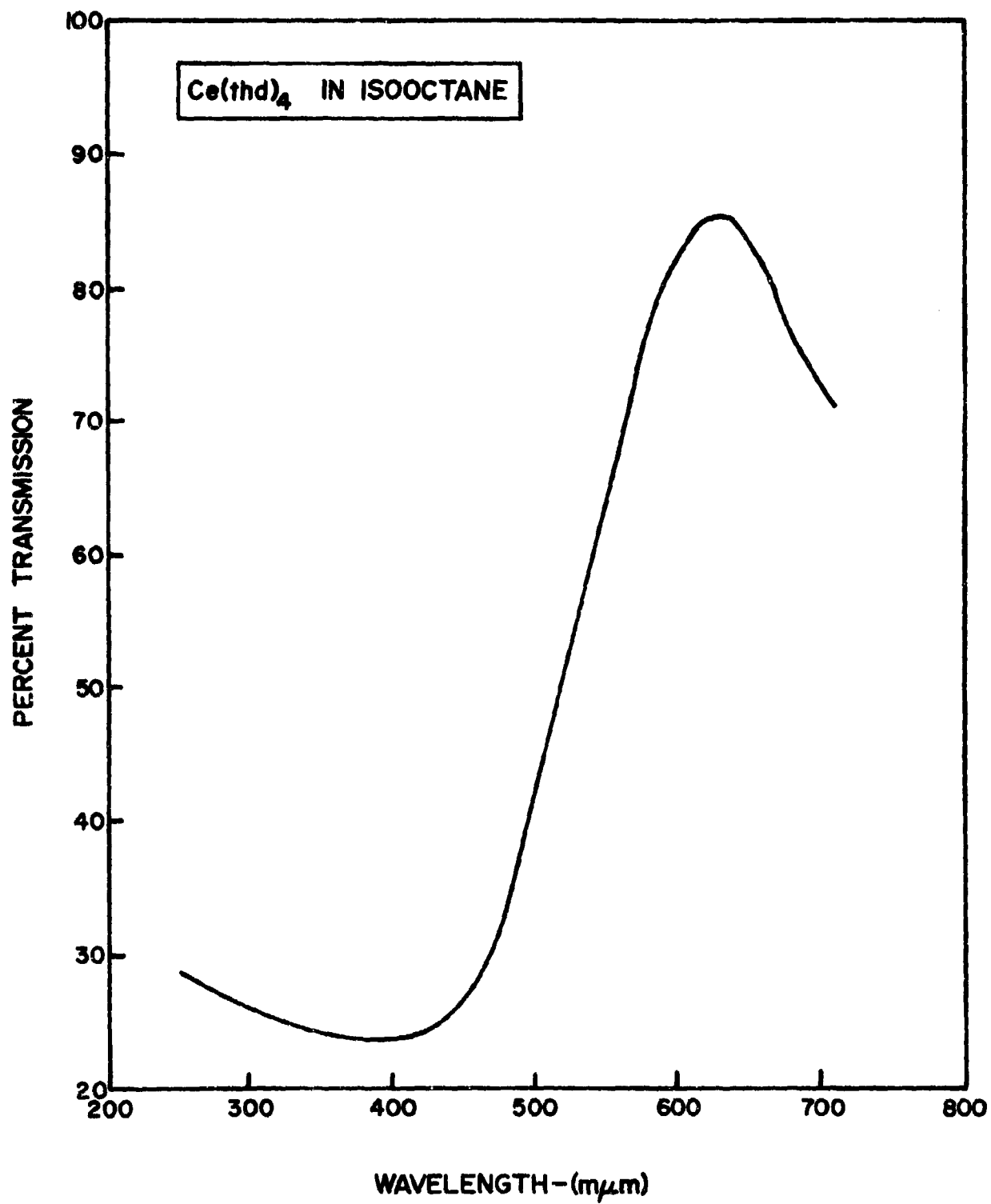


Figure 3. Transmissivity vs. Wavelength for a Dilute Solution of $\text{Ce}(\text{thd})_4$ in Isooctane.

showed a solvent loss. After nine days of intermittent operation, sample (V) had precipitate in it but not as much as its comparison companion (VI). This raises the possibility that the addition of an oxidizing agent may be beneficial and a mildly acidic one even more beneficial. Oxygen can react with the tertiary hydrogen in isooctane to form the peroxy compound, which may be expected to be somewhat acidic. See also the experiments in which excess H(thd) was added to the solutions.

After nine days both of the samples in front of the fluorescent lamp (I, III) had sediment in them. However, the one purged with argon (I) had visibly less quantity. At the time of this writing these samples have been standing 19 months. Exposure to the fluorescent light ended after several months. The as-prepared sample (III) has a quantity of reddish-brown material on the bottom of the jar as well as a coating on the walls up to the liquid level. The bottle purged with the argon (I) had only a thin transparent coating on the walls and bottom. The sample (II) showed the formation of a moderate amount of brownish sediment on the bottom of its container over a period of 19 months.

These results may be compared to observations on two samples prepared earlier for engine testing and only half consumed. After 21 months these solutions still retain good color. However, there is a yellowish precipitate on the bottom of each bottle, with an apparently larger quantity of precipitate present in the more concentrated solution. This difference in color of the solid phase, yellowish vs. reddish-brown, is pronounced. The highly opaque nature of the more concentrated solutions may limit the absorption of light to the surface and in this way change the process.

6. The Effect of H(thd)

Tests were made on the effect of H(thd) on the stability of the solutions. There are at least two ways in which this material might be efficacious. Since H(thd) is naturally acidic, the acid/alkaline nature of the solution would become slightly more acidic. Because cerium compounds are insoluble in strongly basic solutions, this would help maintain solubility if the root cause of the decomposition were a gradual sweetening of the solution. Leaching from the glass vessels might be such a cause. It should be emphasized that the degree of acidity/alkalinity of which we are speaking here is small. A second way in which the H(thd) might function is by reforming the original compound, $RE(thd)_x$, from the decomposed molecule.

In the initial test of this type 100 ml of solution containing 14.3 millimoles $Ce(thd)_4$ per gallon of isooctane was prepared and split into two 50-ml samples. To one of these samples 5 ml of H(thd) was added; the ligand added was impure, having a yellow color. The untreated sample served as a control. Both samples were placed before a fluorescent lamp bulb (Sylvania FC8T9-CW-RS). Four days later, the untreated sample showed a definite amount of yellowish precipitated material against the glass, at the level of the interface on the side closest to the fluorescent bulb. With the passage of time this sample progressively deteriorated, producing a beige precipitate on the surfaces and a urine-colored solution. In contradistinction to this, the addition of the 5 ml H(thd) has preserved the additive solution to this very day, a period in excess of nineteen months, with no sign of any change.

Two 50-ml samples (A, B) of 14.3 millimoles $\text{Ce}(\text{thd})_4$ per gallon isooctane were prepared. To one of these (B) was added $\text{H}(\text{thd})$ in such amount as to give 14.3 millimoles $\text{H}(\text{thd})$ per gallon isooctane; i.e., $\text{H}(\text{thd})/\text{Ce}(\text{thd})_4=1$. The two samples were then placed in front of a fluorescent lamp bulb (Westinghouse, 15 watt daylight). This tube seemed to be bluer than the tube used previously. The untreated sample (A) showed decomposition over a period of four days; on the fifth day the decomposition was very extensive. Sample (B) began to show decomposition after 12 days.

A 50-ml solution containing 15 millimoles $\text{Ce}(\text{thd})_4$ plus 12.1 millimoles $\text{H}(\text{thd})$ per gallon ASTM 80 PRF was prepared and put into an oven at 65°C as part of the accelerated aging tests described in the following section. An identical sample was placed in front of a fluorescent bulb (Westinghouse, 15 watt daylight). After 6 days, the solution in front of the light still looked clear. Eventually precipitate formed, but the solution never did completely decompose. Like many other samples, the solution appeared to deteriorate to a certain undefined degree and thenceforth exhibited little, if any, visible change. The solution in the oven showed much decomposition within a two-day period. Precipitated material was on the bottom of the sample jar; the color of the solution, while still red, had lightened and the solution was now translucent rather than transparent.

A set of three additional samples containing increasing amounts of $\text{H}(\text{thd})$ in the ratios $\text{H}(\text{thd}) : \text{Ce}(\text{thd})_4 = 2, 3, \text{ and } 4$ were prepared and tested in the oven at 65°C as part of the accelerated aging tests. The solution used was drawn from a sample prepared for motor testing that began to break down even though stored in the dark. Its concentration was 15 millimoles $\text{Ce}(\text{thd})_4$ per gallon ASTM 80 PRF. The added quantities of $\text{H}(\text{thd})$ did not cause the decomposition to stop immediately, but the rate of change did seem to be affected. It would seem the effectiveness of adding $\text{H}(\text{thd})$ is highly dependent on the amount used.

7. Accelerated Aging Tests

The effect of temperature on the decomposition of the additive solutions was studied at 65°C . Samples containing 14.3 millimoles $\text{Ce}(\text{thd})_4$ per gallon of solvent were prepared in isooctane and carbon tetrachloride with (I, II) and without (III, IV) 10% excess $\text{H}(\text{thd})$, respectively. Within one day the sample in isooctane (III) had become orange-colored, indicating instability. One day later this solution (III) was straw-colored. A precipitate was noted on the fifth day of the test but may have been present sooner. After eight days samples (I) and (IV) appeared to have a few particles suspended in the solution; upon shaking, though, the solution appeared to possess essentially its original qualities of color and clarity. Solution (II) remained unchanged.

8. The Effect of Antioxidant

Cerium (IV) is normally a strong oxidizing agent. However, the electron-rich ligand thd apparently stabilizes the tetravalent oxidation state and solutions of $\text{Ce}(\text{thd})_4$ are surprisingly stable compared with other ceric β -diketonates. In an attempt to stabilize further the $\text{Ce}(\text{thd})_4$ - containing fuel

solutions against decomposition, a commercial antioxidant was added. This antioxidant is 2,6-di-tertiarybutyl-4-methyl-phenol, also termed 2,6-di-terbutyl-p-cresol, designated DX570. A 50-ml solution containing 15 millimoles $\text{Ce}(\text{thd})_4$ and 0.10 millimoles DX570 per gallon ASTM 80 PRF was placed into the oven in the accelerated aging test. After five days at 65°C sediment began to be evident in the sample. The apparent stability of this combination is considerably better than resulted when $\text{H}(\text{thd})$ was added. The molar ratio of DX570: $\text{Ce}(\text{thd})_4$ was 1:150; the time @ 65°C was 5 days. For the molar ratio $\text{H}(\text{thd})$: $\text{Ce}(\text{thd})_4$ of 0.8:1, the time @ 65°C was 2 days. Therefore, the desirability of making further tests on DX570 or a similar material is indicated.

9. Compatibility

Some common materials of construction were tested for compatibility in the following way. Small pieces of copper, type 306 stainless steel, brass, cold rolled steel, aluminum, black and red gasket rubber were washed by soaking in toluene, acetone, toluene, and three isooctane rinses successively. The samples were then placed into individual soft glass vials, immersed by a solution of 14.9 millimoles $\text{Ce}(\text{thd})_4$ per gallon isooctane, and polyethylene caps were then snapped onto the vials. The vials were well shaken, then stored in total darkness and checked periodically over a two-week period. No visible changes were observed. Ethyl Corporation tests conducted with ASTM D130-60 ("Copper Corrosion Test") are described in Appendix E. Tests were conducted using PRF-80 and three commercial gasolines. Additive concentrations studied were 0.0, 4.2, and 12.6g $\text{Ce}(\text{thd})_4$ per gallon. All twelve samples received a 1-A rating.

SECTION VI

TOXICITY

It is obvious that, before widespread use of these new compounds can be made, thorough toxicity tests must be undertaken on both the additives and their products of combustion. Toxicity information on these additives is extremely limited.

Scientists at the EPA Environmental Toxicology Laboratory in Cincinnati, Ohio, have requested samples of the lanthanide thd chelates and initiated a very thorough and extensive study to determine acute toxicity and chronic effects of the additives themselves, as well as the combustion products of the additives. They have begun oral toxicity tests on Ce(thd)_4 and have not detected, to date, any obvious problems in mice fed daily 10 mg Ce(thd)_4 in mineral oil per kg body weight. No conclusions can be drawn until much more extensive tests have been completed. The EPA also plans to make some radioactively-labelled Ce(thd)_4 to facilitate monitoring uptake, storage, and removal of cerium from test animals.

The only other information on thd chelates available, to our knowledge, was obtained in other laboratories [13] as segments of a study to screen new compounds for anti-cancer activity. In these tests groups of mice were given intraperitoneal injections of Ce(thd)_4 , La(thd)_3 , Pr(thd)_3 , and Nd(thd)_3 (in various carriers) at several dose levels. The mice were checked after five days for fatalities that might have been attributable to the particular compound being screened. No fatalities were observed for these compounds, even at the highest dose level, i.e., 400 mg/kg body weight.

Limited acute toxicity studies of H(thd) [14] indicate that the organic portion of the molecule is relatively non-toxic. Tests conducted included acute oral toxicity, acute dermal toxicity, acute vapor inhalation toxicity, eye irritation, and primary skin irritation. For H(thd) the data indicate: acute oral toxicity, 7.6 g/kg; acute dermal toxicity, > 10.2 g/kg; acute vapor inhalation toxicity, > 2.83 mg/l air; eye irritation test, minimally irritating; skin irritation test, moderately irritating. The above results permit assignment of the rating by Federal Hazardous Substances Labeling Act criteria of "Not Toxic" to H(thd) .

Until detailed toxicity data on these specific compounds are obtained, it will be necessary to rely principally on the information about cerium and the other lanthanide compounds reported in the literature. Sax [15] indicates that "the toxicity of cerium compounds may be taken to be that of cerium, except when the anion has a toxicity of its own." On the other hand he states that "cerium tartrate has been found to produce a direct injurious action on the hearts of small animals." Insoluble cerium salts are stated to be non-toxic even in large doses; e.g. cerium oxalate is used to prevent vomiting in pregnancy, the average dose being 0.05 to 0.5 gram.

Toxicity hazard rating codes for cerium itself are as follows [15]:

Acute Local : 0
Acute Systemic: Ingestion 1.
Chronic Local : 0
Chronic Systemic: Ingestion 1; Inhalation 1.

The codes are based on a scale of 0 to 3, with 0 the lowest toxicity. A rating of 0 is given for substances which produce "(a) No harm under any conditions; (b) Harmful only under unusual conditions or overwhelming dosage." A rating of 1 is assigned to substances which cause "readily reversible changes which disappear after end of exposure." It would seem that application of generalizations to specific cerium compounds is uncertain and unwarranted; therefore, final conclusions must await the results of the EPA study.

It has been reported [16] that the low oral toxicity of the rare earths is undoubtedly due to poor intestinal absorption, as shown by chronic feeding experiments. None of the cerium group chlorides caused internal organ damage to rabbits fed at levels of 0.01%, 0.1%, or even 1% of the diet for 90 days [16,17]. The work of Oelkers and Vincke [17] is particularly interesting because they showed that administration of large doses of the chlorides of the most abundant lanthanides (cerium, lanthanum, praseodymium, and neodymium) had no appreciable effect on the blood chemistry or internal organs of rabbits. In general, compounds of the cerium group elements appear to be less toxic than those of the yttrium group elements [4,5,6]. This generalization appears to be true not only for oral toxicity but for inhalation toxicity as well. Haley [16], Brakhnova [18], and Izraelson [19] have reviewed the pharmacology and toxicology of rare earth elements and the reader is referred to the numerous original articles cited in these reviews for detailed information on the various rare earth compounds studied.

Since the expected products of combustion of the additives are oxides, it is worthwhile to consider the experience in the industrial hygiene of workers exposed to much higher concentrations of rare earth oxides than would ever be expected to arise even in heavy traffic. Rare earth oxides have several industrial uses. Cerium oxide has long been used extensively in glass polishing. It is also used as a catalytic coating for ovens to promote the low temperature oxidation of fats and greases, preventing the build-up of carbonaceous deposits. Brakhnova [18] has reviewed the data available on the oxides of the rare earths and has recommended a maximum permissible concentration (MPC) of $6000 \mu\text{g}/\text{m}^3$ for the oxides of the cerium group and $4000 \mu\text{g}/\text{m}^3$ for the yttrium group. It is interesting to compare this with his recommended MPC for lead and its organic compounds ($10 \mu\text{g}/\text{m}^3$).

It is also worthwhile to review some typical urban air levels of lead to approximate what levels of additive particulates the general public might expect to encounter in the air. According to the 1969 NASN quarterly composite air sampling data [20], lead levels in the air of several U.S. cities range from < 1 to $4.6 \mu\text{g}/\text{m}^3$; the median value for all urban sites was $1.0 \mu\text{g}/\text{m}^3$. While this includes lead from non-automotive sources and does not account for possible differences in distribution, sinks, or rain wash-out efficiencies between lead and cerium, it does nonetheless provide a general idea of what to expect from an additive used to approximately the same extent that the lead alkyls were used in 1969. At that time lead was

used in gasoline at about 2.5 grams/gallon. Since known values of lead concentration along busy highways almost never exceed $30 \mu\text{g}/\text{m}^3$ [20], this can serve as an initial working upper limit for lanthanide exhaust particulate concentrations.

Two studies have been performed on workers in a nuclear facility who accidentally inhaled radioactive europium oxide [21,22]. In the two individuals 84% and 92%, respectively, of the europium was eliminated in the feces in the first 48 hours after exposure [21]. The time required for biological removal of half of the europium in the lungs was 360-390 days [21,22]. Although rare earth compounds are often shown to exhibit remarkably similar chemistry, one should not conclude that the other rare earths will necessarily behave analogously to europium.

Berke [23] has used radioactive isotopes to study the effect of aerosols generated from solutions of cerium, europium, ytterbium, and yttrium on: deposition and retention of inhaled particulates in dogs; lung clearance mechanisms; organ and tissue distribution; the elimination route and its magnitude.

Experiments were reported by Mogilevskaya and Raikhlin, cited by Izraelson [19], in which oxides of specific rare earth elements were introduced, in the form of 50 mg of dust suspension in 0.6 ml sterile physiological solution, by intratracheal administration to white rats. Their findings were that "in contrast to yttrium oxide, cerium oxide did not cause serious changes in the pulmonary tissue and there was no diffuse or nodular fibrous reaction." Further, "we had clearly shown that the dusts of the oxides of rare earth elements studied, exert different degrees of fibrotic effect." It should be noted also that the inhalation of any dust may be expected to give rise to some emphysematous changes in lung tissue.

It should be stated that while the lanthanide oxides are the thermodynamically expected combustion products, one should not expect chemically pure oxides to be present in the exhaust gases. Therefore, because of the unknown and complex nature of the actual exhaust particulates, toxicity studies will necessarily be required on the actual materials in any event. Extrapolation from data on chemically pure compounds, while it may prove indicative, will not be sufficient.

From the admittedly incomplete information now available it appears that problems in handling the new additives may require much less sophisticated handling techniques than are presently needed for the lead alkyls. If nothing unforeseen develops during the toxicity testing of the new additives, there will accrue other benefits, by virtue of lower exposure to toxic lead compounds (or high aromatic fuels), to the millions of people who inevitably spill, breathe, or even wash their hands in gasoline in spite of warnings not to do so. As with any new compound, due care should be taken in handling or testing these additives until they are proven to be innocuous, as they are now thought to be.

SECTION VII

PRODUCTS OF COMBUSTION

An important property which must be considered when evaluating a candidate antiknock additive is the amount of wear which may be produced within the engine by the additive or its products of combustion. The 0 to 10 Moh scale (wherein talc is assigned a value of 1 and diamond a value of 10) provides an indication of the relative hardness of various materials.

The expected combustion products of the rare earth chelate additives are the metal oxides. These rare earth oxides have Moh hardnesses of about 5. While lead alkyls produce combustion products with lower relative hardnesses, other additives which have oxides possessing intermediate hardnesses have been used in the past. For example, manganese oxides have hardnesses of 5-6 while iron oxides range from 5.5 to 6.5. By comparison, cerium oxide has a hardness of 5 [24]. Ultimately, however, the question of whether wear will be a problem can be answered only by long term tests.

SECTION VIII

RAW MATERIALS

The basic materials from which the new additives can be made are rare earth ores, neopentanoic acid, and acetone. The rare earths are rare in name only, and abundant U.S. reserves are available for at least as long as petroleum reserves are expected to last. For example, cerium is more abundant in the earth's crust than lead. Monazite and bastnasite are the most important rare earth ores. The Mountain Pass, California, deposit of bastnasite contains over 2,000,000 tons of cerium [25]. There are extensive monazite deposits in Tennessee, California, Idaho, and Florida.

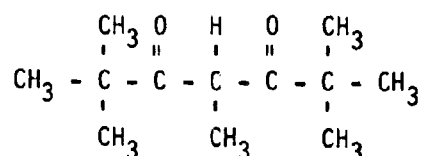
It may not be necessary to use a purified rare earth, such as cerium, to make the additive since all the lanthanide-thd chelates tested show antiknock activity. In this case the much cheaper unseparated or partially separated material can be used instead. The cost of mixed rare earth chlorides has been estimated by various sources at 20-30 cents per lb [26], and the rare earths may become much cheaper if they become available as by-products of thorium mining for new nuclear reactors.

Sweet and Parlett [27] have provided evidence that the synthesis of the chelates from the ligand and water-soluble lanthanide salts can be accomplished in virtually quantitative yield by inexpensive solvent extraction techniques. A process can be envisioned in which countercurrent incoming streams of H(thd) dissolved in a solvent, e.g., gasoline, and water carrying the leach solution from the rare earth ores react to form the chelate, stripping the metals from the aqueous solution. Alternatively, batch processes can be used. Neither method requires any heat or special equipment. Because of the low toxicity expected, the additive can probably be easily handled without the expensive precautions required in handling the highly toxic lead additives.

Acetone is used to make pinacolone. The ligand H(thd) is synthesized by a Claisen condensation of the pinacolone and neopentanoic acid in the presence of a base such as sodium hydride or sodium methoxide. While H(thd) is a highly effective chelating agent, we are continuing our search for other ligands that can be made less expensively or will yield an even more effective additive. One such ligand may be the condensation product of methyl isobutyl ketone with ethyl acetate. Another is obtained by Claisen condensation of methyl isobutyl ketone with an ester of neopentanoic acid. The strategy in these instances would be to find a methyl ketone that is less expensive than pinacolone and yet would yield a chelate with the desired solubility, volatility, and antiknock properties.

Yet another approach is to avoid a condensation reaction altogether in synthesizing the diketone. According to the literature this can be accomplished in a one-step synthesis by the acid dichromate oxidation of triisobutylene [28]. Isobutylene is one of the cheapest raw materials one can

envision. The work of Miner [28] showed that 2,2,4,6,6-pentamethyl-3,5-heptanedione (trivial name, 1,1-dipivaloylthane)



is one of the principal oxidation products of triisobutylene.

This ligand is very closely related to H(thd), differing only by the presence of a methyl group attached to the methine carbon rather than a hydrogen atom. Miner's experiments were done repeatedly on a reasonably large scale and reportedly gave consistently good results. Typically 60 lbs of triisobutylene (Rohm and Haas) and 85.4 lbs of technical grade sodium dichromate (dissolved in 16 liters of water) were placed in a 50 gallon kettle. To this was added incrementally 36 liters (66 kg) of conc. sulfuric acid in 64 liters of water. Thirty liters of 50% sulfuric acid were added at once and an additional 30 liters over a period of five hours. The reaction was allowed to proceed without cooling until the temperature of the reaction mixture reached 38°C, at which point water was run through the jacket until the temperature fell to 30°C. The remainder of the acid was then added at a rate of about 6 liters per hour, with the temperature of the reaction mixture held between 30°C and 40°C by occasional cooling. The stirring of the reaction mixture was continued until the temperature of the mixture had fallen to within 2 or 3 degrees of room temperature. The reaction mixture was then steam-distilled, introducing high pressure steam at 140°C into the jacket, periodically replenishing water by adding earlier distilled water fractions. The distillation was continued until the ratio of water to oil exceeded 20:1 or until solid appeared in the distillate. The distillate was further fractionated by redistillation. A neutral fraction boiling at 91°C at 18 mm (205°C at 730 mm.) and having a refractive index, $n_D^{20} = 1.4320$, was identified as 1,1-dipivaloylthane. It was obtained in 9-18% yield, depending on which fraction and isomeric composition of triisobutylene was used as starting material; no attempt was made to optimize the yield of this particular product. Ericson and Fernelius [29] have determined that the formation constants of this ligand with beryllium and uranyl are similar to those of acetylacetone.

One can also contemplate the use of naturally occurring β -diketones such as those that are present in wheat straw and other agricultural waste products. The principal β -diketones in the wax of Triticum compactum wheat stems are 8- and 9- hydroxyhentriacontan-14, 16-dione [30,31]. Beta-diketones constitute about 18% of the wax fraction from some wheat varieties. Hexane extracts of straw from one of the more popular varieties (Arthur) of wheat grown in the Midwest are known to contain β -diketones; the β -diketones were detected in the straw several months after harvest [32]. Glaucous lines of barley have the β -diketone, hentriacontan-14,16-dione, in their surface lipids [33]. Waxes from various grasses and Eucalyptus and Acacia species contain 50% or more β -diketones [34,35].

U.S. Patent 3,004,070 describes the synthesis of 1,3- β -diketones in high yield (94% in one example) by condensation of disubstituted ketene dimers or co-dimers with aromatic hydrocarbons in the presence of a Friedel-Crafts catalyst such as aluminum chloride.

Obviously the efficacy of such other chelates as antiknock agents as well as the economics of their production must be assessed before decisions can be made regarding which chelate(s) will ultimately be most attractive. As seen in the performance data the ability of a lanthanide to act as an anti-knock agent is a sensitive function of the character of the ligand shell. Cerium octoate and $\text{Ce}(\text{acac})_4$ are ineffective and several lanthanide β -diketonates suffer serious deficiencies such as insufficient solubility and (perhaps) insufficient volatility.

SECTION IX

ALTERNATE METHODS OF ADDITIVE INTRODUCTION

As a matter of possible interest, there may be unique potential advantages if the rare earth additives are proven innocuous enough that they can be handled by the consumer. One can conceive of the possibility of the motorist adding an antiknock agent on demand as a powder, pellets, or a concentrated solution similar to various conditioners presently being marketed for use by pouring into the gasoline tank. In this way the motorist need add only enough to adjust a base fuel to the requirements of his particular engine. Still another possible method would be to add the antiknock compound with the oil in two-cycle engines.

SECTION X

DISCUSSION

1. Performance

A review of the performance test data (Tables I-VII) indicates that the most marked improvement in octane number effected by $\text{Ce}(\text{thd})_4$ occurred in the SPN (Supercharge Performance Number) tests. Two fuels were used for this purpose, ASTM Isooctane PRF and premium grade, Pb-free Amoco. In both instances (Figures 1 and 2, respectively, for the PRF and Amoco fuels) $\text{Ce}(\text{thd})_4$ clearly outperformed TEL on a grams of metal per gallon basis.

Much more modest improvements were obtained in the RON and MON tests, the latter number being the least sensitive to the effect of the cerium additive. Comparative MON's are shown in Fig. 4 for fuel RMFD-254-72, a representative gasoline used by the CRC Road Octane Group for evaluation of road octane requirements of automobiles. This fuel was selected upon the basis of tests by the U.S. Army Fuels and Lubricants Research Laboratory (AFLRL) on a variety of fuels differing widely in octane number and hydrocarbon composition. It demonstrated the greatest increase in motor octane number with the cerium additive. At a level of approximately 1.5 grams of cerium per gallon of fuel, an increase in RON and MON of 3.5 and 2.0, respectively, was obtained in RMFD-254-72. This is to be contrasted with RON's and MON's of 90 and 87, respectively, measured in ASTM 80 PRF at the same additive level of concentration.

It is interesting to compare the behavior of the cerium additive and TEL in both these fuels. For RMFD-254-72, TEL added in the same millimole concentration as $\text{Ce}(\text{thd})_4$ produced increases in RON and MON of 8.7 and 9.7, respectively; in ASTM 80 PRF the comparable ΔON increases were 14.5 and 15.9. These antiknock additives exhibited exactly reverse effects on the two fuels. The cerium compound increases the RON more than the MON while TEL does the opposite. This characteristic of TEL is true for all ASTM isooctane/n-heptane PRF blends. This fact and the differing behavior of cerium and related additives suggest that some rationalization of their relative effectiveness be attempted in terms of differences in the three modes of octane number testing.

The three test methods have already been compared in a previous section of this report. One of the most important differences among them appears to be in the intake systems and the modes of introducing the fuel-air charge into the cylinder. The Supercharge Method provides the most direct admission to the combustion chamber, the Motor Method the least and the Research Method is between the two. Furthermore, in the Motor Method an electric immersion heater is installed in the intake manifold to heat the incoming mixture and presumably increase the severity of the test. For full-boiling range gasolines (conventional automotive fuels) the degree of fractionation of the fuels may be expected to vary with each of the test procedures, being least for the Supercharge and most for the Motor Method. Thus the fuel in the intake system will tend to become enriched in the

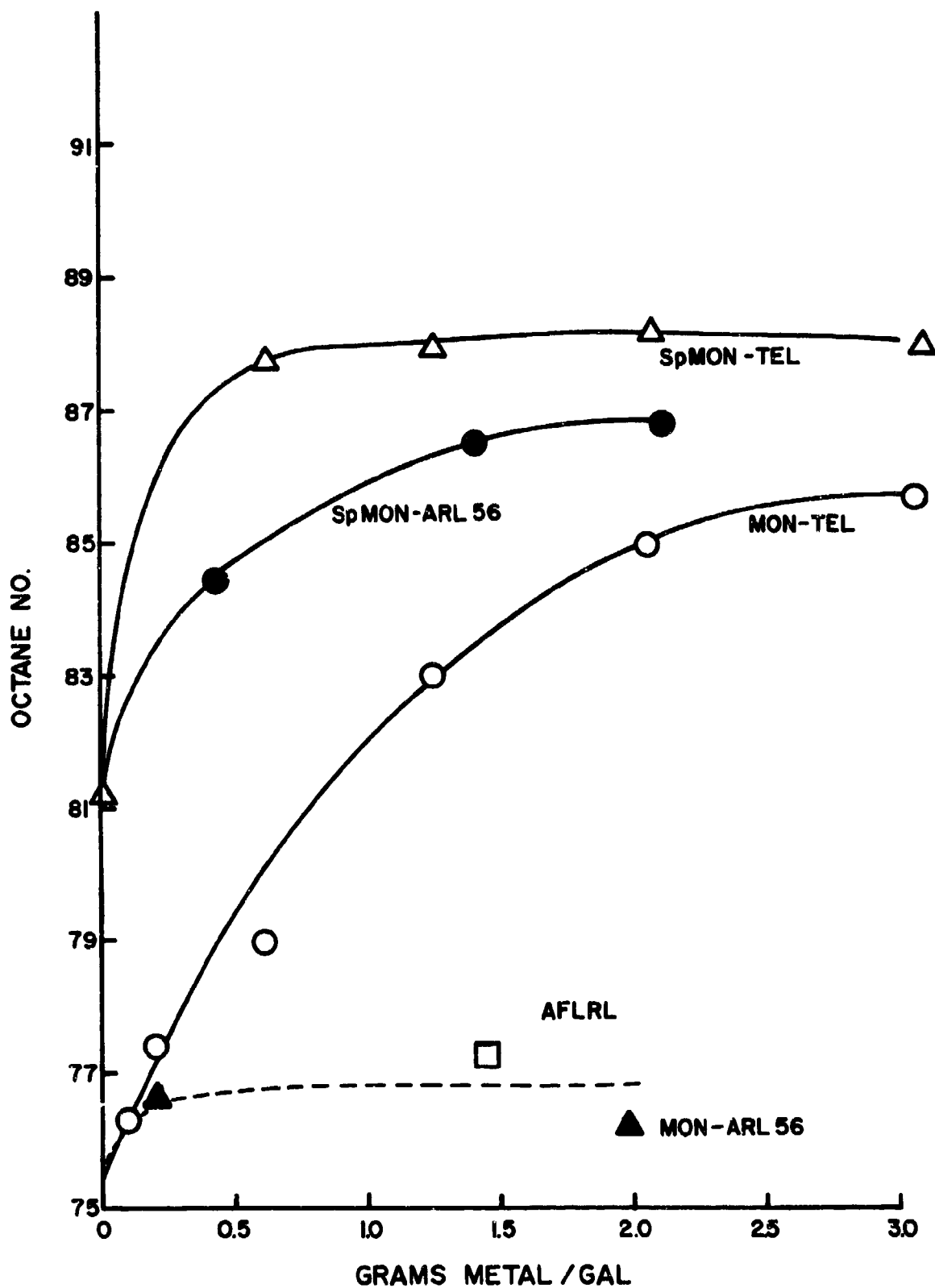


Figure 4. Comparison of Motor Octane Number with Special Motor Octane Number for ARL-56 and TEL in AL-4458-G Fuel Blend.

heavy end as the light ends enter the engine cylinder preferentially. One may reasonably assume that this tendency will be greater for the Motor Method than for the Research Method. Furthermore, since the light ends contain more of the knock-prone unsaturated compounds than the heavy ends, one may expect that the MON will be lower than the RON. This behavior is indeed observed in the usual commercial gasolines. If an additive of low vapor pressure is added to the gasoline, it too will tend to become enriched in the heavy ends and be present in a lesser concentration in the engine cylinder. When the fuel has a narrow boiling range, as in the case of ASTM isooctane/n-heptane PRF fuels, this tendency to accumulate will be reduced, and larger concentrations of the additive will be admitted to the combustion chamber. TEL has a vapor pressure much higher than that of pure $\text{Ce}(\text{thd})_4$ under engine intake conditions. Thus the cerium compound may be anticipated to experience a much larger accumulative effect than TEL. Nevertheless, it should perform better in ASTM PRF fuels than in full-boiling gasolines, for the reasons cited. The test results indicate exactly this behavior. Much higher RON's and MON's are observed in ASTM 80 PRF than in gasolines. For TEL dissolved in the isooctane/n-heptane blend, the heater blade apparently serves to vaporize additional additive in sufficient quantities to overcome segregation tendencies, and the MON exceeds the RON.

To determine the effect of mixture heating and longer path length (geometry) on octane number in the Motor Method, a series of tests using ASTM 80 PRF and RMFD-254-72 were conducted with the heater blade turned off. Results were inconclusive for the first of these fuels but did indicate that mixture temperature did not have a large effect, as might have been expected. However, quite another situation prevails for the case of the full-boiling gasoline, as shown in Fig. 4. Turning off the heater blade power produces a dramatic increase in special motor octane number (SpMON) for the cerium additive and one less spectacular for the TEL. The temperature effect is measured by the differences in ordinate at zero additive, 6 octane numbers. The difference between motor octane numbers for TEL without heater blade power (SpMON) and with power (MON) decreases with increasing concentration - one may assume as a result of increased vaporization on the heater blade. On the other hand, the difference between SpMON and MON increases with increasing amount of $\text{Ce}(\text{thd})_4$ due to the fact that the effectiveness-concentration curve appears to approach a limiting value at 0.5-1.0 grams of cerium/gallon. This circumstance may be attributed to the fact that the cerium additive has a low enough vapor pressure that it remains primarily in the heavy residue of the fractionated gasoline. The very deleterious effect of the heater blade in the Motor Method on $\text{Ce}(\text{thd})_4$ is graphically displayed in Fig. 5, which indicates that the special motor octane number approaches the RON as the cerium content increases. It appears that sufficient additive gets into the fuel-air charge to overcome the geometric effect of about 2.5 octane numbers at zero additive, though the reason for this is not readily apparent.

The previous data suggest that $\text{Ce}(\text{thd})_4$ will be a very effective anti-knock agent if it can be admitted into the engine cylinder without losses in the intake system. The Supercharge Method results appear to support this view. The fuel is sprayed directly into a heated air stream just upstream of the intake valve. Fractionation of the fuel and deposition of the additive

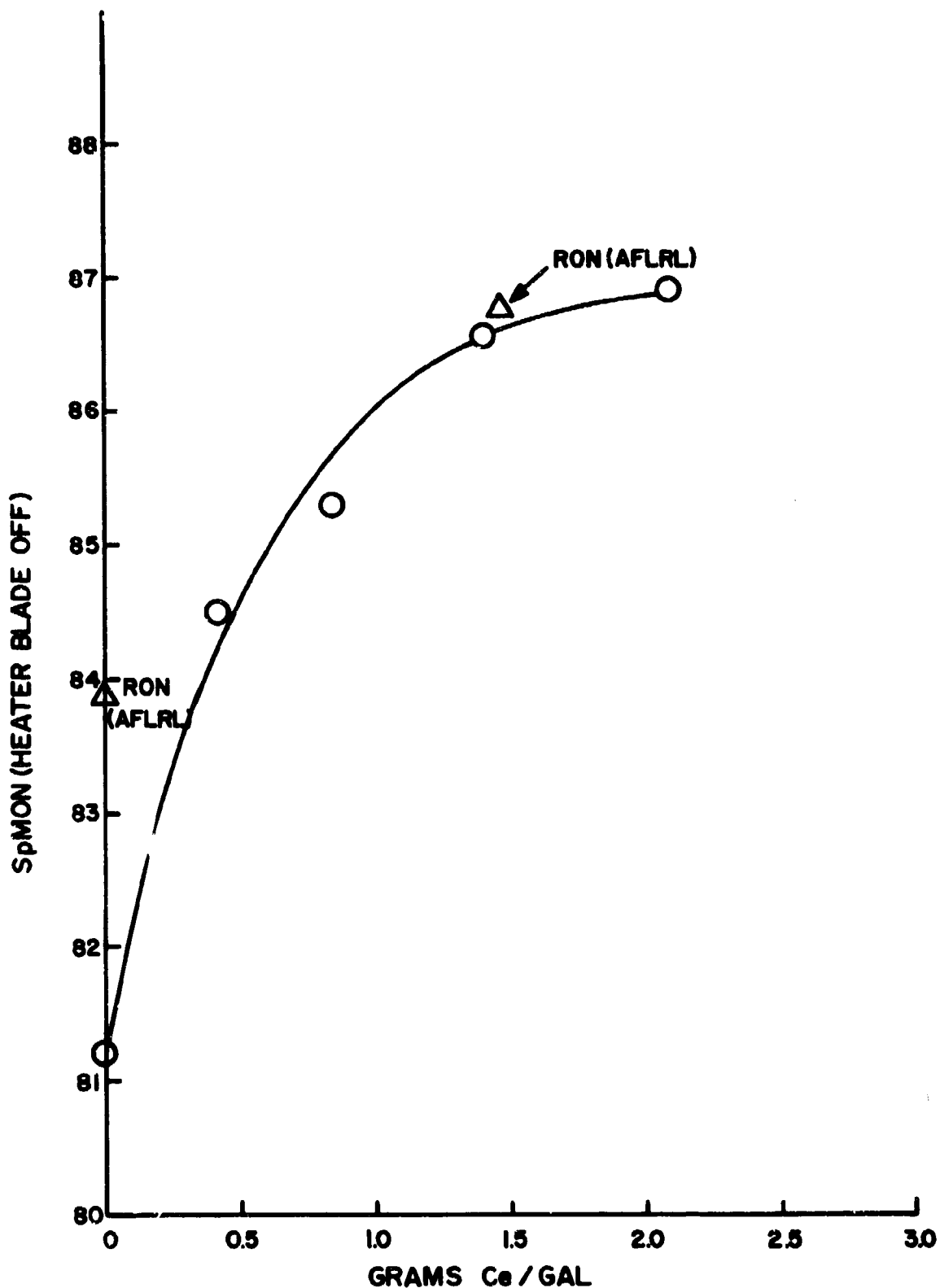


Figure 5. Comparison of Research Octane Number with Special Motor Octane Number for $\text{Ce}(\text{thd})_4$ in AL-4458-G Fuel Blend.

are minimized and more of the antiknock agent enters the cylinder than is the case for the Research and Motor methods with the observed striking increases in SPN.

Tests (RON and MON) conducted by AFLRL (Appendix D) indicated that $\text{Ce}(\text{thd})_4$ was rather ineffective in fuels of high aromatic content. To assess this properly, they ran a toluene reference fuel and an alkylate feed stock containing some 95% of saturates. As expected, negligible octane improvement was obtained for the toluene reference fuel, while significant performance increases were demonstrated for the alkylate feed stock. It is worthy of note that in this instance the RON and MON of the neat fuel were virtually identical and that a greater MON than RON was achieved with TEL. Fuel performance with antiknock agents may be related as much to physical (fractionation, vaporization, etc.) as to chemical effects.

As already mentioned, the least sensitive of the octane rating methods to lanthanide antiknock agents (MON) was selected for tests of ligand structure and metal atom variation on performance. Consequently, the results are not highly differentiated with composition. They do, however, indicate that the activity of cerium antiknock agents is dependent upon the nature of the ligand and that, for the thd complexes, cerium is superior to praseodymium, neodymium, lanthanum, samarium, terbium, holmium, and erbium. Surprisingly, the mixed rare earth thd complexes performed equally to $\text{Ce}(\text{thd})_4$ in RMFD-254-72 but were inferior to it at equal molar concentration in ASTM 80 PRF. As a matter of interest, a manganese antiknock agent (methylcyclopentadienyl manganese tricarbonyl) was tested in RMFD-254-72. Its performance exceeded that of $\text{Ce}(\text{thd})_4$ slightly at the same molar concentration, but the difference in octane number improvement is considered to be within the experimental error of the measurement.

Separate comparison Supercharge Method tests were made on the thd complexes of cerium, praseodymium, neodymium, and ytterbium in ASTM Iso-octane PRF. The latter three exhibited approximately the same SPN and were decidedly inferior to $\text{Ce}(\text{thd})_4$ at the same molar concentration levels. However, all three yielded higher SPN's than an equivalent molar quantity of TEL. These findings suggest that all of the rare earth metals probably have some effectiveness as antiknock agents and that cerium is the best.

It has previously been noted that performance tests on $\text{Ce}(\text{thd})_4$ additive were conducted by both the Sun Oil Company and Ethyl Corporation (Exhibits F and E, respectively). Of these, the results obtained by Sun are considered to be of the greatest practical interest and importance. Sun, using the Modified Uniontown Method, measured road octane numbers in two 1973 model cars. At a level of 1.0 gram of cerium per gallon, road octane number was improved by 2.2 numbers for one car and 1.3 numbers in the other. Increase of the cerium content to 3.0 grams per gallon yielded no significant improvement in road octane number. The same behavior was observed in the MON tests, save that the improvement in octane number was approximately half that obtained in road testing. Both MON and road octane tests (in one car) at intermediate concentrations indicated that the optimum

level of cerium addition was approximately 0.5 gram/gallon, which caused an increase in the road octane number in the Ford from 90.2 to 92.2. Quite a different behavior was observed for TEL in the same base fuel. In this instance, approximately the same improvement in road octane number was obtained in each car, increases ranging from 3.2 numbers at the lower to approximately 6.0 numbers at the higher level of concentration; the increase in MON significantly exceeded that for the road octane number; and both values increased with increase of Pb concentration from 1.0 to 3.0 grams/gallon.

Ethyl Corporation's tests on three commercial Pb-free regular grade gasolines showed the usual trend in octane numbers. The RON's exceeded the MON's, and the increase in MON's with cerium additive were about one-third those with TEL at equivalent molar quantities. However, their results differed from ours and those of the Sun Oil Company in exhibiting an increasing effect with increasing cerium content up to the maximum level tested (2 grams/gallon). The maximum change in MON was obtained with Amoco regular gasoline; its increase of 2.8 numbers exceeded any obtained in tests by all the other laboratories.

Synergism has been observed between $\text{Ce}(\text{thd})_4$ and organic co-additives in the antiknock performance of mixtures. In our tests with RMFD-254-72 gasoline we have observed (Table V) that addition of halogenated organic compounds, e.g., 1,2-dichloroethane or 1,4-dibromopentane, together with $\text{Ce}(\text{thd})_4$, causes an increase of about one octane number in the MON above that when $\text{Ce}(\text{thd})_4$ was used alone. Furthermore, Young [42] has claimed that increases of 1.5 to 2 octane numbers were produced in road octane number tests when small amounts (0.02-0.05 grams/gal.) of t-butyl formate or t-butyl acetate were added. Obviously these indications of synergistic activity should be explored more fully.

2. Stability

The stability testing performed in this laboratory has been described in detail previously. To summarize the results briefly, solutions of $\text{Ce}(\text{thd})_4$ in isooctane are sensitive to light, decomposing under its influence; bubbling air through such solutions does not impair their stability, and the additive shows no tendency to hydrolyze in the presence of water. Accelerated aging tests at 65°C induced decomposition in a solution of $\text{Ce}(\text{thd})_4$ in isooctane. This process was inhibited to some extent by the addition of an antioxidant, DX-570. Very limited tests indicated compatibility with the usual materials found in automotive fuel supply and engine systems.

Ethyl Corporation conducted tests on water contact, existent gum, oxidation induction period, and copper corrosion on the three commercial gasolines (Sohio, Amoco, and Marathon) as well as ASTM 80 PRF at two levels of concentration of the cerium additive, 0.67 and 2.03 grams of metal/gallon. The water contact tests confirmed our own in demonstrating that the additive was stable to hydrolysis. All four fuels received 1A ratings in the ASTM D130-60 "Copper Corrosion Tests" at all additive concentrations. The existent gum tests, ASTM D381-70, yielded satisfactory gum values for PRF-80, marginal results for Marathon, and unsatisfactory results for

Sohio and Amoco. All three commercial gasolines failed the ASTM D525-55 "Oxidation Induction Period" test, indicating that their oxidation stability was seriously impaired by $\text{Ce}(\text{thd})_4$. The paraffinic PRF-80 was unaffected by the presence of additive, suggesting that $\text{Ce}(\text{thd})_4$ may interact with the olefins and/or aromatics present in commercial gasolines.

3. Exhaust Emissions

Very limited testing by the Sun Oil Company indicated that the cerium compound had no adverse effect on the usual pollutants of concern in engine exhaust emissions. In fact, the results suggested that a slight reduction in unburned hydrocarbon and CO concentration might be obtained with the use of this additive, but the data are too preliminary to be conclusive. In view of the reported efficacy [36-40] of the rare earth oxides as catalysts for reduction of noxious engine exhaust emissions, further testing is definitely in order. Rare earth oxides reportedly catalyze the oxidation of unburned hydrocarbons in exhaust [36], and have been used as oven coatings to facilitate oxidation of oils, greases, and carbonaceous residues in self-cleaning ovens [41]. An EPA-sponsored study [40] has shown that rare earth oxides also catalyze the decomposition of oxides of nitrogen. The rare earth oxides are not known to catalyze the oxidation of SO_2 , and so may not present the problem of increased sulfuric acid pollution caused by platinum-group catalytic converters. Indeed, the use of rare earth additives may even lower the sulfur dioxide emission. Rare earths are used in steel-making as sulfur getters because they combine with sulfur to form rather stable rare earth oxysulfides.

Two types of studies should be made. The effect on the exhaust emissions of using rare earth additives should be examined at various exhaust converter temperatures and geometries. An independent study should also be made to determine whether inexpensive rare earth oxides can be substituted for platinum catalysts in exhaust converters. One of the problems noted by other workers is the relatively low surface area of commercial rare earth oxide preparations. We have obtained electron micrographs of the particulate products of combustion of gasoline containing $\text{Ce}(\text{thd})_4$ and have observed that the particles appear very spongy and apparently have a much higher surface area than commercial samples of CeO_2 . This is not surprising since the particles are formed by agglomeration of fragments formed by combustion of isolated $\text{Ce}(\text{thd})_4$ molecules.

4. Conclusions and Recommendations

a. Road octane testing of $\text{Ce}(\text{thd})_4$ additive in two 1973-model cars demonstrated improvements of 1.5 and 2.9 octane numbers at the maximum concentration level of 3.0 grams of metal/gallon. These exceeded the improvements in motor octane number. The optimum concentration level appeared to be 0.5-1.0 gram cerium/gallon. Very little increase in octane number was obtained at higher cerium content.

b. The maximum effect of the cerium additive was observed in the Supercharge Test Method (ASTM D 909-67), in which its performance as an antiknock agent exceeded that of TEL at equivalent metal weight concentrations. Its performance in the RON and MON tests was significantly

inferior to that of TEL. Our test data suggest that $\text{Ce}(\text{thd})_4$ is an effective antiknock agent if it can be admitted into the engine cylinders without losses in the intake system and that it might be most effective in fuel-injection engines.

c. Within the scope of our tests, cerium was found to be superior to the other rare earth metals, though a mixture of rare earth thd complexes in gasoline demonstrated an effectiveness about equal to that of $\text{Ce}(\text{thd})_4$. This latter finding has promising implications for reduction of the cost of such compounds used as antiknock agents.

d. Tests to date indicate that $\text{Ce}(\text{thd})_4$ tends to promote gum formation in and to reduce markedly the oxidation stability of gasoline. It is believed that formulations can be developed to overcome these deficiencies.

e. The limited data available on the toxicity of cerium compounds suggest that these additives and their combustion products would be much less toxic than is the case for the lead alkyls.

f. The synergistic effect of using other additives together with the rare earth chelates should be studied extensively.

g. Preliminary exhaust emission testing suggests that the cerium additive may reduce to some extent the unburned hydrocarbon and CO content of engine exhaust gases. Further testing should be performed to demonstrate the reality and magnitude of this effect. The effect of the use of rare earth additives on emissions of oxides of nitrogen and sulfur should also be explored under a variety of operating conditions.

h. In independent studies, combustion-generated rare earth oxide particulates should be examined as possible catalytic beds in exhaust converters.

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APPENDIX A

DEFINITIONS, PHYSICAL PARAMETER VALUES, ETC. EMPLOYED

Variations in the values cited for physical constants from source to source occur. To preserve internal consistency the following set of equivalencies were used throughout the work:

$$3785.3 \text{ ml} = 1 \text{ U.S. Gallon}$$

$$1 \text{ atm} = 14.696 \text{ psia}$$

$$\frac{2 \text{ ml dilute TEL}}{400 \text{ ml fuel}} = \frac{2 \text{ ml TEL}}{\text{U.S. Gallon}} = \frac{2.11 \text{ gram Pb}}{\text{U.S. Gallon}}$$

Reference: ASTM Manual for Rating Motor, Diesel, and Aviation Fuels, 1972. p. 169 pp. 208.1.4.2, 208.1.4.3)

$$\frac{1 \text{ ml dilute TEL}}{400 \text{ ml}} = \frac{1.055 \text{ gram Pb}}{\text{U.S. Gallon}}$$

$$\text{density of Pb(C}_2\text{H}_5)_4 = 1.659 \text{ gram/ml @ } 18^\circ\text{C}$$

$$\text{density of TEL fluid} = 1.647 \frac{\text{gram Pb(eth)}}{\text{ml Tel fluid}}$$

Acronyms and Symbols

The following acronyms occur during the text for brevity:

RdON	road octane number
MON	motor octane number, ASTM D2700
RON	research octane number, ASTM D2699
SON	supercharge octane number, ASTM D909
SPN	supercharge performance number, ASTM D909
SpMON	special motor octane number

$$\text{SPN} = (3)(\text{SON} - 100) + 100$$

$$\text{Pb(eth)}_4 = \text{TEL} = \text{tetraethyl lead M.W.} = 323.43$$

$$\text{TCP} = \text{tricresylphosphate M.W.} = 368.37$$

$$\text{DX570 2,6-ditert-butyl-p-cresol M.W.} = 220.36$$

ARL-56 tetrakis (2,2,6,6 - tetramethyl-3,5 - heptanedionato) cerium (IV)
M.W. = 873.21

Methylcyclopentadienyl manganese tricarbonyl M.W. = 219.10

LIST OF ABBREVIATIONS

		Mol Wt
thd	2,2,6,6-tetramethyl-3,5-heptanedionato	183.27
tdh	1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato	195.16
dibm	diisobutyrylmethanato	155.22
dnp	1,3-di(2-naphthyl)-1,3-propanedionato	323.37
mhd	6-methyl-2,4-heptanedionato	141.19
acac	acetylacetonato	99.11
hen	14,16-hentriacontanedionato	463.81
facam	d-3-trifluoroacetylcamphorato	234.22
tfa	1,1,1-trifluoro-2,4-pentandionato	153.08
hfa	1,1,1,5,5,5-hexafluoro-2,4-pentandionato	207.05
fcd	6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato	295.18

APPENDIX C. REPORT ON TESTING CONDUCTED BY
U.S. ARMY FUELS AND LUBRICANTS
RESEARCH LABORATORY

U.S. ARMY FUELS AND LUBRICANTS RESEARCH LABORATORY

**8500 CULEBRA ROAD—P.O. DRAWER 28510
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USAFRLRL

1 November 1972

**Technical Director
U. S. Army Coating & Chemical Laboratory
Attn: AMXRD-CF, Mr. H. L. Ammlung
Aberdeen Proving Ground, Md. 21005**

**Subject: Evaluation of ARL 56 as an Antiknock Additive in Full
Boiling Range Fuels**

Dear Sir:

A material developed by the Aerospace Research Laboratory which showed promise of being an effective antiknock additive was submitted to AFLRL for evaluation in full boiling range gasolines. Preliminary evaluations by the Aerospace Laboratory indicated the material to be effective in iso-octane and blends consisting of n-heptane and iso-octane.

For this work five full boiling range gasolines were selected which varied widely in research and motor octane numbers and in hydrocarbon type composition. The analytical data for these fuels are shown in Table 1. Four of the gasolines selected were full boiling range unleaded reference gasolines (RMFD-) manufactured by Phillips Petroleum Company and used by the CRC Road Octane Group for Evaluation of road octane requirements of automobiles. The fifth fuel was a base fuel used in the manufacture of referee grade combat gasoline MIL-G-45016(MR) but containing no lead or other additives. This base fuel was prepared by Howell Hydrocarbons.

The material being evaluated was identified as ARL 56 and was added along with a stabilizer to one gallon of each gasoline, in an amount determined by Aerospace Research Laboratory personnel which was equivalent on a mole basis to 2 ml of tetraethyl lead. An 80 octane, primary reference fuel was also treated with ARL 56 and the stabilizer. One gallon samples of each fuel containing 2 ml of tetraethyl lead were also prepared. The lead analyses for these samples are shown in Table 2.

Research and motor octane numbers were determined on each sample by ASTM methods D 2699 and D 2700 respectively, and the results are shown in Table 3. After all numbers were determined the research octane numbers for AL-4457-G + ARL 56 and AL-4457-G + 2 ml TEL were repeated and these results are shown in the Table. Since the base fuel octane numbers were furnished by the gasoline suppliers, the research and motor octane numbers of three of these gasolines, without addition of ARL 56 or TEL, were also determined and are shown in the Table. Some deviation was found between the numbers supplied with the base fuels and those determined at AFLRL; however, this deviation is small and does not affect the conclusions from this work.

Table 4 shows the hydrocarbon composition, sulfur content and octane numbers for the base fuel along with the octane number increases resulting from the addition of ARL 56 and TEL. The average research octane number increase observed with the addition of ARL 56 to full boiling range fuels was 2.9 numbers as compared to 7.3 numbers average increase with the addition of 2 ml of TEL to the same gasolines. The average motor octane number increase with addition of ARL 56 was 0.6 number while the average increase with 2 ml of TEL was 7.4 numbers. In the primary 80 octane reference fuel the addition of ARL 56 produced a 10 number increase in research octane and 7.0 number increase in motor octane.

It is concluded that ARL 56 is an effective antiknock agent in a blend of n-heptane and iso-octane; however, it is considerably less effective in full boiling range gasolines containing a variety of hydrocarbon types. This difference in response to various fuel compositions may be due to a lack of synergism between the additive and specific hydrocarbon components or the additive's volatility characteristics. In an effort to shed further light on the problem, selected fuel blending stocks will be obtained and evaluated for octane numbers using ARL 56. These stocks will include high and low volatility saturate components and high boiling aromatic-olefin-saturate blends.

Very truly yours,

R. D. Quillian, Jr.
Director



Alan A. Johnston, Manager
Fuels and Lubricants Applications

AAJ:tc
Encl

cc: ARL

Table I. Analyses of Base Gasolines

	AL-4140-G *		AL-4141-G		AL-4456-G		AL-4457-G		AL-4458-G	
	RMFD-424-71		RMFD-243-71		RMFD-243-71		RMFD-252-72		RMFD-254-72	
API Gravity	60.1		56.0		60.4		61.7		59.9	
Reid Vapor Press., psi	7.0		7.3		8.4		7.0		7.8	
ASTM Distillation, F										
IBP	96		102		94		111		101	
10%	138		138		133		142		135	
30%	182		185		181		165		165	
50%	224		225		220		195		197	
70%	279		255		260		239		234	
90%	367		340		336		299		297	
EP	420		422		386		382		398	
FIA, Vol %										
Aromatics	18.6		33.3		26.3		16.0		19.7	
Olefins	35.1		20.3		2.7		9.8		15.0	
Saturates	46.3		46.4		71.0		74.2		65.3	
RON	84.0		91.2		90.6		91.0		83.3	
MON	75.9		80.5		82.5		82.5		75.3	
Sensitivity	8.1		10.7		8.1		8.5		8.0	
Lead, g/gallon	<0.03		<0.03		0.029		0.0006		0.005	
Exist. Gum, mg/100 ml	14.1		3.2		0		-		-	
Stability, Min	1440 +		1440 +		1620 +		1440 +		1440 +	
Copper Corrosion, 212°F	1A		1B		1A		-		-	
Total Sulfur, ppm	623		321		70		150		160	

* Army Fuels and Lubricants Code No.

Table 2. Lead Content of Fuels with 2 ml TEL Added
Atomic Absorption Analyses

<u>Sample</u>	<u>Lead, g/gal</u>
AL-4140-G + TEL	2.13
AL-4141-G + TEL	2.13
AL-4456-G + TEL	2.20
AL-4457-G + TEL	2.18
AL-4458-G + TEL	2.15

Table 3. Research and Motor Octane Numbers

	<u>RON</u>	<u>MON</u>
AL-4140-G (RMFD-242-71)	84.0 ⁽¹⁾	75.9 ⁽¹⁾
AL-4140-G + ARL 56	88.0	75.1
AL-4140-G + 2 ml TEL	91.9	80.8
AL-4141-G (RMFD-243-71)	91.2 ⁽¹⁾	80.5 ⁽¹⁾
AL-4141-G + ARL 56	93.2	80.7
AL-4141-G + 2 ml TEL	97.5	86.7
AL-4456-G	90.6 ⁽²⁾ 91.7 ⁽⁵⁾	82.5 ⁽²⁾ 83.8 ⁽⁵⁾
AL-4456-G + ARL 56	92.7	83.0
AL-4456-G + 2 ml TEL	97.0	90.8
AL-4457-G (RMFD-252-72)	91.0 ⁽¹⁾ 91.4 ⁽⁵⁾	82.5 ⁽¹⁾ 83.3 ⁽⁵⁾
AL-4457-G + ARL 56	93.6 93.6 ⁽⁴⁾	83.0
AL-4457-G + 2 ml TEL	98.1 97.6 ⁽⁴⁾	90.5
AL-4458-G (RMFD-254-72)	83.3 ⁽¹⁾ 83.8 ⁽⁵⁾	75.3 ⁽¹⁾
AL-4458-G + ARL 56	86.8	77.3
AL-4458-G + 2 ml TEL	92.0	85.0
80 Octane PRF	80.0 ⁽³⁾	80.0 ⁽³⁾
80 Octane PRF + ARL 56	90.0	87.0

(1) Phillips Petroleum Company data-average of data from several laboratories.

(2) Howell Hydrocarbons data.

(3) Primary reference fuel blend-80% iso-octane, 20% n-heptane.

(4) Repeat values.

(5) Army Laboratory check of fuel supplier's octane data.

Table 4. Fuel Composition and Octane Number Increase

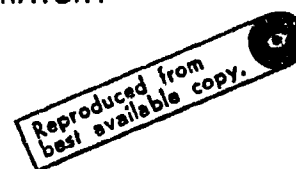
	AL-4140-G RMFD-242-71	AL-4141-G RMFD-243-71	AL-4456-G	AL-4457-G RMFD-252-72	AL-4458-G RMFD-254-72	80 Octane PRF
Aromatics, v%	18.6	33.3	26.3	16.0	19.7	0
Olefins, v%	35.1	20.3	2.7	9.8	15.0	0
Sulfur, wt %	0.062	0.032	0.007	0.015	0.016	0
Base fuel RON	84.0	91.2	90.6	91.0	83.3	80.0
RON increase with ARL-56 [*]	4.0	2.2	2.1	2.6	3.5	10.0
RON increase with 2 ml TEL [*]	7.9	6.3	6.4	7.1	8.7	-
Base fuel MON	75.9	80.5	82.5	82.5	75.3	80.0
MON increase with ARL-56 [*]	-0.8	0.2	0.5	0.5	2.0	7.0
MON increase with 2 ml TEL [*]	4.9	6.2	8.3	8.0	9.7	-

^{*} Both ARL-56 and TEL were added to each gasoline in concentrations of 0.0105 moles/gal.

APPENDIX D. FINAL REPORT ON TESTING
CONDUCTED BY U.S. ARMY FUELS
AND LUBRICANTS RESEARCH LABORATORY

U.S. ARMY FUELS AND LUBRICANTS RESEARCH LABORATORY

8500 CULEBRA ROAD--P.O. DRAWER 28510
SAN ANTONIO, TEXAS 78284



USAFRLRL

29 November 1972

Director
U. S. Army Mobility Equipment Research
and Development Center
Coating and Chemical Laboratory
Attn: SMEFB-CL, Mr. H. L. Ammlung
Aberdeen Proving Ground, Maryland 21005

Subject: Hydrocarbon Composition Affects on ARL-56 Antiknock Agent

Dear Sir:

Preliminary evaluation of the Aerospace Research Laboratory's ARL-56 fuel additive (reference letter report dated 1 November 1972) indicated that the additive's antiknock response was drastically inhibited when used in full boiling range unleaded gasolines. Therefore, additional studies have been undertaken to define which fuel characteristics hinder the additive's effectiveness. Two major factors were considered, 1) fuel volatility, and 2) fuel hydrocarbon composition.

Fuel Volatility--ARL-56 has proven effective in raising the octane number of a hydrocarbon blend of 80% isooctane-20% n-heptane, a rather low volatility fuel (RVP 1.6). For comparison a 50% isooctane-50% n-pentane, a much higher volatility blend (RVP 9.6) was evaluated with the following results.

<u>Fuel</u>	<u>RON</u>	<u>MON</u>
80% isooctane - 20% n-heptane	80.0	80.0
+ ARL-56	90.0	87.0
+ TEL	94.5	95.9
50% isooctane - 50% n-pentane	78.0	78.6
+ ARL-56	86.3	85.4
+ TEL	92.4	91.7

The change in volatility appeared to have little or no effect on ARL-56's octane improvement capability. In Tables 1 through 5 are presented the distillation data on the five fuels used during the initial ARL-56 evaluation (1 November report) and were obtained using a gas chromatograph technique. No trends between the fuel boiling point distribution and ARL-56 octane number response could be defined.

Fuel Hydrocarbon Composition--For this phase two special hydrocarbon blends were used for comparison against AL-4458-G results obtained in the 1 November studies. AL-4458-G was a full boiling range fuel composed of 19.7% aromatics, 15.0% olefins, 65.3% saturates and 0.016% sulfur. The two new blends consisted of a toluene reference fuel made up of 77% toluene - 23% n-heptane, and an alkylate feed stock consisting of 0.5% aromatics, 4% olefins and 95.5% saturates. These latter two fuels were blended with TEL and ARL-56 producing the following octane data.

<u>Fuel</u>	<u>RON</u>	<u>MON</u>
Toluene Reference	92.5	81.2
+ ARL-56	93.3	81.4
+ TEL	99.0	86.6
Alkylate	94.0	94.3
+ ARL-56	99.3	97.9
+ TEL	102.3	103.6
AL-4458-G	83.8	75.3
+ ARL-56	86.8	77.3
+ TEL	92.0	85.0

From these data a trend does appear which shows that aromatics may be the major ARL-56 inhibitor. This study was not broad enough to define whether or not specific aromatic compounds are important, however, their presence does significantly reduce ARL-56's octane improvement capability. These results may answer the question as to why ARL-56 failed to produce octane improvement in a commercial no-lead fuel (normally containing a high aromatic concentration).

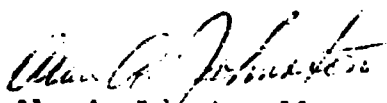
As a secondary item AL-4458-G was blended with 0.47 ml TEL and the same concentration of ARL-56 as used previously. This combination produced:

<u>Fuel</u>	<u>RON</u>	<u>MON</u>
AL-4458-G	83.8	75.3
+ ARL-56	86.8	77.3
+ TEL	92.0	85.0
+ TEL 0.47 ml, ARL-56	87.1	80.7

No significant synergistic effect was noted. Also for ARL's information Table 6 and 7 provide detailed compositional data on AL-4458-G which they intend to use in future studies. These data were obtained by an AFLRL gas chromatography procedure to give the probable composition of this fuel. However, some components may overlap each other and are shown as two or more materials for a single retention code. No further work on ARL-56 is planned at this time.

Very truly yours,

R. D. Quillian, Jr.
Director


Alan A. Johnston, Manager
Fuels and Lubricants Applications

AAJ:el

Enclosures

cc: Dr. Kent Eisentraut (ARL) ✓

-----BOILING POINT DISTRIBUTION BY GC-----
 U.S. ARMY FUELS & LUBRICANTS RESEARCH LABORATORY

SAMPLE I.D.: GASOLINE 12-4140-C
 SAMPLE 4 ANALYSIS 1
 TEST PROCEDURE #: SURVEY

CALIBRATED ON: NOV 15
 ANALYZED ON: NOV 15
 AREA: 871992

% OFF	DEG F	% OFF	DEG F
0.5	27	23.0	153
1.0	36	24.0	159
2.0	36	25.0	159
3.0	67	30.0	186
4.0	74	35.0	202
5.0	74	40.0	212
6.0	74	45.0	212
7.0	82	50.0	236
8.0	89	55.0	245
9.0	89	60.0	263
10.0	96	65.0	285
11.0	96	70.0	298
12.0	96	75.0	328
13.0	103	80.0	341
14.0	122	85.0	370
15.0	129	90.0	396
16.0	129	95.0	422
17.0	135	96.0	430
18.0	135	97.0	439
19.0	141	98.0	448
20.0	141	99.0	456
21.0	153	99.5	473
22.0	153	100.0	532

Figure 1

-----BOILING POINT DISTRIBUTION BY GC-----
 U.S. ARMY FUELS & LUBRICANTS RESEARCH LABORATORY

SAMPLE I.D.: GASOLINE AL-71-1-G
 SAMPLE 1 ANALYSIS 1
 TEST PROCEDURE #: SURVEY

CALIBRATED ON: NOV 15
 ANALYZED ON: NOV 15
 AREA: 1762784

% OFF	DEG F	% OFF	DEG F
0.5	27	23.0	153
1.0	36	24.0	159
2.0	67	25.0	164
3.0	67	30.0	197
4.0	67	35.0	207
5.0	67	40.0	231
6.0	67	45.0	241
7.0	74	50.0	241
8.0	74	55.0	241
9.0	74	60.0	241
10.0	74	65.0	245
11.0	74	70.0	268
12.0	74	75.0	285
13.0	82	80.0	298
14.0	89	85.0	328
15.0	96	90.0	362
16.0	96	95.0	400
17.0	103	96.0	409
18.0	129	97.0	417
19.0	129	98.0	435
20.0	135	99.0	448
21.0	141	99.5	456
22.0	153	100.0	543

Figure 2

-----BOILING POINT DISTRIBUTION BY GC-----
 U.S. ARMY FUELS & LUBRICANTS RESEARCH LABORATORY

SAMPLE I.D.: GASOLINE 71-4456-G
 SAMPLE 3 ANALYSIS 1
 TEST PROCEDURE #: SURVEY

CALIBRATED ON: NOV 15
 ANALYZED ON: NOV 15
 AREA: 865115

% OFF	DEG F	% OFF	DEG F
0.5	15	23.0	151
1.0	33	24.0	151
2.0	33	25.0	156
3.0	72	30.0	184
4.0	72	35.0	200
5.0	72	40.0	205
6.0	72	45.0	215
7.0	72	50.0	234
8.0	72	55.0	239
9.0	72	60.0	239
10.0	72	65.0	257
11.0	86	70.0	288
12.0	86	75.0	292
13.0	86	80.0	322
14.0	86	85.0	339
15.0	93	90.0	356
16.0	107	95.0	386
17.0	126	96.0	394
18.0	126	97.0	399
19.0	133	98.0	411
20.0	133	99.0	416
21.0	139	99.5	437
22.0	139	100.0	557

Figure 3

-----BOILING POINT DISTRIBUTION BY GC-----
 U.S. ARMY FUELS & LUBRICANTS RESEARCH LABORATORY

SAMPLE I.D.: GASOLINE AL-4457-C
 SAMPLE 2 ANALYSIS 1
 TEST PROCEDURE #: SURVEY

CALIBRATED ON: NOV 15
 ANALYZED ON: NOV 15
 AREA: 887827

% OFF	DEG F	% OFF	DEG F
0.5	52	23.0	129
1.0	67	24.0	129
2.0	67	25.0	129
3.0	67	30.0	135
4.0	74	35.0	153
5.0	74	40.0	170
6.0	74	45.0	191
7.0	82	50.0	207
8.0	89	55.0	236
9.0	103	60.0	241
10.0	109	65.0	241
11.0	109	70.0	245
12.0	122	75.0	281
13.0	122	80.0	285
14.0	129	85.0	294
15.0	129	90.0	324
16.0	129	95.0	362
17.0	129	96.0	375
18.0	129	97.0	392
19.0	129	98.0	405
20.0	129	99.0	426
21.0	129	99.5	448
22.0	129	100.0	594

Figure 4

-----BOILING POINT DISTRIBUTION BY GC-----
 U.S. ARMY FUELS & LUBRICANTS RESEARCH LABORATORY

SAMPLE I.D.: GASOLINE AL-4458-G
 SAMPLE 1 ANALYSIS 1
 TEST PROCEDURE #: SURVEY

CALIBRATED ON: NOV 15
 ANALYZED ON: NOV 15
 AREA: 837775

% OFF	DEG F	% OFF	DEG F
0.5	26	23.0	128
1.0	35	24.0	128
2.0	35	25.0	128
3.0	66	30.0	146
4.0	74	35.0	191
5.0	88	40.0	201
6.0	95	45.0	206
7.0	108	50.0	211
8.0	108	55.0	211
9.0	103	60.0	216
10.0	108	65.0	231
11.0	115	70.0	245
12.0	122	75.0	285
13.0	128	80.0	285
14.0	128	85.0	298
15.0	128	90.0	332
16.0	128	95.0	387
17.0	128	96.0	400
18.0	128	97.0	421
19.0	128	98.0	447
20.0	128	99.0	502
21.0	128	99.5	547
22.0	128	100.0	597

Figure 5

Figure 6

High Resolution Gas Chromatographic Analysis

Code	Hydrocarbon	Weight, %
P3	Propane.....	0.000
O2	Propene (propylene).....	0.000
P5	2-Methylpropane (isobutane).....	0.144
O3;O6	1-Butene; 2-Methylpropene (isobutene).....	0.010
P4	31°F n-Butane.....	2.777
O11	3-Methyl-1-butene.....	0.000
O5	trans-2-Butene.....	0.079
N15	Cyclobutane.....	0.000
P8	2,2-Dimethylpropane (neopentane).....	0.040
O4	cis-2-Butene.....	0.041
P7	2-Methylbutane (isopentane).....	1.826
O7	1-Pentene.....	0.148
O10	2-Methyl-1-butene.....	0.284
P6	9.7°F n-Pentane.....	1.222
O9	trans-2-Pentene.....	0.431
O8	cis-2-Pentene.....	0.237
O12	2-Methyl-2-butene.....	0.654
O28	3,3-Dimethyl-1-butene.....	0.002
P12	2,2-Dimethylbutane.....	4.767
CO1	Cyclopentene.....	0.081
N23	Cyclopentane.....	16.937
O20	4-Methyl-1-pentene.....	0.000
O19	3-Methyl-1-pentene.....	0.573
O27	2,3-Dimethyl-1-butene.....	0.000
N12	1,1,2-Trimethylcyclopropane.....	0.000
P13;O24	2,3-Dimethylbutane; 4-Methyl-cis-2-pentene.....	1.124
P10;O25	2-Methylpentane; 4-Methyl-trans-2-pentene.....	0.092
N18	1,1-Dimethylcyclobutane.....	0.000
N9	1-Methyl-1-ethylcyclopropane.....	0.000
N22	1,trans-3-Dimethylcyclobutane.....	0.604
P11	3-Methylpentane.....	0.000
N8	Isopropylcyclopropane.....	0.000
N11	1-Methyl-trans-2-ethylcyclopropane.....	0.000
O18	2-Methyl-1-pentene.....	0.234
N14	1,cis-2,trans-3-Trimethylcyclopropane.....	0.000
N20	1,trans-2-Dimethylcyclobutane.....	0.000
N21	1,cis-3-Dimethylcyclobutane.....	0.000
O13	1-Hexene.....	0.000
O26	2-Ethyl-1-butene.....	0.000

Code	Hydrocarbon	Weight, %
P9	156°F n-Hexane.....	0.527
O16	cis-3-Hexene.....	0.164
O17;CO3	trans-3-Hexene; 3-Methylcyclopentene.....	0.297
O21	2-Methyl-2-pentene.....	0.277
O22	3-Methyl-cis-2-pentene.....	0.000
O15;N13	trans-2-Hexene; 1, cis-2, cis-3-Trimethylcyclopropane	
CO4	4-Methylcyclopentene.....	0.000
O14	cis-2-Hexene.....	0.147
N10	1-Methyl-cis-2-ethylcyclopropane.....	0.000
N19	1, cis-2-Dimethylcyclobutane.....	0.134
N7	n-Propylcyclopropane.....	0.000
O23	3-Methyl-trans-2-pentene.....	0.000
N16;N17	Methylcyclobutane; Ethylcyclobutane.....	0.236
N24	Methylcyclopentane.....	0.387
O56	4, 4-Dimethyl-1-pentene.....	0.000
O29	2, 3-Dimethyl-2-butene.....	0.005
P18	2, 2-Dimethylpentane.....	0.211
P20	2, 1-Dimethylpentane.....	0.002
P22;O63	2, 2, 3-Trimethylbutane; 4, 4-Dimethyl-trans-2-pentene	0.010
A1;O65;O54	Benzene; 2, 3, 3-Trimethyl-1-butene; 3, 3-Dimethyl-1-pentene.....	0.542
CO2	1-Methylcyclopentene.....	0.000
N102;O62	Cyclohexane; 4, 4-Dimethyl-cis-2-pentene.....	1.715
P21;O55	3, 3-Dimethylpentane; 3, 4-Dimethyl-1-pentene.....	0.056
O53	2, 4-Dimethyl-1-pentene.....	0.007
O59	2, 4-Dimethyl-2-pentene.....	0.138
O36	3-Methyl-1-hexene.....	0.000
CO21;O51;O52	Cyclohexene; 3-Ethyl-1-pentene; 2, 3-Dimethyl-1-pentene.....	1.010
P15;P19	2-Methylhexane; 2, 3-Dimethylpentane.....	3.631
O38	5-Methyl-1-hexene.....	0.000
O46;O47	2-Methyl-cis-3-hexene; 2-Methyl-trans-3-hexene....	0.000
N26;O42	1, 1-Dimethylcyclopentane; 4-Methyl-cis-2-hexene....	0.760
P16;O37;O64	3-Methylhexane; 4-Methyl-1-hexene; 3-Methyl-2-ethyl-1-butene.....	0.189
CO12;CO17;O43	3, 3-Dimethylcyclopentene; 4, 4-Dimethylcyclopentene; 4-Methyl-trans-2-hexene.....	0.000
O45	5-Methyl-trans-2-hexene.....	0.147
P17	3-Ethylpentane.....	0.256
N29	1, cis-3-Dimethylcyclopentane.....	0.000
O44;O60	5-Methyl-cis-2-hexene; 3, 4-Dimethyl-cis-2-pentene..	0.393

Code	Hydrocarbon	Weight, %
N30	1, trans-3-Dimethylcyclopentane	0.000
N28	1, trans-2-Dimethylcyclopentane	0.000
O61;CO9	3, 4-Dimethyl-trans-2-pentane; 1, 3-Dimethylcyclopentene	0.045
O35	2, Methyl-1-hexene	0.077
CO10	1, 4-Dimethylcyclopentene	0.135
P14;O30;O49	n-Heptane; 1-Heptene; 3-Methyl-trans-3-hexene	20.204
O50	2-Ethyl-1-pentene	0.000
P37	2, 2, 4-Trimethylpentane	0.000
O41	3-Methyl-trans-2-hexene	0.204
O48;O39	3-Methyl-cis-3-hexene; 2-Methyl-2-hexene	0.000
O34;O33	trans-3-Heptene; cis-3-Heptene	0.000
O57	3-Ethyl-2-pentene	3.536
O40;O58	3-Methyl-cis-2-hexene; 2, 3-Dimethyl-2-pentene	0.130
N27	1, cis-2-Dimethylcyclopentane	0.000
O32	trans-2-Heptene	0.376
O31	cis-2-Heptene	0.000
CO6	3-Ethylcyclopentene	0.000
CO7	4-Ethylcyclopentene	0.000
N25	Ethylcyclopentane	0.063
P40	2, 2, 3, 3-Tetramethylbutane	0.045
P28	2, 2-Dimethylhexane	0.007
N39	1, 1, 3-Trimethylcyclopentane	0.811
CO11	1, 5-Dimethylcyclopentene	0.000
CO23	3-Methylcyclohexene	0.247
CO24	4-Methylcyclohexene	0.000
P31	2, 5-Dimethylhexane	0.000
P30	2, 4-Dimethylhexane	0.097
P36	2, 2, 3-Trimethylpentane	0.049
N45	1, trans-2, cis-4-Trimethylcyclopentane	0.083
P32	3, 3-Dimethylhexane	0.200
A2;N42	Methylbenzene (toluene); 1, trans-2, cis-3-Trimethylcyclopentane	2.794
P39	2, 3, 4-Trimethylpentane	0.115
P38	2, 3, 3-Trimethylpentane	0.069
P29;N38	2, 3-Dimethylhexane; 1, 1, 2-Trimethylcyclopentane	0.000
P34	2-Methyl-3-ethylpentane	0.344
P24;P26;P33	2-Methylheptane; 4-Methylheptane; 3, 4-Dimethylhexane	1.145
P35	3-Methyl-3-ethylpentane	0.000
P27;N43;N44	3-Ethylhexane; 1, cis-2, cis-4-Trimethylcyclopentane; 1, cis-2, trans-4-Trimethylcyclopentane	0.000

Code	Hydrocarbon	Weight, %
P25	3-Methylheptane	0.000
N41	1, cis-2, trans-3-Trimethylcyclopentane	1.150
O66	1-Octene	0.008
P74	2, 2, 4, 4-Tetramethylpentane	0.000
N36;N37;N35	1-Methyl-cis-3-ethylcyclopentane; 1-Methyl-trans-3-ethylcyclopentane; 1-Methyl-trans-2-ethylcyclopentane	0.037
N33	1-Methyl-1-ethylcyclopentane	0.000
P62	2, 2, 5-Trimethylhexane	0.164
N40	1, cis-2, cis-3-Trimethylcyclopentane	0.036
P23	258° n-Octane	1.319
P61	2, 2, 4-Trimethylhexane	0.137
N32	Isopropylcyclopentane	0.052
N34	1-Methyl-cis-2-ethylcyclopentane	0.036
P66	2, 4, 4-Trimethylhexane	0.031
P65	2, , 5-Trimethylhexane	0.012
N31	n-Propylcyclopentane	0.085
P47	2, 2-Dimethylheptane	0.063
P73;P49	2, 2, 3, 4-Tetramethylpentane; 2, 4-Dimethylheptane ...	0.000
P60	2, 2, 3-Trimethylhexane	0.092
P57;P69	2-Methyl-4-ethylhexane; 2, 2-Dimethyl-3-ethylpentane.	0.029
P55;P51	4, 4-Dimethylheptane; 2, 6-Dimethylheptane	0.258
P50;P54	2, 5-Dimethylheptane; 3, 5-Dimethylheptane	0.020
P71	2, 4-Dimethyl-3-ethylpentane	0.011
P52	3, 3-Dimethylheptane	0.000
A3	Ethylbenzene	0.516
P63;P138	2, 3, 3-Trimethylhexane; 2, 2, 5, 5-Tetramethylhexane..	0.000
P56	2-Methyl-3-ethylhexane	0.031
P64	2, 3, 4-Trimethylhexane	0.000
A6	1, 4-Dimethylbenzene (p-xylene)	4.035
A5	1, 3-Dimethylbenzene (m-xylene)	4.000
P72	2, 2, 3, 3-Tetramethylpentane	0.000
P48;P59;P67	2, 3-Dimethylheptane; 3-Methyl-4-ethylhexane; 3, 3, 4-Trimethylhexane	0.000
P53;P58	3, 4-Dimethylheptane; 3-Methyl-3-ethylhexane	0.000
P46	4-Ethylheptane	0.137
P75	2, 3, 3, 4-Tetramethylpentane	0.594
P44;P45	4-Methyloctane; 3-Ethylheptane	0.000
P42	2-Methyloctane	0.432
P43	3-Methyloctane	0.000
P70	2, 3-Dimethyl-3-ethylpentane	0.000

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Code	Hydrocarbon	Weight, %
A4	1, 2-Dimethylbenzene (o-xylene)	1.895
P68	3, 3-Diethylpentane	0.000
P125	2, 2-Dimethyl-4-ethylhexane	0.029
P137	2, 2, 4, 5-Tetramethylhexane	0.095
P135;P106	2, 2, 3, 5-Tetramethylhexane; 2, 2, 4-Trimethylheptane ..	0.037
P108	2, 2, 6-Trimethylheptane	0.061
P115	2, 4, 6-Trimethylheptane	0.011
P41;P107 303'F	n-Nonane; 2, 2, 5-Trimethylheptane	0.034
P113	2, 4, 4-Trimethylheptane	0.300
P116	2, 5, 5-Trimethylheptane	0.000
A8	Isopropylbenzene (cumene)	0.045
P140	2, 3, 3, 5-Tetramethylhexane	0.000
P136	2, 2, 4, 4-Tetramethylhexane	0.000
P130	2, 5-Dimethyl-3-ethylhexane	0.024
P147	2, 2, 4-Trimethyl-3-ethylpentane	0.018
P118	3, 3, 5-Trimethylheptane	0.042
P86;P112	2, 5-Dimethyloctane; 2, 3, 6-Trimethylheptane	0.000
P98;P124; P142	2-Methyl-4-ethylheptane; 2, 2-Dimethyl-3-ethylhexane; 2, 3, 4, 5-Tetramethylhexane	0.000
P114	2, 4, 5-Trimethylheptane	0.000
P83	2, 2-Dimethyloctane	0.000
P144	2, 4-Dimethyl-3-isopropylpentane	0.075
P95;P93	4-n-Propylheptane; 4, 4-Dimethyloctane	0.000
P105	2, 2, 3-Trimethylheptane	0.000
P102	3-Methyl-5-ethylheptane	0.045
P86;P96	2, 5-Dimethyloctane; 4-Isopropylheptane	0.000
P134	2, 2, 3, 4-Tetramethylhexane	0.000
P150;P91	2, 2, 3, 4, 4-Pentamethylpentane; 3, 5-Dimethyloctane ..	0.057
P99	2-Methyl-5-ethylheptane	0.000
P110;P88	2, 3, 4-Trimethylheptane; 2, 7-Dimethyloctane	0.000
A7	n-Propylbenzene	0.301
P128	2, 4-Dimethyl-3-ethylhexane	0.000
P109	2, 3, 3-Trimethylheptane	0.000
P133	2, 2, 3, 3-Tetramethylhexane	0.000
P87	2, 6-Dimethyloctane	0.000
P104;P111; P92	4-Methyl-4-ethylheptane; 2, 3, 5-Trimethylheptane; 3, 6-Dimethyloctane	0.000
P127	2, 3-Dimethyl-4-ethylhexane	0.000
P129	2, 4-Dimethyl-4-ethylhexane	0.000
A10;P89;P97	1-Methyl-3-ethylbenzene; 3, 3-Dimethyloctane; 2-Methyl-3-ethylheptane	0.000

Code	Hydrocarbon	Weight, %
P119	3, 4, 4-Trimethylheptane	0.000
P111	2, 3, 4, 4-Tetramethylhexane	0.000
A11;P117	1-Methyl-4-ethylbenzene; 3, 3, 4-Trimethylheptane ...	0.831
P94;P101; P132	4, 5-Dimethyloctane; 3-Methyl-4-ethylheptane; 3, 4-Dimethyl-3-ethylhexane.....	0.000
P120	3, 4, 5-Trimethylheptane	0.000
P131;P103	3, 3-Dimethyl-4-ethylhexane; 4-Methyl-3-ethylheptane	
P90	3, 4-Dimethyloctane	0.350
P82;P100; P126	4-Ethyloctane; 3-Methyl-3-ethylheptane; 2, 3-Dimethyl-3-ethylhexane	0.000
P123	3, 4-Diethylhexane	0.000
P84	2, 3-Dimethyloctane	0.000
P139	2, 3, 3, 4-Tetramethylhexane	0.000
A14	1, 3, 5-Trimethylbenzene (mesitylene)	0.518
P60	5-Methylnonane	0.000
A9	1-Methyl-2-ethylbenzene.....	0.000
P79	4-Methylnonane	0.008
P149	2, 2, 3, 3, 4-Pentamethylpentane	0.057
P122	3, 3-Diethylhexane	0.000
P81	3-Ethyloctane.....	0.000
P121	2-Methyl-3-isopropylhexane.....	0.327
P77	2-Methylnonane.....	0.095
P78	3-Methylnonane.....	0.127
A18	tert-Butylbenzene (2-phenyl-2-methylpropane)	0.001
A13;P145; P146;P148	1, 2, 4-Trimethylbenzene; 2-Methyl-3, 3-diethylpentane; 2, 2, 3-Trimethyl-3-ethylpentane; 2, 3, 4-Trimethyl- 3-ethylpentane	1.231
P143	3, 3, 4, 4-Tetramethylhexane.....	0.000
A16	Isobutylbenzene (1-phenyl-2-methylpropane)	0.030
A17	sec-Butylbenzene (2-phenylbutane).....	0.044
P76	3x5' n-Decane.....	0.013
A23	1-Methyl-3-isopropylbenzene (m-cymene)	0.015
A12	1, 2, 3-Trimethylbenzene.....	0.246
A24	1-Methyl-4-isopropylbenzene (p-cymene).....	0.007
A38	2, 3-Dihydroindene (indan)	0.167
A22	1-Methyl-2-isopropylbenzene (o-cymene).....	0.000
A26	1-3-Diethylbenzene.....	0.029
A20	1-Methyl-2-propylbenzene	0.091
A21;A15	1-Methyl-4-propylbenzene;n-Butylbenzene (1-phenyl- butane).....	0.165
A25;A32	1, 2-Diethylbenzene; 1, 3-Dimethyl-5-ethylbenzene	0.000

Code	Hydrocarbon	Weight, %
A27	1, 4-Diethylbenzene.....	0.190
A19	1-Methyl-2-propylbenzene.....	0.009
A80	1-Phenyl-2, 2-dimethylpropane.....	0.000
A33	1, 4-Dimethyl-2-ethylbenzene.....	0.030
A31;A79	1, 3-Dimethyl-4-ethylbenzene; 2-Phenyl-3-methylbutane	0.161
A29;A91	1, 2-Dimethyl-4-ethylbenzene; 1-Methyl-3-tert-butylbenzene.....	0.271
A30	1, 3-Dimethyl-2-ethylbenzene.....	0.000
A39	1-Methyl-2, 3-dihydroindene (1-methylindan).....	0.012
A76	3-Phenylpentane.....	0.000
A40	2-Methyl-2, 3-dihydroindene (2-methylindan).....	0.002
A95	1-Ethyl-3-isopropylbenzene.....	0.001
A78	2-Phenyl-2-methylbutane.....	0.000
A48	1-Methyl-4-tert-butylbenzene.....	0.000
A75;A44	2-Phenylpentane; 1-Ethyl-2-isopropylbenzene.....	0.089
A28;A88;A85	1, 2-Dimethyl-3-ethylbenzene; 1-Methyl-3-isobutylbenzene; 1-Methyl-3-sec-butylbenzene.....	0.007
A60	1, 3-Dimethyl-5-isopropylbenzene.....	0.003
A45	1, 2-Dimethyl-5-isopropylbenzene (3, 4-dimethylcumene)	0.112
P151 5856	Undecane.....	0.060
A84;A87;A89	1-Methyl-2-sec-butylbenzene; 1-Methyl-2-isobutylbenzene; 1-Methyl-4-isobutylbenzene.....	0.154
A61	1, 4-Dimethyl-2-isopropylbenzene.....	0.000
A96	1-Ethyl-4-isopropylbenzene.....	0.000
A36	1, 2, 4, 5-Tetramethylbenzene (durene).....	0.003
A86;A77	1-Methyl-4-sec-butylbenzene; 1-Phenyl-2-methylbutane	
A35	1, 2, 3, 5-Tetramethylbenzene (isodurene).....	0.000
A49	1-Phenyl-3-methylbutane (Isopentylbenzene).....	0.000
A58;A59	1, 3-Dimethyl-2-isopropylbenzene; 1, 3-Dimethyl-4-isopropylbenzene.....	0.000
A90	1-Methyl-2-tert-butylbenzene.....	0.009
A67	1-Methyl-3, 5-diethylbenzene.....	0.000
A93	1-Ethyl-3-n-propylbenzene.....	0.129
A57;A42	1, 2-Dimethyl-4-isopropylbenzene; 5-Methyl-2, 3-dihydroindene (5-methylindan).....	0.000
A54	1, 3-Dimethyl-5-n-propylbenzene.....	0.044
A56	1, 2-Dimethyl-3-isopropylbenzene.....	0.000
A92	1-Ethyl-2-n-propylbenzene.....	0.171
A66	1-Methyl-3, 4-diethylbenzene.....	0.053
A55	1, 4-Dimethyl-2-n-propylbenzene.....	0.034
A63;A94;A82	1-Methyl-2, 4-diethylbenzene; 1-Ethyl-4-n-propylbenzene; 1-Methyl-2-sec-butylbenzene.....	0.028

Code	Hydrocarbon	Weight %
A34	1, 2, 3, 4-Tetramethylbenzene (prehnitene).....	0.023
A45; A41	n-Pentylbenzene; 4-Methyl-2, 3-dihydroindene (4-methylindan).....	0.030
A62	1-Methyl-2, 3-diethylbenzene.....	0.018
A83; A64	1-Methyl-4-n-butylbenzene; 1-Methyl-2, 5- diethylbenzene.....	0.035
A43; A53; A52	1, 2, 3, 4-Tetrahydronaphthalene; 1, 3-Dimethyl-4-n- propylbenzene; 1, 3-Dimethyl-2-n-propylbenzene...	0.010
A81	1-Methyl-2-n-butylbenzene.....	0.050
A65	1-Methyl-2, 6-diethylbenzene.....	0.140
A51	1, 2-Dimethyl-3-n-propylbenzene.....	0.091
A50	1, 2-Dimethyl-3-n-propylbenzene.....	0.060
A71	1, 3, 5-Trimethyl-2-ethylbenzene.....	0.017
A71; A72	1, 2, 4-Trimethyl-5-ethylbenzene; 1, 2, 4-Trimethyl-6- ethylbenzene.....	0.000
P152	421°F Dodecane.....	0.055
A69	1, 2, 3-Trimethyl-5-ethylbenzene.....	0.000
A70	1, 2, 4-Trimethyl-5-ethylbenzene.....	0.000
A37	Naphthalene.....	0.000
A47	3, 5-Diisopropyltoluene (3, 5-Diisomethyltoluene).....	0.000
A68	1, 2, 3-Trimethyl-4-ethylbenzene.....	0.190
P153	456°F Tridecane.....	0.002
A74	Pentamethylbenzene.....	0.000
Unknown		1.684
TOTAL		100.000

Olefins	10.209
Naphthenes	23.126
Saturates	44.312
Aromatics	20.669

VIGAS*A-----ARMY FLRL GAS CHROMATOGRAPHIC ANALYSIS--

SAMPLE 2, ANALYSIS 1
 SAMPLE IDENTIFICATION:
 SAMPLE NAME: AL 4458-G
 CALCULATION METHOD: INTSTD
 STANDARD FILE NAME: /AROM/

<u>COMPONENT</u>	<u>RETENTION TIME</u>	<u>VOLUME %</u>
BENZENE	1182	0.247
TOLUENE	1376	2.192
ETHYLBENZENE	1530	1.176
M+P-XYLENE	1551	6.685
O-XYLENE	1587	1.530
CUMENE	1621	0.033
C9+	1662	0.242
UNKNOWN	1682	0.971
UNKNOWN	1706	0.531
UNKNOWN	1738	1.123
UNKNOWN	1814	0.896
UNKNOWN	1857	0.442
UNKNOWN	1888	0.045
UNKNOWN	1916	0.344
UNKNOWN	1959	0.446
UNKNOWN	2010	0.401
UNKNOWN	2055	0.121
UNKNOWN	2099	0.145
UNKNOWN	2148	0.261
UNKNOWN	2167	0.084
UNKNOWN	2291	0.041
UNKNOWN	2533	0.088

		18.043

REFERENCE PEAK TIME: 1182 SECONDS
 TIME TOLERANCE: 1%
 INTERNAL STANDARD TIME & AREA: 999 SECONDS & ***** COUNTS

11/7/71

Figure 7

APPENDIX E. REPORT ON TESTING CONDUCTED BY
ETHYL CORPORATION

ETHYL CORPORATION TESTS OF ARL-56

FINAL REPORT

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Test Objective

The objective of this work was to evaluate the potential of ARL-56 as a commercial antiknock agent. ARL-56 is a cerium chelate received from Dr. R. Sievers, Wright-Patterson Air Force Base, Ohio.

Test Methods and Results

The test methods and results follow under paragraph headings which correspond to those of the Testing Agreement of August 2, 1973, copy attached.

Part I. A. a. Research and Motor Octane Numbers

A comparison was made of the antiknock effectiveness of TEL and ARL-56. Concentrations of TEL were 1.0 and 3.0 g Pb/gal and concentrations of ARL-56 were 0.67 and 2.03 g Ce/gal. These concentrations are equivalent on a metal gram-atom basis. Details are given in Table 1.

Table 1

Test Concentrations of TEL and ARL-56

<u>Millimoles additive/gal.</u>	<u>Lead</u>		<u>Cerium</u>	
	<u>g Pb/gal.</u>	<u>g TEL/gal.</u>	<u>g Ce/gal.</u>	<u>g ARL-56/gal.</u>
4.83	1.0	1.56	0.67	4.2
14.48	3.0	4.68	2.03	12.6

Five test fuels were used: namely, PRF-80, PRF-90; and commercial lead-free regular-grade Schio, Amoco, and Marathon gasolines. The results of the study are tabulated in Table 2 and presented graphically in Figures 1-8.

Examination of the data shows that the relative effectiveness of the two antiknocks changes with concentration. Figures 1 and 2 show that ARL-56 is 33% as effective as TEL by Research Method and 16% as effective by Motor Method. These comparisons were made on an equal weight-of-metal basis and are averages of tests in three commercial gasolines at the octane response obtained with 0.5 g Pb/gal.

Water Contact - The stability of ARL-56 to hydrolysis was determined in the following manner. One quart blends of each of the three commercial fuels were stored for three days with 2.0 volume% of distilled water. A comparative test was made with TEL. Research and Motor Octane determinations following storage showed no significant change in octane effectiveness for either antiknock. The octane values following water contact are shown in Table 3, and the baseline values appear in Table 2.

Part I. A. b. Special Motor Octane Number

The heater blades on the Motor Method engine were cleaned before the work in Part I. A. a. was started. At the conclusion of this work, the heater blades showed no sign of deposits. This suggests that ARL-56 is not decomposed by the heater blades. As a result of this observation, the Special Motor Octane Number work was omitted.

Part I. A. c. Carburetor and Intake System Deposits

After rating ARL-56 solutions, a long wash-out time is required to return the engine to baseline condition. This is the result of ARL-56 depositing on the inside surfaces of the intake system. Visual observation showed that this begins immediately downstream from the carburetor venturi with PRF fuels and farther downstream with gasolines. The more volatile PRF fuels gave much longer wash-out times than the gasolines. Some deposition was noted on the intake valve shroud of the Motor engine and an orange deposit was noted in the center of the piston of the Research engine. In general it is difficult and time-consuming to rate fuels containing ARL-56. After the engine has returned to baseline condition by running on non-additive fuel, there is no evidence of deposits in the carburetor or intake system. Consequently, no photographs were taken.

Part II. Inspection Test Screening

Three ASTM Fuel inspection tests have been run. ASTM D130-60 "Copper Corrosion Test" was run on PRF-80 and all three commercial gasolines with 0.0, 4.2, and 12.6g ARL-56/gal. All twelve samples received a 1-A rating.

ASTM D381-70 "Existent Gum" was run in the same four fuels with the same additives. This test is valuable because it correlates with induction-system problems in vehicles. Generally speaking, gum values of less than 7.0 mg/100 ml are considered satisfactory. The PRF-80 was satisfactory, the Sohio gasoline proved to give marginal results, and the other two gasolines gave unsatisfactory gum values when ARL-56 was present. The data are shown in Table 4. The gum residue is not ARL-56 because residues were thoroughly washed with hexane before weighing. Furthermore only a small residue was formed with PRF-80.

ASTM D525-55 "Oxidation Induction Period" was run on the same fuels. This test directly measures resistance to oxidation by exposing the fuel to a pure oxygen atmosphere of 100 psi at 100°C. A satisfactory fuel resists oxidation (shown by pressure drop) for at least three hours (180 min). Many fuels show no oxidation in 24 hours (1440 minutes). However all three gasolines containing ARL-56 gave values of less than 180 minutes which shows that the oxidation stability of these gasolines was seriously impaired by ARL-56. Apparently olefins and/or aromatics are involved in this instability because the paraffinic PRF-80 was unaffected. The data are shown in Table 4.

Table 4

Fuel Inspection Tests

<u>Additive</u>	<u>D381-70 Existent gum mg/100 ml</u>		
	<u>None</u>	<u>4.2g ARL-56/gal</u>	<u>12.6g ARL-56/gal</u>
PRF-80	0.0	1.2	3.4
Sohio	0.2	18.8	22.6
Amoco	0.8	19.8	22.2
Marathon	0.0	8.4	4.0

<u>Additive</u>	<u>D525-55 Induction Period, minutes</u>		
	<u>None</u>	<u>4.2g ARL-56/gal</u>	<u>12.6g ARL-56/gal</u>
PRF-80	1440+	1440+	1440+
Sohio	795	120	30
Amoco	960	30	15
Marathon	1440+	30	30

Synergism of TEL and ARL-56

We have determined the antiknock effectiveness of

- a. 0.1 g Ce/gal as ARL-56
- b. 1.0 g Pb/gal (TEL)
- c. 0.1 g Ce + 1.0 g Pb/gal (TEL)

in the three commercial fuels. The purpose of this work was to investigate the possibility of a synergistic effect of the two antiknocks.

Our results show that there is no antiknock synergism for this mixture of TEL and ARL-56. The results are tabulated in Table 5. An average of 0.54 Research Octane increase was realized from 0.1 g Ce/gal. Both 1.0 g Pb/gal and 1.0 g Pb + 0.1 g/gal gave a Research gain of 4.70. Therefore, the effectiveness of the ARL-56 was lost in the presence of 1.0 g Pb/gal.

The Motor Method response of 0.1 g Ce/gal was not large enough to detect, and no synergy was observed with Pb.

J. B. Hinkamp
J. B. Hinkamp

JBH/jkh
9-26-73

Table 5

Research and Motor Octane Numbers

Fuel	Additive				Δ Octane Value		
	None	0.1g Ce as ARL-56	1.0g Pb	0.1g Ce +1.0g Pb	0.1g Ce as ARL-56	1.0g Pb	0.1g Ce +1.0g Pb
Research							
Sohio	92.52	93.03	96.86	96.86	0.51	4.34	4.34
Amoco	91.48	92.00	96.43	96.39	0.52	4.95	4.91
Marathon	91.55	92.13	96.35	96.35	0.58	4.80	4.80
Avg.	91.85	92.39	96.55	96.53	0.54	4.70	4.68
Motor							
Sohio	83.49	83.49	86.78	86.78	0.0	3.29	3.29
Amoco	83.03	83.03	86.83	86.83	0.0	3.80	3.80
Marathon	82.00	82.00	85.59	85.59	0.0	3.59	3.59
Avg.	82.84	82.84	86.40	86.40	0.0	3.56	3.56

TABLE 1
Antiknock Data on TEL and ARL-56

of

100

95-1447-2000/2001

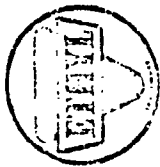
Pb 3.0g/cal

APR 56 12.60/PM

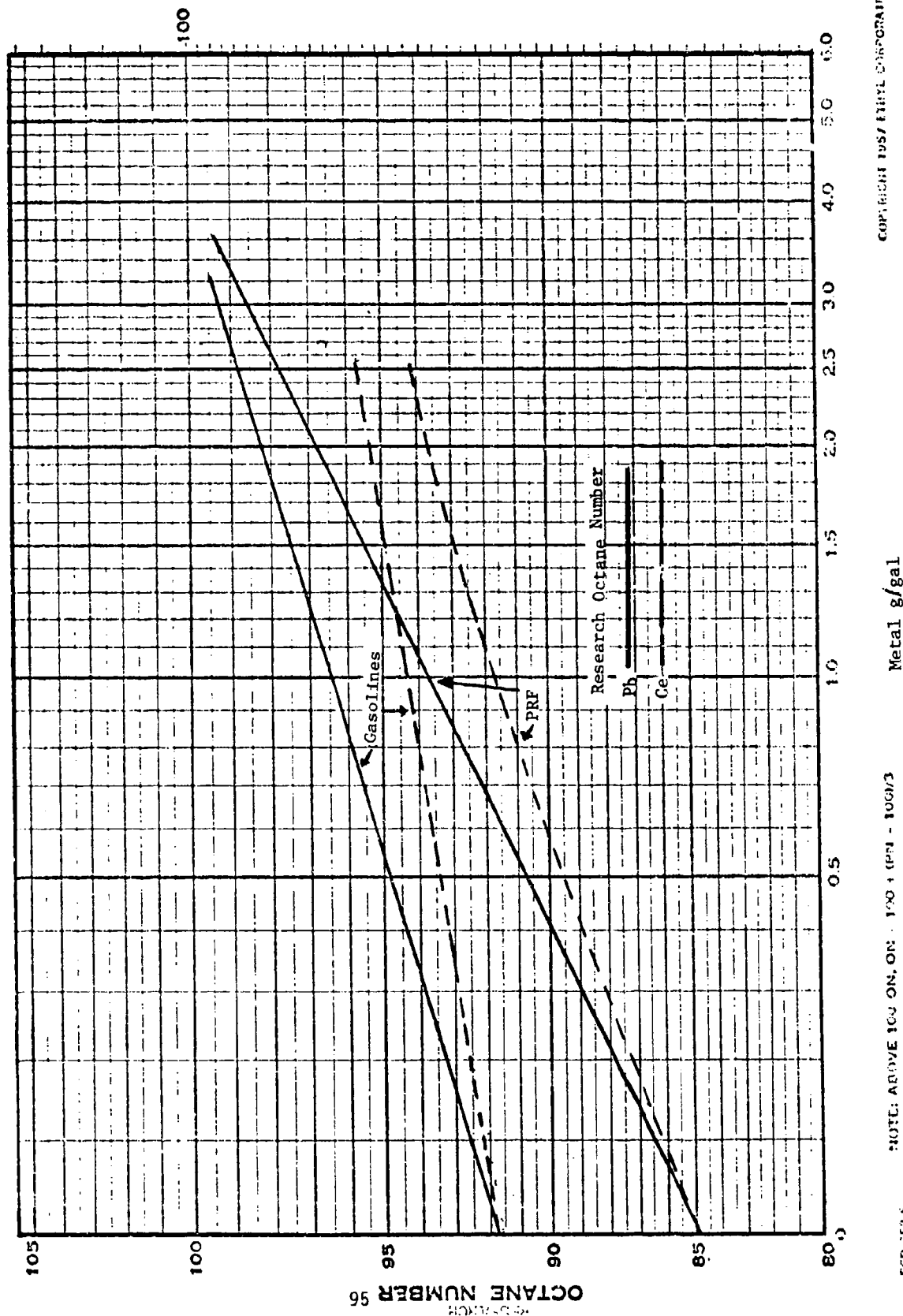
Additive:	None	Octane Number	Δ	Octane Number	Δ	Octane Number	Octane
Research							
REF-80	80.00	89.91	9.91	85.72	5.72	95.70	15.70 9.42
REF-90	89.99	97.55	7.56	95.30	5.31	101.51	11.52 8.11
Avg.	85.00	93.73	8.74	90.51	5.52	98.60	13.61 8.76
Schlo	92.05	96.65	4.60	94.25	2.20	99.83	7.78 3.73
Amoco	91.55	96.61	5.06	93.96	2.41	99.24	7.69 3.81
Marathon	92.00	96.27	4.27	93.53	1.53	98.89	6.89 3.15
Avg.	91.87	96.51	4.64	93.91	2.05	99.32	7.45 3.56
Motor							
REF-80	80.01	92.03	12.02	89.53	9.52	98.31	18.30 13.49
REF-90	90.01	101.20	11.19	98.70	8.69	107.12	17.11 11.66
Avg.	85.01	96.62	11.60	94.12	9.12	102.72	17.70 12.58
Schlo	83.49	86.88	3.39	84.31	0.82	90.86	7.37 1.94
Amoco	83.03	86.98	3.95	84.52	1.49	90.41	7.38 2.76
Marathon	82.00	85.69	3.69	83.03	1.03	88.85	6.85 1.98
Avg.	82.84	86.52	3.63	83.95	1.11	90.04	7.20 2.23

Table 3 Hydrolytic Stability

94



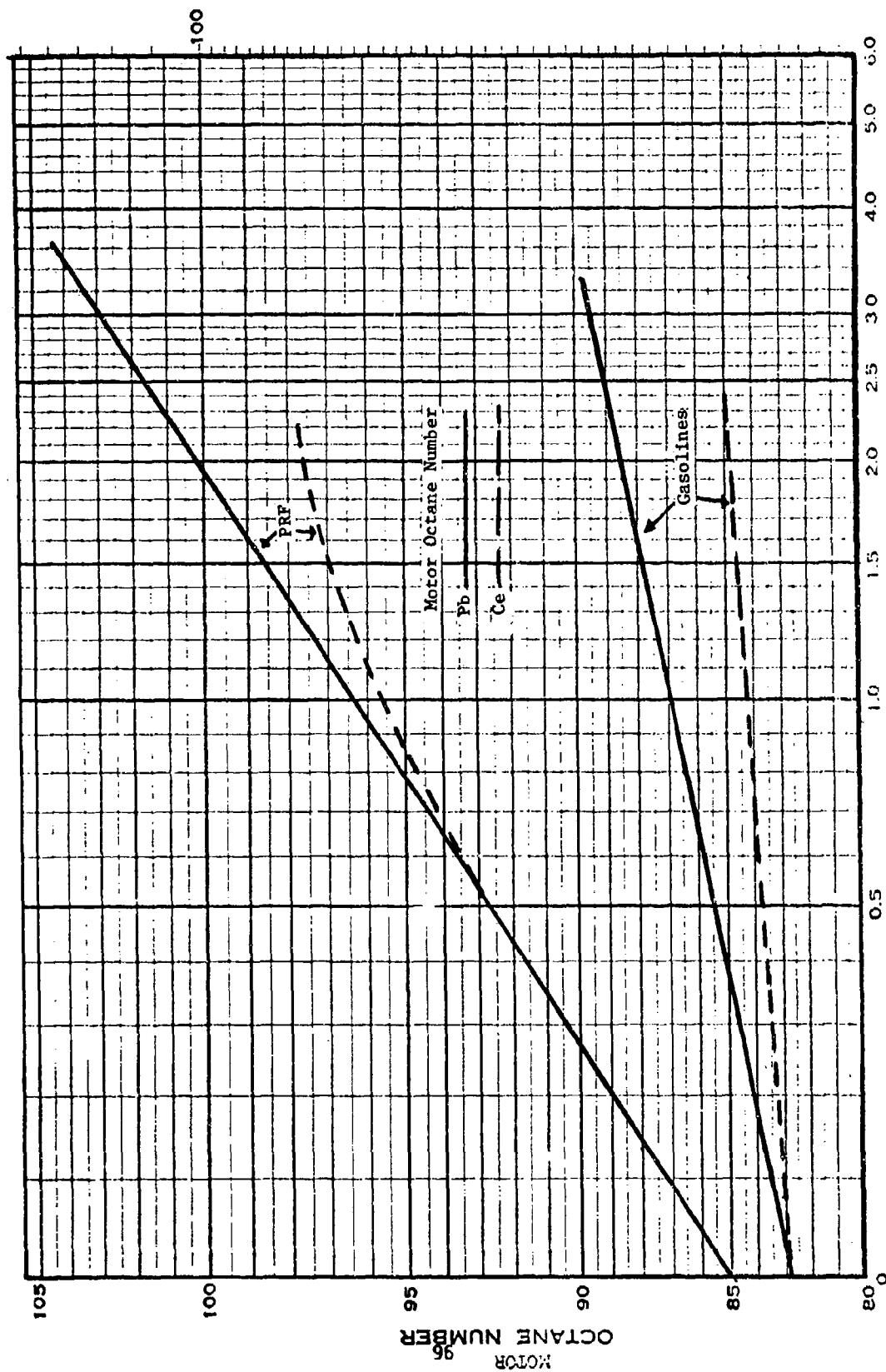
ETHYL CORPORATION TETRAETHYLLEAD SUSCEPTIBILITY CHART



ETHYL CORPORATION

TETRAETHYLLEAD SUSCEPTIBILITY CHART

Figure 2



ECD 850-F

NOTE: ABOVE 100 ON. ON = 100 + (PN - 100)/3

Metal g/gal

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Figure 3

WITNESSED BY _____ DATE _____
 PLOT BY _____ DATE _____
 TEST DATED _____ DATA SHEET NO. _____
 FILES G & H _____
 FIRM CORPORATION RESEARCH LABORATORIES AT _____
 ORIGINAL OF FIRST REPORT [] REPT. NO. []

Δ
Research
Octane
Number

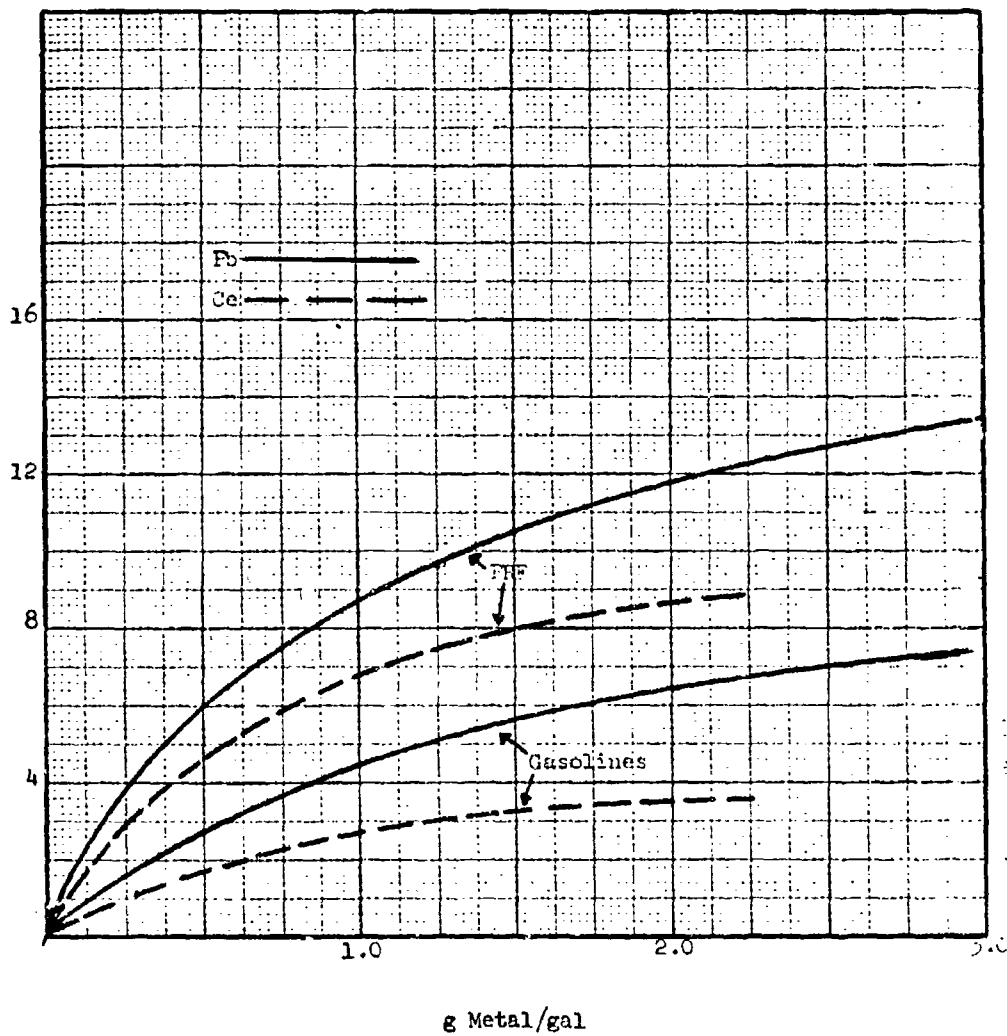


Figure 4

WITNESSED BY _____
DATE _____
PLOT BY _____
DATE _____
TEST DATES _____
DATA SHEET NO. _____

FILES G & H _____
ETHYL CORPORATION RESEARCH LABORATORIES AT _____
ORIGINAL ☐ FIRST REPLICATES ☐ REPLICATES ☐

Δ
Motor
Octane
Number

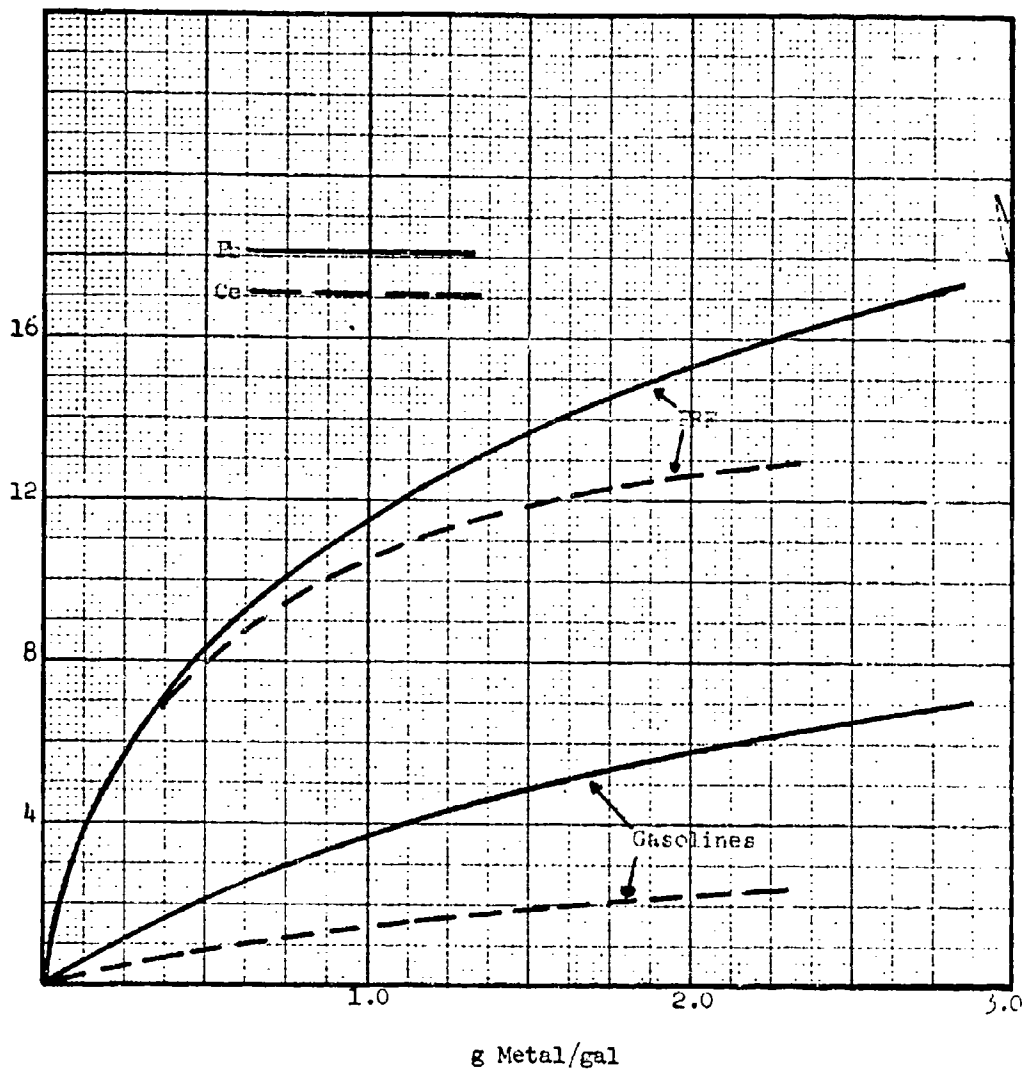


Figure 5

SEE NUMBER
CHART SHEET

WITNESSED BY _____
PLOT BY _____
TEST DATES _____
DATE _____
DATA SHEET NO. _____

FILES Q & M _____
ETHYL CORPORATION RESEARCH LABORATORIES AT _____
ORIGINAL ☐ FIRST REPLY ☐ REPLY ☐

Research
Octane
Number

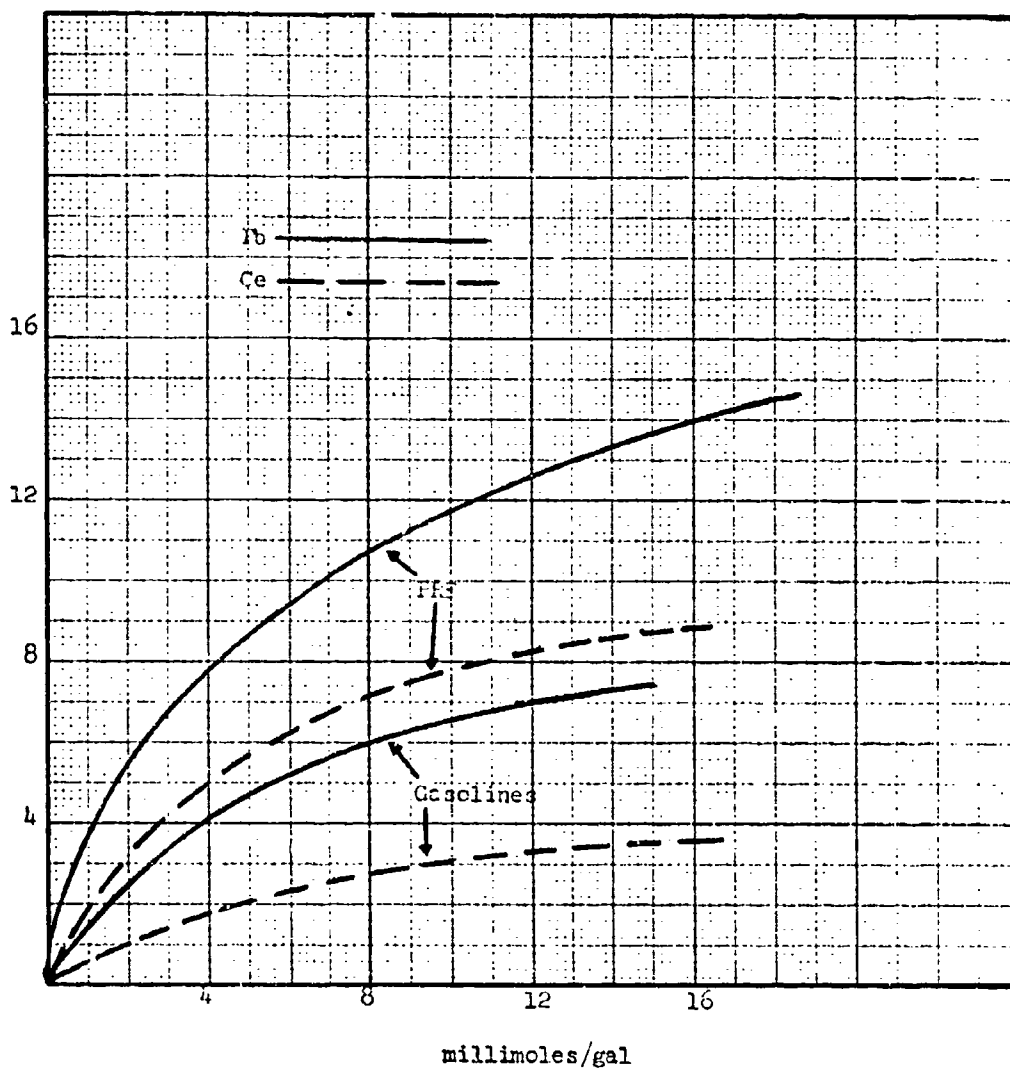


Figure 6

WITNESSED BY _____ DATE _____
 PLOT BY _____ DATE _____
 TEST DATES _____ DATA SHEET NO. _____

FILED IN _____
 RESEARCH CORPORATION RESEARCH LABORATORIES AT _____
 ORIGINAL ☐ FIRST REPRINT ☐ REPRINT ☐

Δ
Motor
Octane
Number

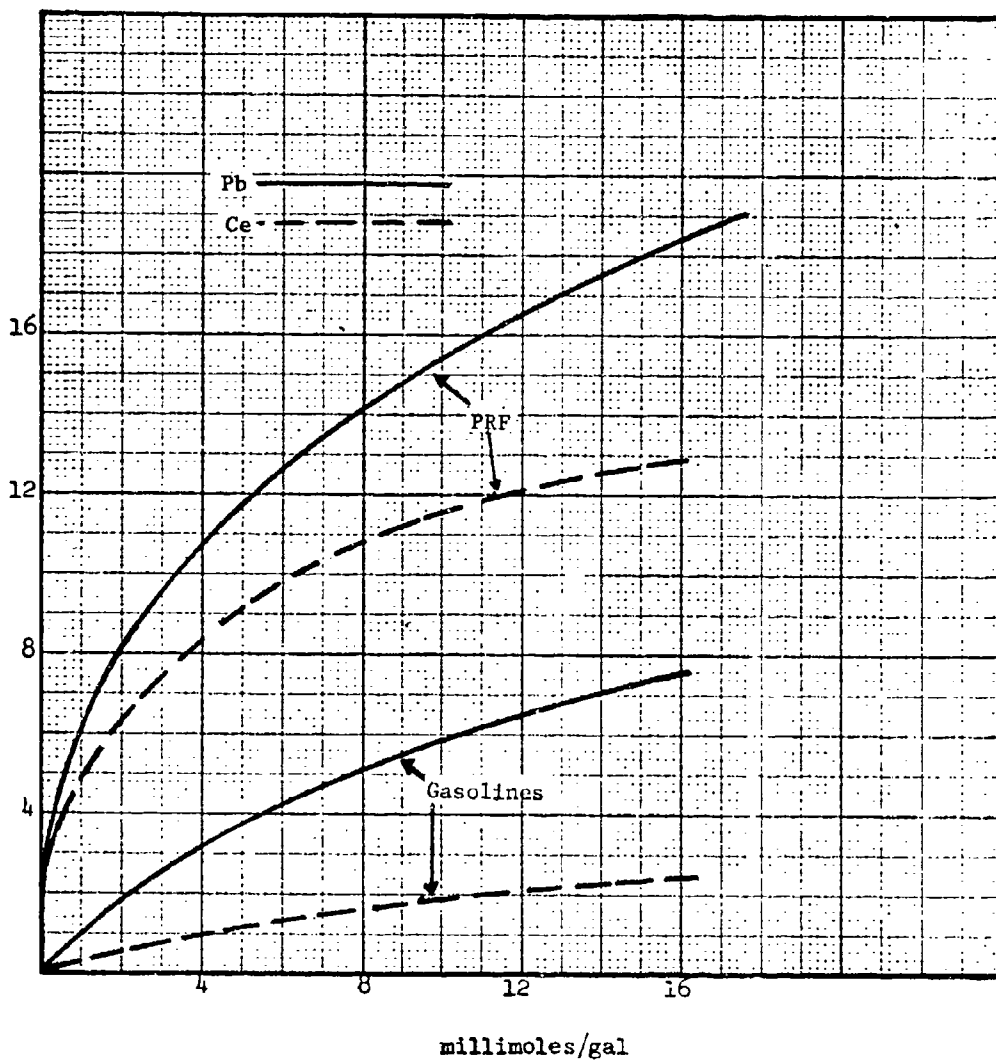


Figure 7

WITNESSED BY _____
 PLOT BY _____
 TEST DATES _____
 DATE _____
 DATA SHEET NO. _____

FILES G & H _____
 FIRMAL CORPORATION RESEARCH LABORATORIES AT _____
 ORIGINAL ☐ FIRST REPORTS ☐ REPEATS ☐

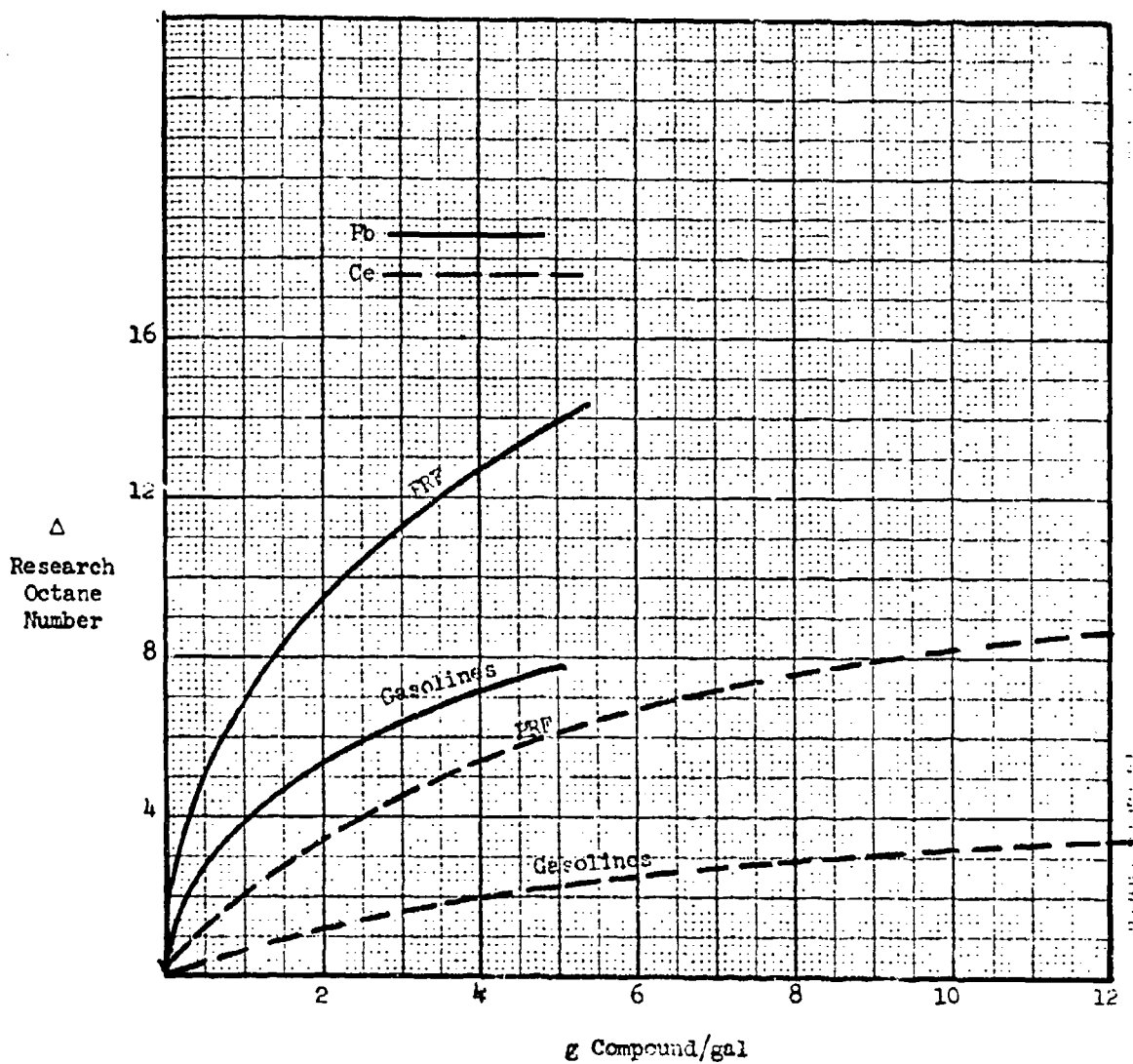
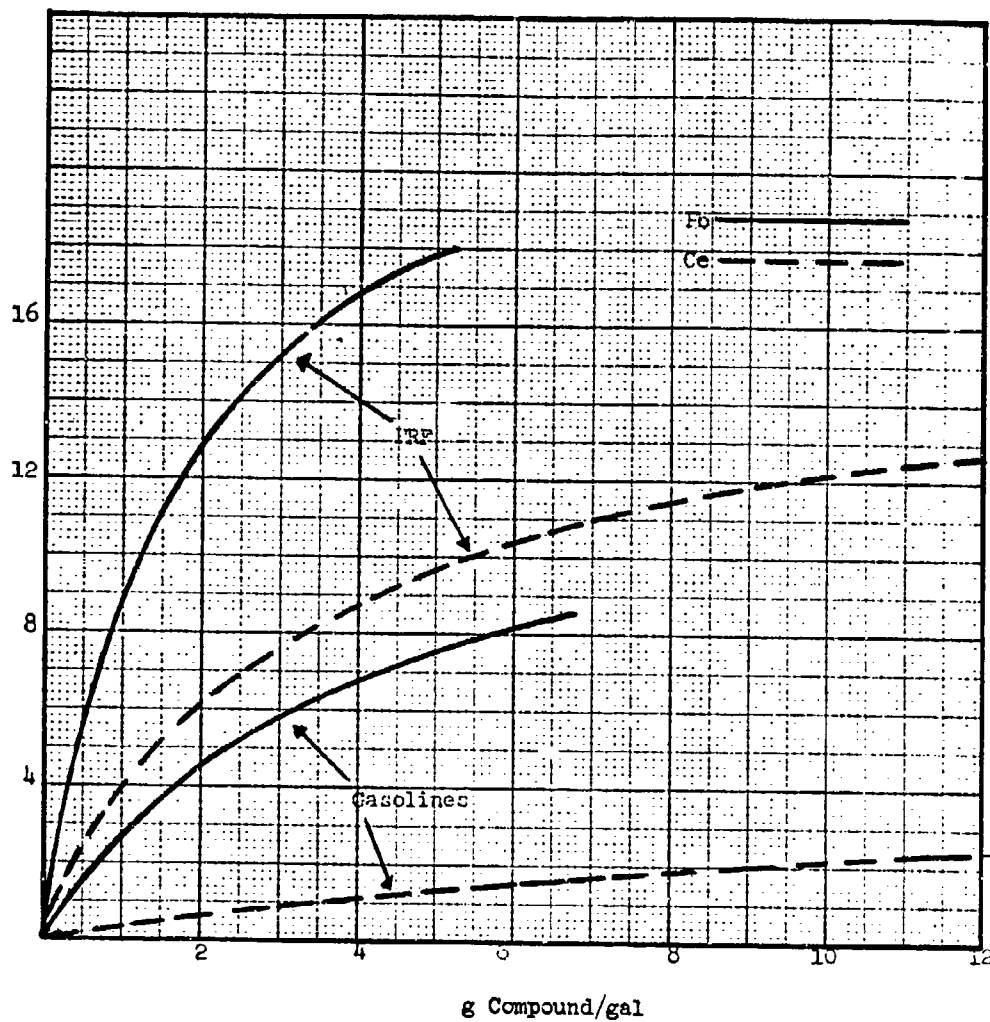


Figure 8

WITNESSED BY _____
 PLOT BY _____
 TEST DATES _____
 DATE _____
 DATA SHEET NO. _____

FILES G & H _____
 ETHYL CORPORATION RESEARCH LABORATORIES AT _____
 ORIGINAL ☐ FIRST REPRINT ☐ REPRINTS ☐

Δ
 Motor
 Octane
 Number



APPENDIX F. REPORT ON TESTING CONDUCTED
BY SUN OIL COMPANY

SUN OIL COMPANY
Research and Development

Applied Research Department
Memorandum Number ARD73-26

Date: December 20, 1973
Project No.: 13-106
Author: J. P. Pandosh

EVALUATION OF WPAF CERIUM COMPOUND ARL-56

SUMMARY

We were asked to evaluate the cerium compound ARL-56 which Wright Patterson Air Force had synthesized. This compound had been tested as an antiknock compound for use in an unleaded fuel since it should not poison noble metal catalyst and is reported to be nontoxic. These claims suggested two areas of study: first, antiknock evaluation in cars with an unleaded base fuel to see if there was any real octane benefit; second, exhaust emissions testing in a 1973 non-catalyst car to see if it caused any change in emissions.

Based on a limited amount of testing, we conclude:

1. WPAF Compound ARL-56 at 0.5- 1 g/gal of cerium (6.23 g of compound) increases the road octane number of a clear fuel by about 1.5 numbers.
2. There is little or no additional octane benefit in adding more than 1 g Ce/gal.
3. ARL-56 has no adverse effect on conventional exhaust emissions.

WPAF ARL-56 would be quite beneficial in an unleaded system even though its octane response is less than that of TEL. This, of course, is provided it doesn't poison catalysts or have any other adverse effects. We believe further octane & emissions testing, especially at the lower levels (1 g/gal or less), is needed in more cars. Should it show the same favorable results in a fleet of cars, it should then undergo durability testing. This would include testing for long range engine deposits, wear, or unfavorable reactions with gasoline or engine oil additives.

Octane Testing

We tested WPAF ARL-56 and compared it to TEL in an ASTM-CFR engine for relative Motor Octane Number response. Motor octane correlates very well with road octane in modern cars using Pb antiknocks. Then, to check if this motor/road correlation also applied to this compound, we next tested it in two 1973 model cars using the Modified Uniontown Method for road octane number. We compared these two compounds on an equivalent grams of metal basis. Table 1 summarizes our results.

When TEL was added at 1.0 and 3.0 g Pb/gal to the clear base fuel, appreciable gains in both MON and road octane number were noted, as expected. When 1.0 & 3.0 g Ce/gal of ARL-56 were added to the same base fuel, the same increases in MON and road were not experienced. Adding 1.0 g Ce/gal ARL-56 gave about 50% of the TEL increase, while 3.0 g Ce/gal ARL-56 gave little or no increase over the 1.0 g/gal dosage. In other words, adding more than 1.0 g Ce/gal had no additional benefit. This phenomenon occurred in testing for both MON & road octane number.

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This prompted us to submit samples at 0.25 & 0.50 g Ce/gal for MON to seek the optimum addition/benefit ratio. Based on the MON results and testing in one car, 0.5 g Ce/gal (or less) seems to be the optimum level. We would liked to have done more testing at this lower addition level, but ran out of compound

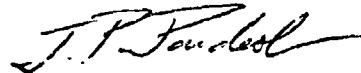
Figures I, II, and III plot the results shown in Table I.

Emissions Testing

We compared 1 g Ce/gal ARL-56 to 1 g Pb/gal TEL using the 1971 Federal Test Procedure Hot Start Cycle in a 1973 400 CID Ford. The following table gives the average of two runs using 4 cycles per run.

<u>Fuel</u>	<u>HC</u>	<u>CO</u>	<u>NOx</u>	<u>Units</u>
Unleaded + 1 g Ce/gal ARL-56	5.40	39.92	7.16	g/cycle
Unleaded + 1 g Pb/gal TEL	5.80	42.57	7.04	g/cycle

Although the ARL-56 looks better in CO, more testing is needed before any definite conclusions can be drawn.



J. P. Pandosh

JPP:cr

TABLE I
EVALUATION OF ARL-56 IN UNLEADED GASOLINE
OCTANE RESULTS

FUEL	ASTM-CFR MON ⁽³⁾		ROAD OCTANE NUMBER			
	TEST ENGINE		1973 BUICK A-222		1973 FORD A-221	
	O.N.	Δ	O.N.	Δ	O.N.	Δ
Base Clear ⁽⁴⁾	84.25	-	89.5	-	90.2	-
Base + 1 g Pb/gal	88.40	(4.2)	92.7	(3.2)	93.45	(3.2)
Base + 3 g Pb/gal	92.30	(8.05)	95.9	(6.4)	95.65	(5.4)
Base + 0.25 g Ce/gal ⁽¹⁾	85.05	(0.8)	-	-	-	-
Base + 0.5 g Ce/gal ⁽¹⁾	85.50	(1.25)	-	-	92.20	(2.0)
Base + 1.0 g Ce/gal ⁽¹⁾	85.50	(1.25)	90.8	(1.3)	92.4	(2.2)
Base + 3.0 g Ce/gal ⁽¹⁾	85.35	(1.10)	91.0	(1.5)	93.10 ⁽²⁾	(2.9)

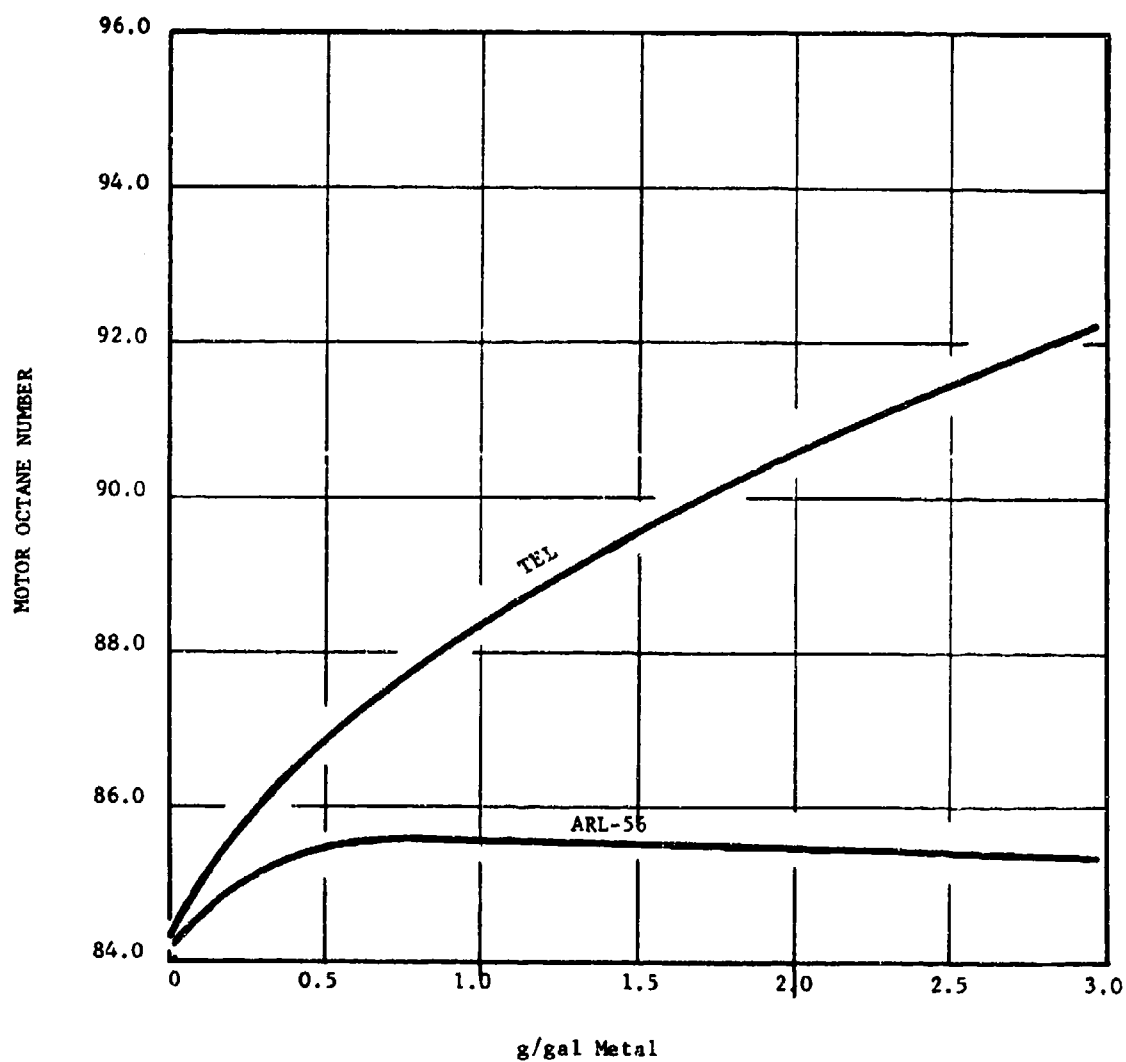
() Numbers in parenthesis are increases from clear base fuel.

(1) Multiply by 6.23 to determine grams of compound.

(2) Adjusted downward by disregarding suspicious data point.

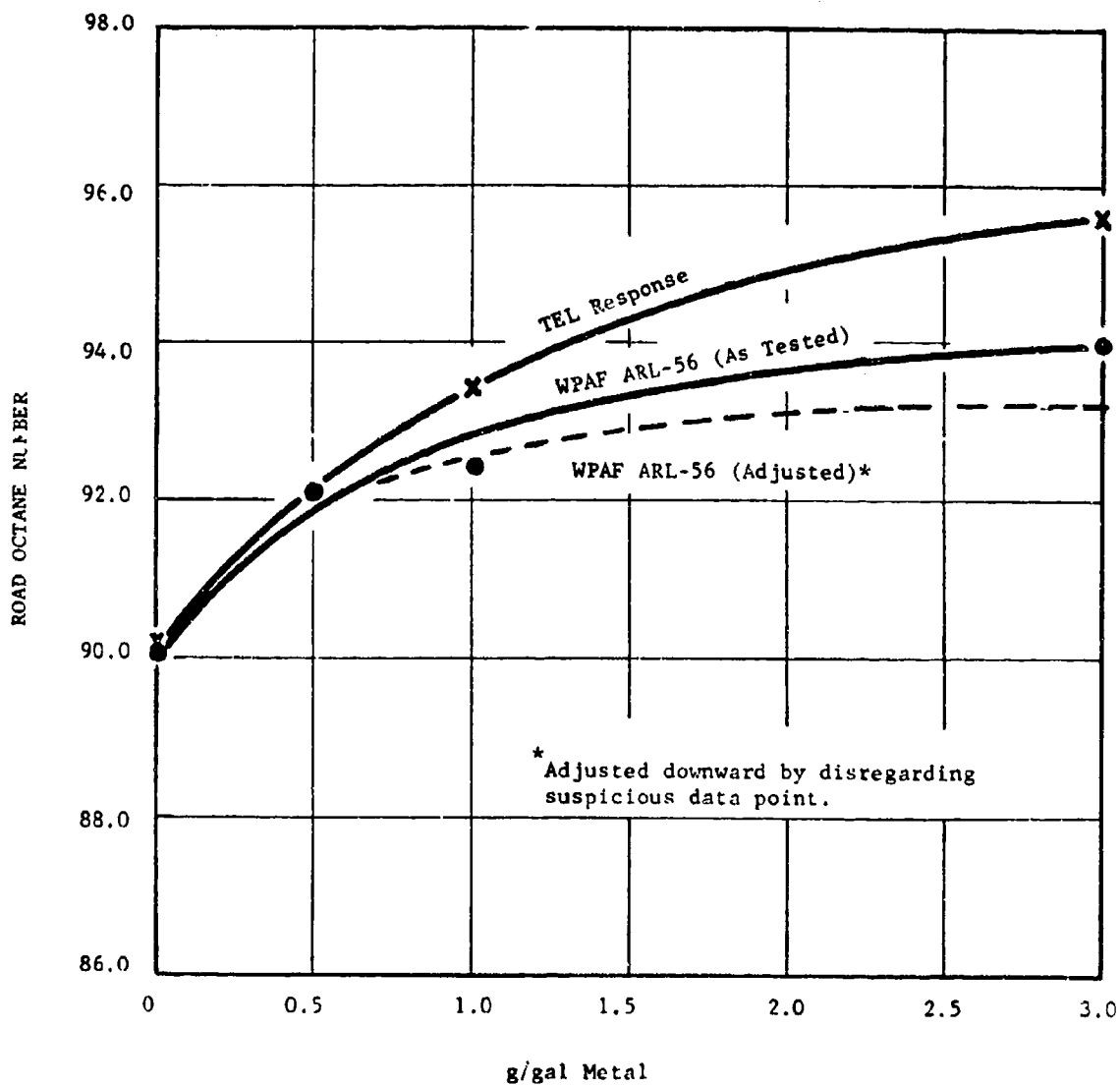
(3) Engine was stabilized for 15 min. prior to reading to minimize possible carryover effect.

(4) Fuel Book Page Number 644006. Fuel had 0.032 g Pb/gal.

EVALUATION OF ARL-56
MOTOR OCTANE DATA

NOTE: Engine was stabilized for 15 min. prior to reading to minimize possible carryover effect.

EVALUATION OF ARL-56
ROAD OCTANE DATA
1973 FORD GALAXIE 500
(400 CID, 2 Bbl)



EVALUATION OF ARL-56
ROAD OCTANE DATA
1973 BUICK ELECTRA 225
(455 CID, 4 Bbl.)

