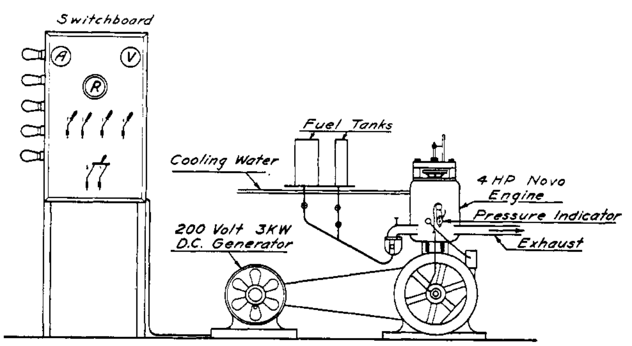
Metallic Colloids and Knock Suppression[1]

H. L. Olin and W. J. Jebens

University of Iowa, Iowa City, Ia.

In an earlier paper[2] were reported the results of work undertaken to test the validity of certain theories which postulated a retarding effect on detonation in the gas-engine cylinder through the agency of metallic colloids present in the burning mixture. Experiments showed that, while prompt response followed the addition of tetraethyl lead and nickel carbonyl to the motor fuel, no appreciable effects were noted when suspensions of specially prepared lead and nickel sols were similarly used.

Shortly before the publication of this paper,[2] Sims and Mardles,[3] working independently on the same problem and evidently employing the same technic, announced results and conclusions diametrically opposite to those found by Olin and co-workers—viz., that lead and nickel sols have the same antiknock activity as solutions of tetraethyl lead and nickel carbonyl containing equivalent amounts of the respective metals. It should be noted that Sims and Mardles prepared the sols by heating nickel carbonyl in boiling hexane for 40 minutes for the nickel colloid and tetraethyl lead at about 250° C. for 30 minutes for the lead.



Apparatus for Testing Motor Fuels

Because of the important bearing of this question on the solution of the general problems of the mechanism of detonation and of its suppression, the writers undertook a systematic review of their earlier work with a view to the detection of possible errors and to the harmonizing of their findings with those of the workers mentioned above.

In any study involving the preparation and use of activated colloids the obviously weak point is the danger of poisoning the active mass, either by hydrolysis in the presence of water, by oxidation, or by interaction with sulfides or with other agents of similar chemical properties. In the second series special pains were taken to avoid trouble of this kind, first by the use of calcium chloride to desiccate the gasoline thoroughly, and second by maintaining an atmosphere of dried and purified nitrogen over all solutions and sols from the time they were prepared to the time they were used. Tests of the gasoline showed the sulfur content to be practically nil.

The colloids were prepared as before by thermal decomposition of the metallo-organic compounds at various given temperatures and stabilized by the addition of small quantities of raw rubber. Working solutions of proper concentration were then made by diluting with gasoline. The tests were made in a newly designed laboratory equipped with a single-cylinder, 4-horsepower vertical engine with variable compression head which allowed a range of compression ratios from 3.75 to 9.0. This was connected by belt with a 3-kilowatt d. c. generator whose output was delivered to a switchboard and dissipated through a variable resistance made up of four 500-watt coils and twenty 40-watt lamps. A Crosby indicator supplied a graphic record of the explosion, but aural evidence of presence or absence of knock was in general the more dependable. A diagram of the apparatus is shown.

Experimental

In making a test run the engine was first operated with the original gasoline. The movable piston head was set for low compression, then gradually lowered until a light knock occurred, and finally to a point where the detonation became pronounced at intervals. This last reading was taken as the highest useful compression ratio (H. U. C. R.). The special fuel was then admitted and a new setting given to the piston head. Table I gives a summary of results obtained with nickel sols.

Table I—Antiknock Properties of Nickel Colloids Prepared at Different Temperatures

Fuel	H. U. C. R.	Increase in H. U. C. R.	Initial Concn. of $Ni(CO)_4$
		Per cent	*Cc. per liter*
Straight gasoline	4.37	..	0
Gasoline with nickel carbonyl	4.70	7.54	5.501
Gasoline with nickel carbonyl heated at 69° C.[a]	4.63	5.94	5.501
Gasoline with nickel carbonyl heated at 77° C.	4.56	4.35	5.501
Gasoline with nickel carbonyl heated at 85° C.	4.41	0.92	5.501

[a] The temperature of boiling hexane, used by Sims and Mardles.

It is readily seen that there is a successive decrease in useful compression ratio as the temperature of decomposition is raised. At 69° C., the boiling point of hexane, the product is nearly as effective as the fuel with undecomposed nickel carbonyl, but at 85° C. the improvement becomes negligible. It appears, therefore, that Sims and Mardles erred in neglecting to effect complete decomposition of their nickel carbonyl and that had they raised the temperature to 85 ° C. or higher their results would have been different.

The validity of this conclusion is further evidenced by data obtained with lead colloids as shown in Table II.

Table II—Antiknock Properties of Lead Colloids Prepared at Different Temperatures

Fuel	H. U. C. R.	Increase in H. U. C. R.	Initial Concn. of Ethyl Lead
		Per cent	*Cc. per liter*
Straight gasoline	4.43	..	0.00
Gasoline with ethyl lead	5.02	13.3	1.00
Gasoline with ethyl lead heated at 250° C.[a]	4.76	7.5	1.00
Gasoline with ethyl lead heated at 275° C.	4.55	2.7	1.00
Gasoline with ethyl lead heated at 300° C.	4.44	0.0	1.00

[a] Temperature employed by Sims and Mardles.

So far as absolute proof with respect to theories postulating a catalytic effect on the part of metallic colloids is concerned, it must be admitted that negative findings leave much to be desired. It is quite possible that in the nascent state at the high temperatures of the explosion chamber their effects are radically different from those exhibited under the conditions described.

[1] Received August 13, 1928.

[2] Ind. Eng. Chem., **18**, 1316 (1926).

[3] *Engineering*, **121**, 774 (1926); *Trans. Faraday Soc.*, 1926 (advance proof).