April 9, 1946. E. BARTHOLOMEW 2,398,281

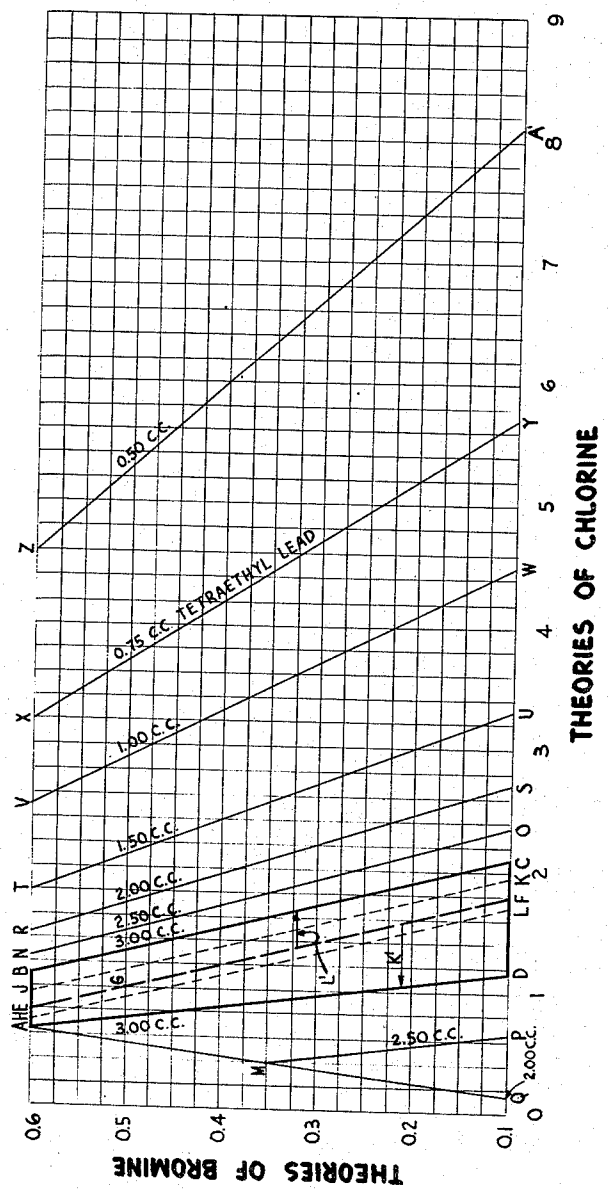
ANTIKNOCK AGENT

Filed July 8, 1944

THEORIES OF BROMINE AND CHLORINE

POINT	A	B	C	D	E	F	G	H	J	K	L	M	N	O
BROMINE	0.60	0.60	0.10	0.10	0.60	0.10	0.50	0.60	0.60	0.10	0.10	0.35	0.60	0.10
CHLORINE	0.65	1.10	2.10	1.15	0.80	1.80	1.00	0.70	0.95	1.95	1.70	0.40	1.24	2.34

POINT	P	Q	R	S	T	U	V	W	X	Y	Z	A'
BROMINE	0.10	0.10	0.60	0.10	0.60	0.10	0.60	0.10	0.60	0.10	0.60	0.10
CHLORINE	0.65	0.15	1.45	2.70	1.80	3.30	2.50	4.50	3.20	5.70	4.60	8.10



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ANTIKNOCK AGENT

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5 Claims. (Cl. 252—386)

This invention relates to the use of halides with lead antiknock compounds to inhibit principally the deposition of lead compounds in engine combustion chambers and on exhaust valves, the burning of exhaust valves and acid corrosion of engine parts.

This application is a continuation-in-part of my application No. 432,859, filed February 28, 1942, for Antiknock agent.

In prior practice, including commercial use, the best results were obtained by the use of one theory of bromine for the lead. In this commercial use the mixture comprised tetraethyl lead and ethylene dibromide. One theory of halogen is the quantity theoretically required for reaction with the lead to form the lead halide, which quantity is two atoms of halogen per atom of lead.

Attempts have been made to replace a part of the bromine with chlorine and to obtain results as good as those given by a mixture containing one theory of bromine and no chlorine. These attempts were successful when small substitutions of chlorine for bromine were made but when further substitutions were made the results did not attain the level set by the one theory of bromine. One commercial practice employs 0.70 theory of bromine and 0.45 theory of chlorine. In the easy operation of an engine the results with this mixture may be as good as with one theory of bromine alone but in heavy duty operation the accumulation of lead compounds in the combustion chamber is greater and exhaust valve life is shorter than when one theory of bromine is used.

This practice has led to a belief that bromine is much more effective and satisfactory than chlorine and that bromine should be the predominating constituent of the corrective agent. I have found that the difficulty of finding a good corrective agent is enhanced by the fact that corrective agents which decrease lead deposition in the combustion chamber may increase acid corrosion of engine parts and particularly of exhaust valves. I have found that both of these difficulties can be overcome and improved results obtained by the use of a corrective agent containing bromine and chlorine, with the chlorine predominating, if the proportions are kept within a defined range.

For example, I have found that a corrective agent comprising one theory of chlorine and one-half theory of bromine for the lead gives results comparable to one theory of bromine. Such an agent may be made readily by the admixture on a volume basis of 404 parts ethylene dichloride and 220 parts ethylene dibromide for use with 1,000 parts tetraethyl lead. This mixture may be dissolved in gasoline and used in a high compression engine as is common practice with antiknock compounds. This mixture, in direct comparison in passenger cars and buses with one containing 0.70 theory bromine and 0.45 theory chlorine, has left combustion chamber residues weighing as much as 50 per cent less than those resulting from the use of the latter. In heavy duty operation the corrective agent containing 0.50 theory bromine and 1.00 theory chlorine gives longer exhaust valve life which, in the case of buses, I have found to be as much as 100 per cent more than that resulting from the use of 0.70 theory bromine and 0.45 theory chlorine. The exhaust valve life in passenger car engines also is increased but to a smaller extent. Thus this mixture lengthens the period between engine overhauls when the need for service arises because of the accumulation of combustion chamber deposits or the failure of exhaust valves. The mixture costs less than a mixture containing 0.70 theory bromine and 0.45 theory chlorine or only one theory of bromine.

This mixture, containing one theory of chlorine and one-half theory of bromine for the lead, is not a critical mixture and may be varied to a small degree with no significant difference in results or to a larger degree with poorer results either in acid corrosion, lead deposits or both. The range of satisfactory mixtures becomes narrower as the concentration of lead in the fuel or the severity of engine operating conditions is increased.

The mixture range is shown more clearly on the accompanying chart. This chart has an abscissa scale marked in theories of chlorine from 0.0 to 9.00 and an ordinate scale marked in theories of bromine from 0.1 to 0.6. For each volumetric concentration of tetraethyl lead, there is a pair of sloping lines, such as AD and BC, which defines the halide mixtures usable therewith. The quadrilateral ABCD and line EF are shown in heavier lines for easier reference. This quadrilateral gives the boundary lines of halide mixtures for concentrations of 3 c. c. tetraethyl lead per gallon of motor fuel. The sloping lines lying to the right of this quadrilateral, such as NO for 2.50 c. c. tetraethyl lead per gallon, and RS for 2.0 c. c. per gallon, are boundary lines of halide mixtures for lower concentrations of tetraethyl lead.

Boundary lines of halide mixtures for concentrations of tetraethyl lead between 2.0 and 3.0 c. c. lying to the left of quadrilateral ABCD are com-

posed in part of terminal line QA and in part of lines parallel to line AD, such as line PM for 2.50 c. c. tetraethyl lead. The left hand boundary of halide mixtures for a lead concentration of 2.5 c. c. per gallon is the bent line PMA and the complete boundary of halide mixtures for this lead concentration is formed by the lines joining the points ANOPMA. The terminal line QA is the left hand boundary line of halide mixtures for tetraethyl lead concentrations of 2.0 c. c. or less per gallon. Boundary lines for concentrations of tetraethyl lead between those shown on the diagram may be interpolated.

On the chart the quadrilateral ABCD has corners denoting halide mixtures as follows: A, the mixture 0.6 theory bromine, 0.65 theory chlorine; B, the mixture 0.6 theory bromine, 1.10 theories chlorine; C, the mixture 0.10 theory bromine, 2.10 theories chlorine; and D, the mixture 0.10 theory bromine, 1.15 theories chlorine. The letter E denotes the preferred quantity of chlorine, 0.8 theory, to be used with 0.6 theory of bromine. The letter F denotes the preferred quantity of chlorine, 1.80 theories, to be used with 0.10 theory of bromine. The line EF shows the preferred quantity of chlorine for use with any desired bromine content between 0.10 and 0.60 theory, for normal conditions of engine operation. This line passes through the point G denoting the halide mixture 0.5 theory bromine, 1.0 theory chlorine used in the specific example. The limits of the theories of chlorine to be used are found by drawing a horizontal line through the theory of bromine chosen and noting the abscissae of the points of intersection of this line with the boundary lines AD and BC. The abscissa of the intersection of the horizontal line thus drawn with the line EF gives the theory of chlorine preferred for use with the theory of bromine chosen.

The smaller qualrilateral having corners HJKL is used in like manner to show variations permissible from line EF without changing substantially the results achieved. On the chart this smaller quadrilateral has corners denoting halide mixtures as follows: H, the mixture of 0.6 theory bromine, 0.7 theory chlorine; J, the mixture 0.6 theory bromine, 0.95 theory chlorine; K, the mixture of 0.10 theory bromine, 1.95 theories chlorine; L, the mixture 0.10 theory bromine, 1.70 theories chlorine.

Under normal conditions of engine operation, halide mixtures lying to the left of line EF, as indicated by arrow K', tend to promote engine deposits and to decrease acid corrosion. Halide mixtures lying to the right of line EF, as indicated by arrow L', tend to decrease engine deposits and to promote acid corrosion. In both cases the effects become more pronounced the farther the halide mixtures depart from those represented by line EF.

The best mixtures for general use where the concentration of tetraethyl lead may be 3.0 c. c. per gallon or less are chosen from within the quadilateral ABCD in the manner described.

As the concentration of tetraethyl lead is decreased below 3.0 c. c. per gallon, the boundary lines are moved outward. For example, for a concentration of 1.5 c. c. per gallon the right hand boundary line is TU and the left hand boundary line becomes the terminal line QA. The optimum halide mixtures for general use with this and lower concentrations of tetraethyl lead are chosen within the area ATUQA in the same mode as described above relative to line EF.

With a tetraethyl lead concentration of 3.0 c. c. per gallon, under severe conditions of engine operation, my preferred halide mixture is denoted by point G on line EF. With mixtures on line EF between 0.37 and 0.6 theory of bromine, the results are substantially the same. Mixtures on line EF below 0.37 theory of bromine have progressively less value as point F is approached. The halide mixture denoted by point F is approximately two-thirds as good as that denoted by point G on the basis of exhaust valve life. This difference of effectiveness of halide mixtures on line EF decreases with decrease in the concentration of tetraethyl lead. At a tetraethyl lead concentration of 1.0 c. c. per gallon all halide mixtures on this line have substantially the same value.

Ethylene dibromide and ethylene dichloride are usually named when considering antiknock agent mixtures, because they are easily made, are relatively inexpensive and react with lead antiknock compounds during combustion. Unstable compounds, such as carbon tetrachloride and dichlorpentane, are not so satisfactory unless a stabilizing agent, of which lecithin is an example, is employed. Ethylene dibromide and ethylene dichloride have lower boiling points than tetraethyl lead but no advantage has been found in using compounds such as benzotrichloride, benzyl bromide and brom-ethylbenzene which have boiling points nearer the boiling point of tetraethyl lead.

The chlorine, bromine, lead antiknock mixtures described may contain any lead compound which has antiknock properties. Experience in this field has shown that the lead alkyl compounds have the greatest utility. The most satisfactory lead alkyls are tetraethyl lead, lead triethyl methyl and lead dimethyl diethyl.

The halides named are but a few of those known to be stable toward lead antiknock compounds when mixed with them outside the engine but which react with the lead antiknock compounds during combustion.

In engine operations under light load conditions, the engine may not differentiate between different mixtures containing halides and lead compounds. Statements made herein are based on engine operations encountered in ordinary commercial practice, which do differentiate between different mixtures containing halide compounds and lead compounds.

The halides may be produced and mixed ready to add to the lead antiknock compound or to gasoline at a location different from that at which the lead compound is made.

I claim:

1. An antiknock agent having a lead antiknock compound in a concentration not greater than 3 c. c. per gallon of fuel, a bromine compound capable of reacting with the lead compound during combustion in an engine and containing between 0.10 and 0.6 theory of bromine, and a chlorine compound capable of reacting with the lead compound during combustion in an engine and having a chlorine content between points of intersection of a horizontal line drawn through the theory of bromine selected and boundary lines for the maximum content of lead antiknock compound to be used per gallon of motor fuel.

2. An antiknock agent having a lead antiknock compound, a bromine compound capable of reacting with the lead compound during combustion in an engine and containing between 0.10 and 0.6 theory of bromine, and a chlorine compound capable of reacting with the lead compound during combustion in an engine, the chlorine content

lying substantially on a point marking the intersection of a horizontal line drawn through the theory of bromine selected and the line EF.

3. An antiknock agent having a lead alkyl antiknock compound, a bromine compound capable of reacting with the lead alkyl compound during combustion in an engine and containing between 0.10 and 0.6 theory of bromine, and a chlorine compound capable of reacting with the lead alkyl compound during combustion in an engine and having a chlorine content between points of intersection of a horizontal line drawn through the theory of bromine selected and lines AD and BC.

4. An antiknock agent having a lead alkyl antiknock compound, a bromine compound capable of reacting with the lead compound during combustion in an engine and containing between 0.10 and 0.6 theory of bromine, and a chlorine compound capable of reacting with the lead compound during combustion in an engine and having a chlorine content between points of intersection of a horizontal line drawn through the theory of bromine selected and lines HL and JK.

5. An antiknock agent having a lead antiknock compound in a concentration not greater than 3 c. c. per gallon of fuel, a bromine compound capable of reacting with the lead compound during combustion in an engine and containing between 0.37 and 0.6 theory of bromine, and a chlorine compound capable of reacting with the lead compound during combustion in an engine and having a chlorine content between points of intersection of a horizontal line drawn through the theory of bromine selected and boundary lines for the maximum content of lead antiknock compound to be used per gallon of motor fuel.

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