## SYMPOSIUM ON VAPOR PHASE OXIDATION OF GASOLINE

## INTRODUCTION

By WILLIAM R. POWER:1

Several years ago, Army Ordnance caused the whole question of gasoline stability and its methods of measurement to be opened for review. In consequence, a panel of the Coordinating Research Council conducted a several year study which employed laboratory and field storage procedures. During this same period some very pronounced vet differing opinions were voiced as to the significance of the ASTM gum test D 381.2 Some in the industry were convinced that induction systems would remain free from objectionable deposits on all gasolines having low ASTM gum values; others were equally sure that certain gasolines would give excessive deposits despite low ASTM gum values. Engine testing was subsequently initiated by the CRC and Ordnance, and data for the more common types of gasoline showed a reasonably good correlation of engine deposit level with ASTM gum. In another engine run, however, excessive deposits formed in the induction system while using a gasoline with a low ASTM gum content. As a result, Ordnance has directed a strenuous search for a supplementary test to D 3812 which would screen out these admittedly rare gasolines.

During this same period, Technical Committee A on Gasoline of ASTM Committee D-2 on Petroleum Products and Lubricants was investigating reported failures of the Induction Period, Method D 525,3 to properly predict the storage stability of gasoline. To better define the seriousness of this problem, an ASTM symposium was held in February, 1954, at Philadelphia. The official title of the symposium was "Gum and Storage Stability of Motor Gasoline" although it might have been more appropriately called "The Trial of the ASTM Induction Period." The papers presented at this symposium were carefully evaluated by Technical Committee A and their conclusions were as follows:

- 1. Gasoline stability was not a major performance problem.
- 2. There did appear to be a need for a more satisfactory screening test to guard against the occasional very unstable gasoline which could cause an epidemic of performance problems.
- 3. The formation of gum might be by way of several different mechanisms. It appeared futile, therefore, to undertake a program to improve or replace the induction period test by means of an empirical correlation with storage stability on a wide variety of fuels.
- 4. There was a need for a fundamental study of the mechanisms of fuel deterioration as they affect performance. Knowledge obtained from the fundamental study would allow the establishment

<sup>&</sup>lt;sup>1</sup> Cities Service Oil Co., Technical Service Lab., East Chicago, Ind.; Chairman of the Symposium.

<sup>&</sup>lt;sup>2</sup> Tentative Method of Test for Existent Gum in Fuels by Jet Evaporation (D 381-54 T), 1955 Book of ASTM Standards, Part 5, p. 178.

<sup>&</sup>lt;sup>3</sup> Method of Test for Oxidation Stability of Gasoline (Induction Period Method) (D 525 – 55), 1955 Book of ASTM Standards, Part 5, p. 254.

of one or more stability tests suitable for specification purposes.

In 1955 the U.S. Bureau of Mines and Stanford Research Inst. began long range programs of basic research into the mechanisms of gum formation. Since the Office of the Chief of Ordnance is sponsoring these studies they are being confined to military gasolines. Technical Committee A is satisfied, however, that the information developed will be applicable to civilian gasoline as well. In the meantime, questions continue to arise: Are the induction system deposits due to a vapor phase oxidation process? Do the usual types of oxidation inhibitors add to or subtract from induction system deposits? Is one type of inhibitor better than another? Is the volatility of the inhibitor a factor? Opinions on these questions have been expressed, sometimes very vigorously, in meetings of Technical Committee A. In an effort to give this subject a good airing and to encourage the substitution of some facts for opinions, this symposium was organized. The papers together with the prepared discussions are expected to serve this purpose.

## By John M. Campbell:4

The gasoline-powered internal combustion engine is today by far the largest source of power in the world. Our 63,000,000 automobiles, trucks and buses represent over 7,000,000,000 hp which is some 50 hp per person.

The successful operation of the gasoline engine in these 63 million individual power plants is predicated on the rapid evaporation of gasoline with air in the induction system aided by heat applied at the walls of the manifold. In order to avoid obstruction of the induction sys-

tem and interference with the heat transfer required for satisfactory evaporating of the fuel, it is essential that this evaporation process be carried out without leaving an appreciable residue on the inside walls of the induction system.

It is of no little historical interest that in 1947 here in Los Angeles one of the car manufacturers first called attention to an epidemic of a black lacquer-like deposit that was accumulating on the throttle plates and throttle bodies and other parts of the induction system. As soon as this problem was identified and called to the attention of the gasoline manufacturers, an intensive investigation was undertaken to remove the components, present in very minute amounts, which had caused this trouble.

From time to time other problems have arisen, such as slight deposit formation at the juncture of the throttle plate and the throttle body when the throttle is in the idle position. Another problem that strikes occasionally is the intake valve deposit. These problems can sometimes be modified by changes in engine design, and it is the car manufacturers' responsibility to keep the susceptibility of the induction system to deposits at a minimum.

Usually, however, the responsibility falls upon the petroleum refiner to take corrective measures when trouble occurs. It is indicative of the high order of technical skill that exists in the petroleum refining industry that we are today producing almost 50,000,000,000 gal of gasoline annually, all of which has to pass through this critical zone where evaporation takes place without leaving a significant amount of residue. Much of the knowledge which has made this possible has been accumulated by the men and the organizations represented on this program today. It is a high tribute to them that the motoring public today is seldom cognizant of this problem in today's automobiles, but con-

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tinued vigilance is called for in order to prevent the recurrence of trouble.

## By R. C. Alden:5

To judge by car and motor fuel advertising, one might easily conclude that octane number is the only thing that makes the wheels go round. Whereas octane number comes in for tons of discussion, the other basic properties of motor fuel come in for ounces of discussion.

That this is so is some sort of a lefthanded tribute to the oil industry. That such important properties as heat of combustion, volatility, and purity can be taken so much for granted is far from being a gift of nature. It is a technical and engineering achievement of the oil industry of the highest order. In my opinion it ranks as an achievement, with the greatly publicized forward look of our partner industry in service to the public.

One small example will illustrate my

point. Shale oil is much in everyone's mind, and one of the major problems in the utilization of shale oil will be the purity of the products obtained.

The present discussion relates to one of the important properties of motor fuel concerning which for many years there has been a general feeling of uneasiness in the oil industry that we may be taking too much for granted. While it is a fact there are no urgent problems crying for solution, it is also a fact that there are some problems even in the civilian field. One thing which convinces us all of the need for more study is the inadequacy of existing testing methods under the extreme conditions imposed by military operations.

It is the purpose of this symposium to review several valuable research projects in the field of the oxidation behavior of gasolines in automotive fuel induction systems. It is a review session. No formal conclusions are to be reached but I am sure we will all be enlightened on this important subject.

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