Evaluation of Two New Ortho-Alkylated Phenols as Lubricant Additives

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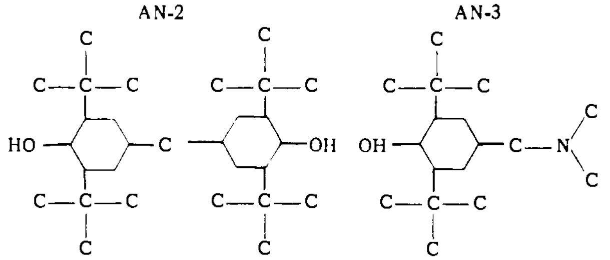
The discovery of the "ortho-alkylation" reaction (*8, 9, 11, 12*) has made available commercially for the first time a series of 2,6-derivatives of phenol and aniline. These products are excellent starting materials for synthesis because of the reactivity of their para positions. 2,6-Di-*tert*-butylphenol is of particular interest because its derivatives contain the hindered phenol structure (*16*) which is characteristic of the more effective phenolic antioxidants.

This paper describes the evaluation of two derivatives of 2,6-di-*tert*-butylphenol as additives in a number of lubricant applications. The compounds evaluated were 4,4′-methylenebis(2,6-di-*tert*-butylphenol), which will be referred to as AN-2, and 2,6-di-*tert*-butyl-α-dimethylamino-*p*-cresol, which will be called AN-3.

AN-2 AN-3



Tests have shown that AN-2 is an excellent antioxidant for petroleum and diester oils used in relatively high-temperature applications, such as those encountered by crankcase oils and transmission fluids. In addition to its antioxidant activity, AN-2 has been observed to minimize ring wear in gasoline engines under several conditions. Moreover, AN-2 is compatible with the most widely used motor-oil additives and frequently exhibits a marked beneficial effect in the presence of these materials.

The second compound, AN-3, is an effective antioxidant in intermediate-temperature applications, such as are encountered by grease and steam turbine oil, where its good color stability is a desirable property. The polarity and alkalinity of the amine group in this compound may impart surface-active properties, such as dispersancy, and protection against rust and wear.

PRIOR STUDIES

Prior studies on phenolic antioxidants have described their preparation (*14*), their relative inhibiting effects in petroleum products, and the mechanisms (*5*) by which they function, based on their oxidation products.

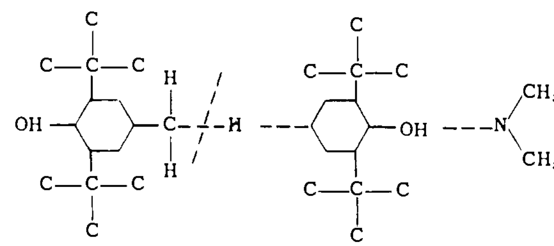
Wasson and Smith (*16*) used a modified Staeger turbine-oil test to study the relationship between phenol substituents and antioxidant activity. Their work showed that a highly effective structure was one in which the 2- and 6-positions were occupied by *tert*-butyl groups and the 4-position by a methyl group. The use of smaller or less branched groups in the 2- or 6-positions resulted in much poorer antioxidants. Replacement of the methyl group in the 4-position by ethyl or *n*-butyl groups produced improved antioxidants, while the presence of *sec*-butyl or *tert*-butyl groups in this position decreased antioxidant effectiveness.

These observations suggest that the 4-position is the most logical one on which to test substituents in experiments designed to modify the 2,6-di-*tert*-butylphenol structure in order to obtain improved antioxidants. For lubricant applications involving elevated temperatures and a considerable degree of aeration, it would be desirable to devise structures having minimum vapor pressures. This suggests the use of structures having higher molecular weights, provided this can be accomplished without sacrificing desirable antioxidant properties.

STRUCTURES OF AN-2 AND AN-3

One of the commercially available antioxidants is 2,6-di-*tert*-butyl-4-methylphenol, a compound which has been widely studied and the antioxidant properties of which are well established (*16*). In comparison with this compound, AN-2 might be visualized as a compound in which a 2,6-di-*tert*-butylphenol group has replaced one of the hydrogens on the 4-methyl group. Similarly, the AN-3 structure represents the substitution of a dimethylamino group for one of the 4-methyl hydrogens.

Structures of AN-2 and AN-3



2,6-di-*tert*-butyl-4-methylphenol AN-2 AN-3

ANTIOXIDANT EVALUATION STUDIES

In the evaluation studies, 2,6-di-*tert*-butyl-4-methylphenol was included in order to provide a comparison with a commercially available compound. A technical grade material was used.

Technical grade AN-2 and AN-3 having a minimum purity of 98% were used. These materials are now available commercially.

Steam-Turbine-Oil Tests. The ASTM method D 943-54 (*1*) entitled "Oxidation Characteristics of Inhibited Steam-Turbine Oils" was employed for the evaluation of steam-turbine oils. This commonly used bench test employs copper and iron wire catalysts, 60 ml. of water and 300 ml. of oil, a 95°C. temperature, and an oxygen feed of 3 liters per hour. Periodic measurements of the acid number of the oil are indicative of oxidation, with acid numbers up to a value of two being permissible.

The results shown in Figure 1 were obtained using a solvent-refined Mid-Continent oil of 95 VI and 200 SUS at 100°F. At each additive concentration, AN-3 was superior to the other two additives. Moreover, use of AN-3 appeared to prevent a sharp break in the acid-number curve. This was particularly evident in the test at 0.5% concentration, during which the acid number remained in the 0.1–2.0 range for several hundred hours. The basicity of AN-3 may be a factor in maintaining acid numbers at this level.

Similar results were obtained at a lower additive concentration of 0.35% when a more highly refined oil (solvent extracted and sulfuric acid–treated) was used. With this oil (98 VI and 168 SUS at 100°F.), AN-3 was again the best of the three additives, as shown in Figure 2.

During the turbine-oil tests, it was observed that a few

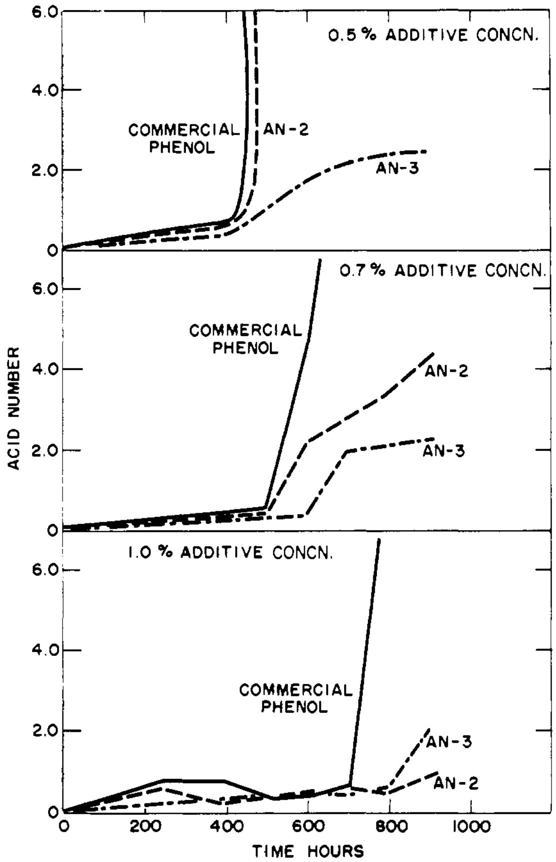


Figure 1. ASTM steam turbine oil oxidation test on 95 VI solvent-refined oil

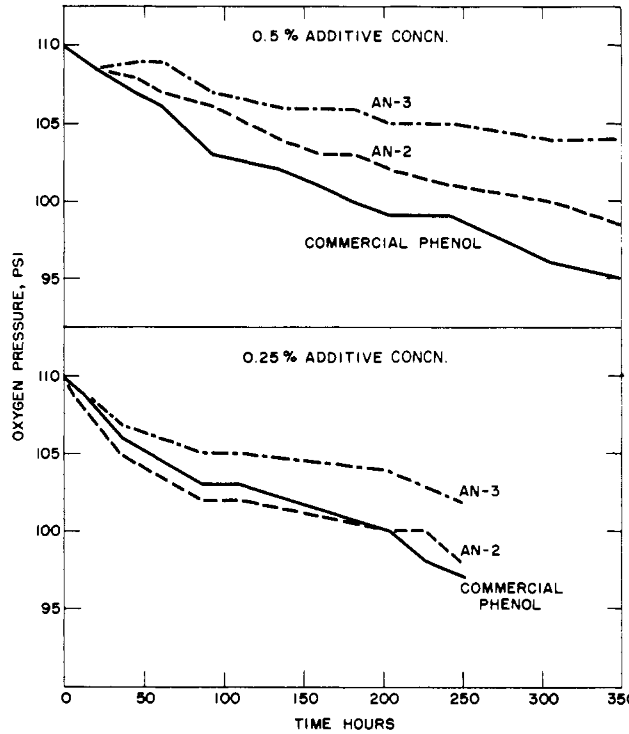


Figure 3. ASTM grease oxidation stability tests at 210° F. on lithium-base grease

crystals collected on the condenser in the top of the oxidation cells. Following the example of Metro (*13*), these crystals were isolated, purified, and identified. For both AN-2 and AN-3, the material was found to be 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde.

This same aldehyde was postulated as the major degradation product of 2,6-di-*tert*-butyl-4-methylphenol by Wasson and Smith (*16*). However, under the turbine-oil test conditions described above, Metro found 2,6-di-*tert*-butyl-1,4-benzoquinone to be the major degradation product.

Grease Tests. The ASTM method D 942-50 (*2*) entitled "Oxidation Stability of Lubricating Greases by the Oxygen Bomb Method," was used for the evaluation of greases. In this procedure, weighed samples of grease are placed in glass dishes and subjected to 110 p.s.i. of oxygen in a stainless steel bomb. Minimum loss of oxygen pressure is the criterion of effective inhibition. Tests were conducted at 210°F. and at the 250°F. level used recently by Calhoun (*3*). The greases employed were a lithium-base

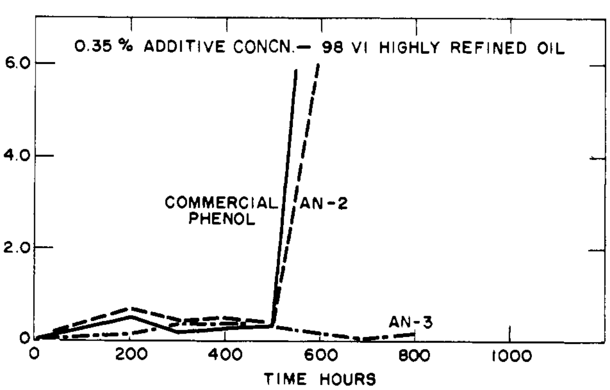


Figure 2. ASTM steam turbine oil oxidation test on solvent-refined and acid-treated oil

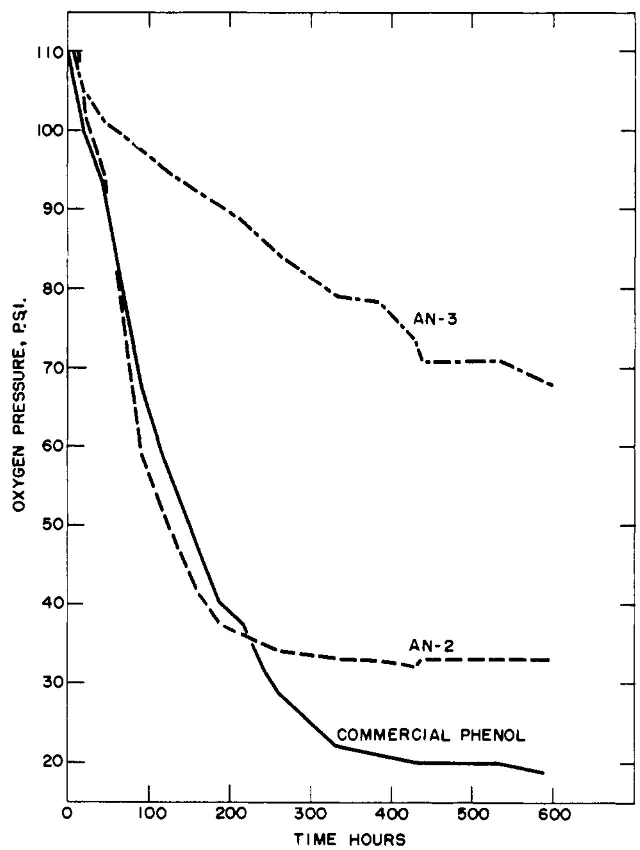


Figure 4. ASTM grease oxidation stability tests at 250° F. on lithium-base grease

grease and a calcium-base grease; neither grease contained an antioxidant.

The three phenolic additives were evaluated at 0.25 and 0.50% concentration in the lithium-base grease at 210°F., and at 0.5% concentration in both greases at 250°F. At

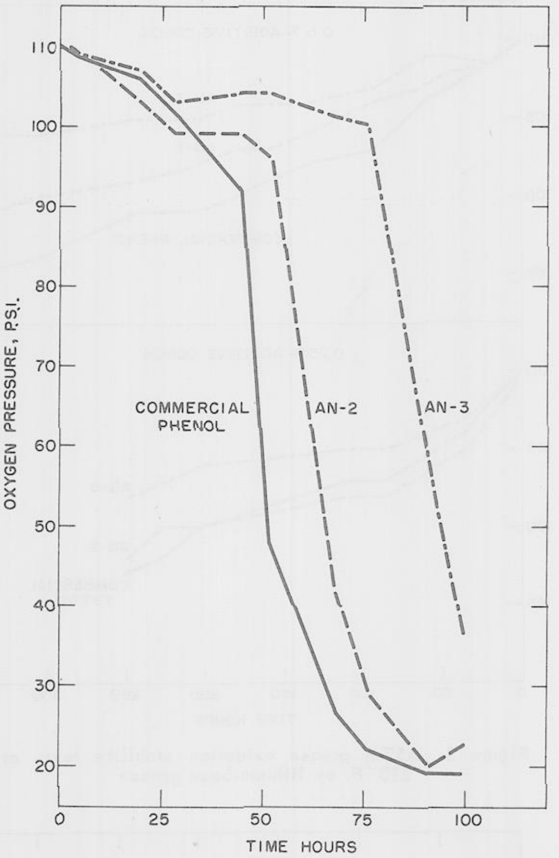


Figure 5. ASTM grease oxidation stability tests at 250° F. on calcium-base grease with 0.5% additive concentration

210° F., AN-3 showed a definite superiority over the other two additives at both concentrations, as shown in Figure 3. AN-2 was slightly better than 2,6-di-*tert*-butyl-4-methylphenol in both tests.

The 250° F. test, which represented a much more severe test condition, caused a wide spread in the oxygen-absorption results and in the appearance of the grease samples. On the basis of pressure drop, AN-3 was by far the most effective antioxidant in both types of grease, as shown in Figures 4 and 5. The superiority of AN-3 also was evident in the appearance of the grease samples at the conclusion of the test. For example, the lithium-base grease containing AN-3 was light-colored and similar to the original grease in texture after 600 hours of 250° F., while the other samples had darkened and undergone considerable change in texture. These results illustrate the good color-stability properties of AN-3 under oxidizing conditions.

In regard to the problem of grease discoloration when exposed to sunlight, AN-3 is color stable on exposure to ultraviolet radiation. Samples of lithium-base grease containing 0.5% of AN-3 were exposed to a General Electric 275-watt sunlamp for 30 hours at a distance of 12 inches. At the end of this time, samples containing AN-3 showed no change in color, while samples containing antioxidants

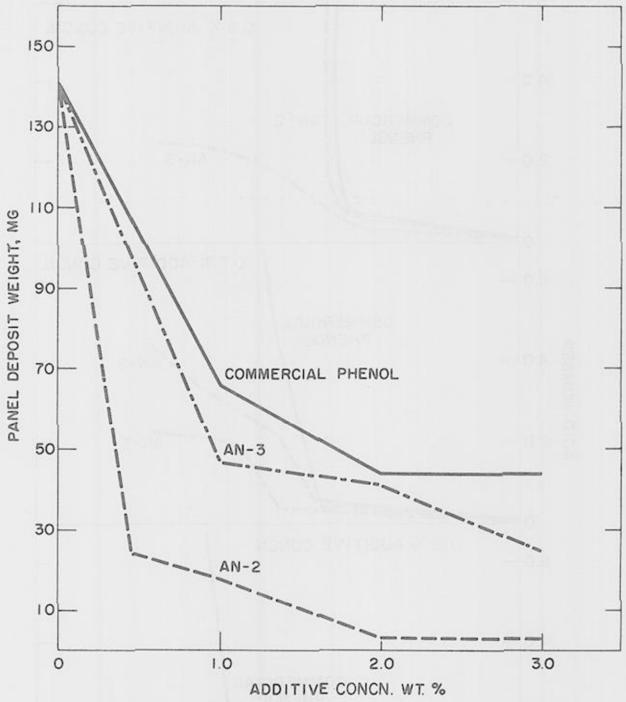


Figure 7. Panel coking test comparison of phenolic antioxidants on dioctyl sebacate, base oil

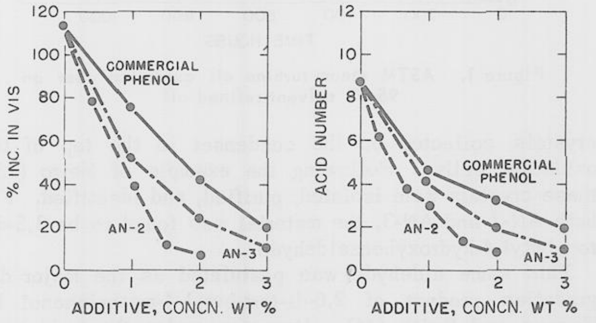


Figure 8. Motor oil oxidation stability test comparison of phenolic antioxidants at 300° F.

of the aromatic amine type underwent considerable darkening. Such a comparison is shown in Figure 6. The samples shown contained, respectively, no additive, 0.5% AN-3, and 0.5% phenyl-α-naphthylamine.

Panel-Coking Tests. Panel-coking tests were conducted in the Panel Coking apparatus (*15*) used to qualify synthetic lubricants for jet engines. The method involves the splashing of a lubricant onto a heated aluminum panel which is maintained at a controlled temperature. The weight of deposit formed on the panel is a measure of the oxidation stability of the lubricant. For these tests, the panel temperature was 600° F., the time was 10 hours, and the splasher was operated for 5 seconds each minute.

Each of the phenolic additives was evaluated in com-

Figure 6. Effect of ultraviolet radiation on additives in lithium-base grease

Left. No additive.
Center. 0.5% AN-3.
Right. 0.5% aromatic amine

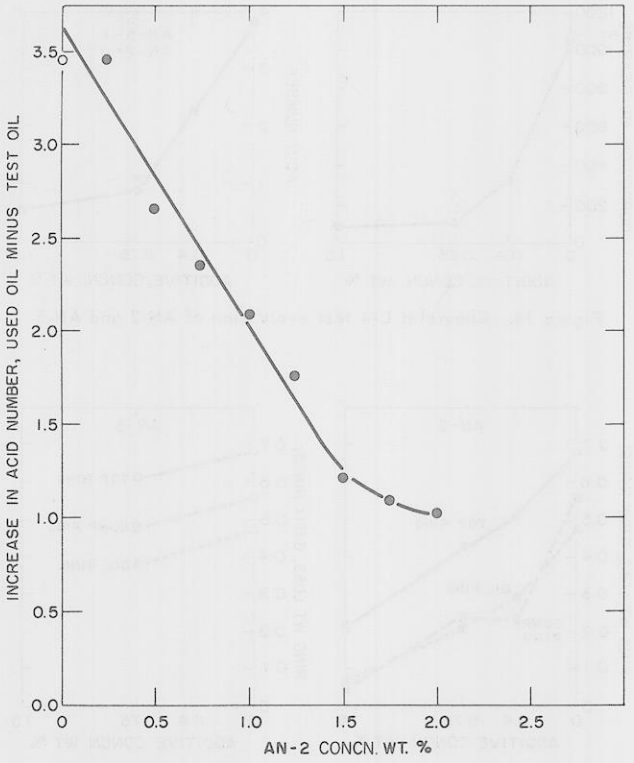


Figure 9. Effect of AN-2 on oxidation stability of automatic transmission fluid

Test oil, commercial automatic transmission fluid

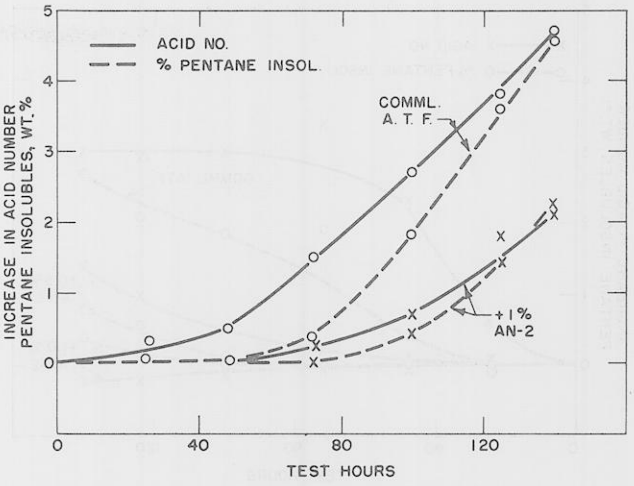


Figure 10. Used oil results from hydramatic transmission tests

mercial dioctyl sebacate at concentrations of 1, 2, and 3%. As shown in Figure 7, use of AN-2 effectively minimized coke formation, giving extremely low results at the higher additive concentrations. AN-3 was moderately effective, while the 2,6-di-*tert*-butyl-4-methylphenol had little value.

Bench-Scale Tests of Motor Oils. Bench-scale tests of motor oils were performed using a modification of a Standard Oil (Ohio) method (*10*) which involves aeration of the oil and iron catalysis. The test conditions were: sample, 100 grams; temperature, 300°F.; time, 20 hours; air rate, 70 liters/hour; and catalyst, 0.05 wt% Fe_2O_3 as soluble soap. The criteria of oxidation were the acid number and the per cent increase in viscosity of the used oil.

A solvent-refined base oil of 95 VI and 200 SUS at 100°F. was used, and each of the phenolic additives was tested in the concentration range of 0 to 3%. In these tests, AN-2 was very effective, as shown in Figure 8, giving relatively complete inhibition at concentrations above 1%. Both AN-3 and 2,6-di-*tert*-butyl-4-methylphenol were moderately effective at concentrations of 2 and 3%, with AN-3 being superior.

An indication of the antioxidant properties of AN-2

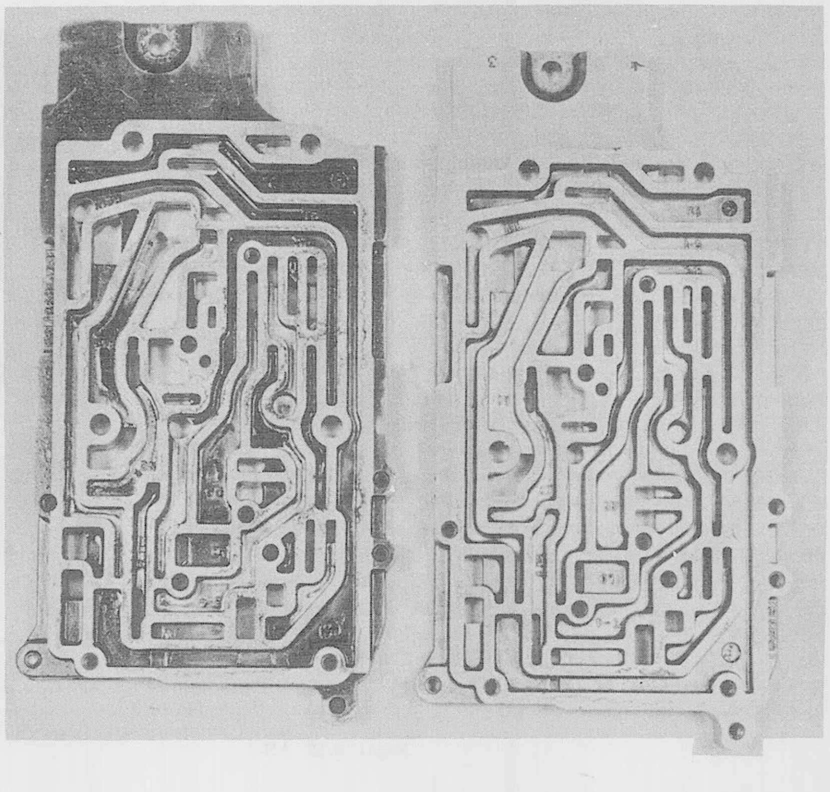


Figure 11. Channel bodies from hydramatic transmission tests on fluid 1

Left. Commercial automatic transmission fluid 1
Right. 1% AN-2

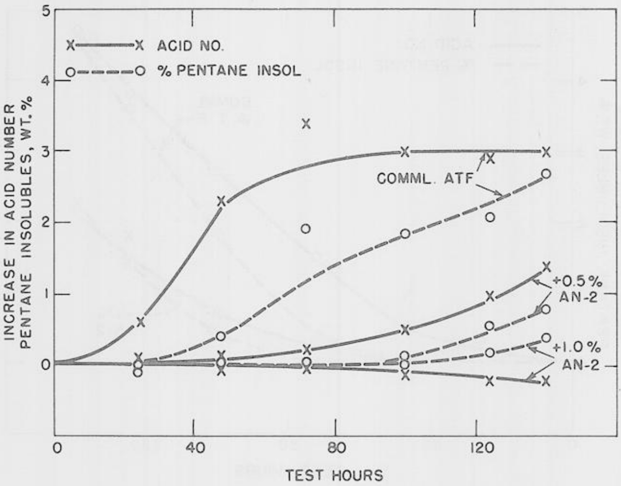


Figure 12. Used oil results from hydramatic transmission tests on fluid 2

when used in combination with other additives is provided by an experiment which employed a commercial Type A automatic transmission fluid as the test oil. The oil, which had a VI (viscosity index) of 136 and a viscosity of 193 SUS (Saybolt Universal seconds) at 100°F., contained high concentrations of several motor-oil additives, as indicated by the following analysis: 0.41% barium, 0.10% zinc, 0.10% phosphorus, and neutralization numbers of 2.04 (acid) and 2.79 (base).

A series of AN-2 concentrations was evaluated in this transmission fluid by using the procedure just described. As shown in Figure 9, there was a linear relationship between concentration and inhibiting effect, as indicated by the change in acid number of the used oils. A corresponding decrease in sludge and varnish formation accompanied the change in acidity. AN-2 concentrations of

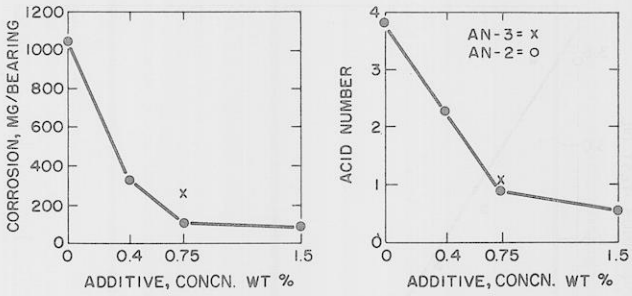


Figure 14. Chevrolet L-4 test evaluation of AN-2 and AN-3

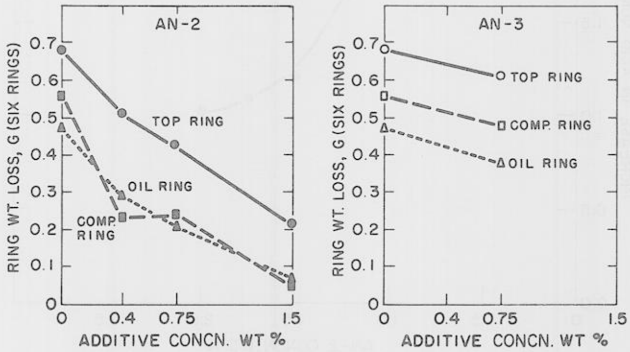


Figure 15. Effect of AN-2 and AN-3 on ring wear in Chevrolet L-4 test

1% or higher showed a large antioxidant effect. These results illustrate the compatibility of AN-2 with an oil containing a variety of commercial additives, and they show that AN-2 is an effective antioxidant in the presence of these additives.

Hydramatic Transmission Tests. To extend these ob-

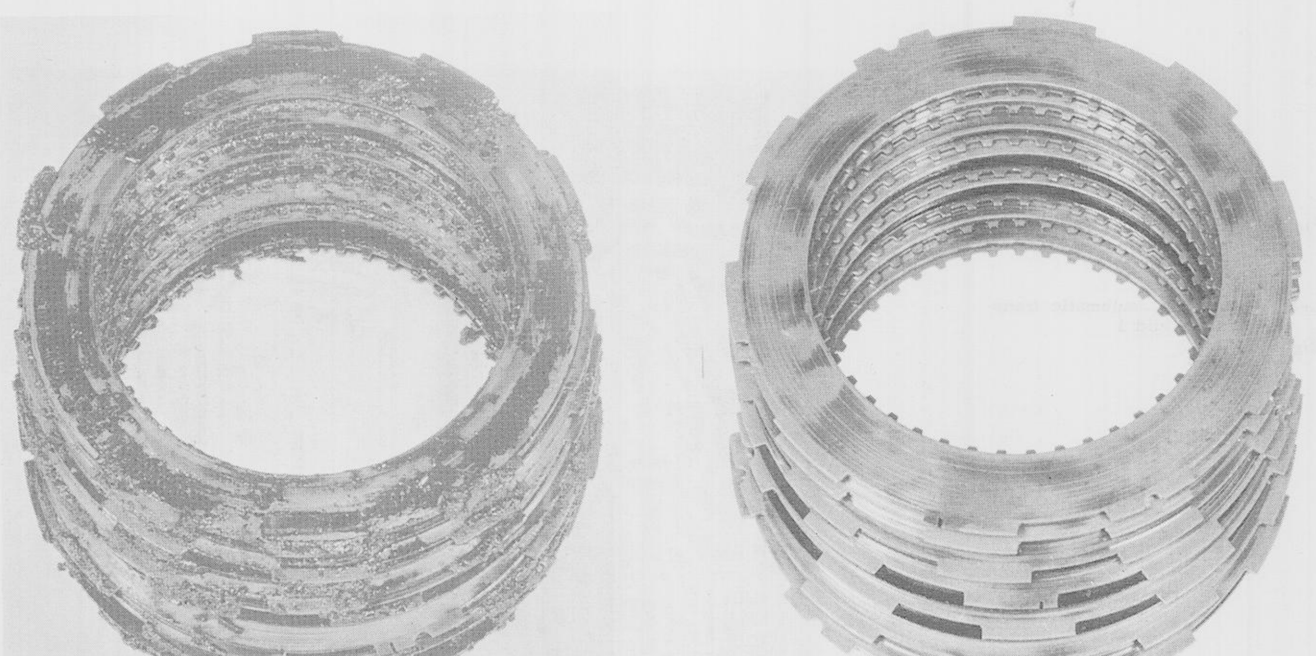


Figure 13. Rear clutch plates from hydramatic transmission test on fluid 2
Left. Commercial automatic transmission fluid 2
Right. 0.5% AN-2

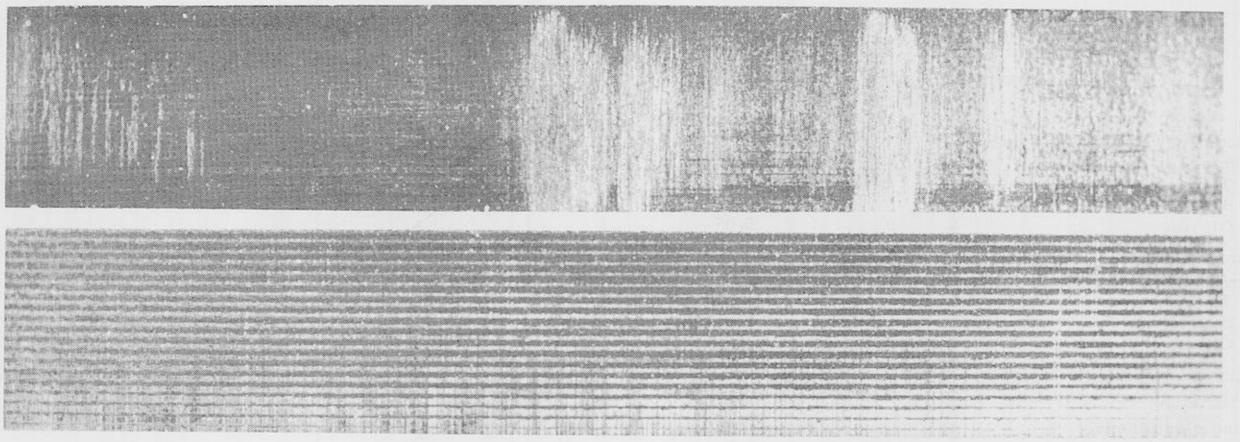


Figure 16. Top rings from Chevrolet L-4 tests

Upper. Base oil
Lower. Base oil + 0.75% AN-2

servations, tests were conducted in a 1957 Oldsmobile Jetaway Hydramatic transmission. The test time was 140 hours, and an oil temperature of 275°F. was maintained. The input speed was 1800 r.p.m., and an 8-second shift cycle from third gear to fourth to third was used. The fluids tested were the commercial fluid described above (fluid #1) and this same fluid with 1% of AN-2 added.

In these tests, AN-2 showed a strong antioxidant effect. As indicated by the used-oil properties shown in Figure 10, the AN-2 extended the induction period by 50 hours, and at the conclusion of the test gave an acid-number increase and pentane-insolubles content which were less than half of those obtained with the commercial fluid.

There was also a marked difference in the visual appearance of the transmissions from these tests. The parts from the test on commercial fluid were heavily sludged and varnished, while those from the test using the fluid containing AN-2 were clean. Typical of the parts from these tests are the channel bodies shown in Figure 11.

A similar study was made using another Type A commercial transmission fluid (fluid 2). This fluid contained a widely used additive package formulation and was different in chemical composition from fluid 1 as indicated by its analysis: 0.75% ash, 0.39% barium, 0 zinc content, 0.023% phosphorus, and 0.45 acid number.

Transmission tests using the above conditions were conducted on the commercial fluid and the fluid containing 0.5 and 1.0% of added AN-2. The base fluid underwent considerable oxidation and, as illustrated in Figure 12, showed a large change in acid number after only 40 test hours. Both AN-2 concentrations gave excellent inhibition with the higher concentration showing virtually no change in used oil properties. Both AN-2 concentrations also gave completely clean transmissions, in contrast to the severe sludging which was observed for the commercial fluid. The rear clutch plates shown in Figure 13 are representative of the parts from these tests, with and without AN-2.

Chevrolet L-4 Tests. The Chevrolet L-4 test (*6*) is a widely used procedure for evaluating the oxidation stability and bearing-corrosion properties of motor oils. A bulk-oil temperature of 280°F. is maintained during the 36-hour test, and two copper-lead bearings are weighed before and after the test in order to measure bearing corrosion.

To evaluate the antioxidant properties of AN-2 a series of concentrations in the range of 0.40 to 1.50% were tested; AN-3 also was tested at 0.75%. The base oil in these tests was a nonadditive SAE 20 blend of solvent-refined neutral and bright stock having a VI of 109 and a viscosity of 372 SUS at 100°F.

At concentrations of 0.75 and 1.5%, AN-2 prevented oil oxidation and bearing corrosion as shown in Figure 14. At the lower concentration of 0.4%, some oxidation occurred, and corrosion was higher than is generally considered acceptable. It is probable that a concentration in the range of 0.40 to 0.75% would give a satisfactory result. The test employing AN-3 at 0.75% concentration showed adequate inhibition, but resulted in higher bearing corrosion than did the use of AN-2 at this concentration.

Both the base oil and the inhibited oils produced piston-skirt varnish ratings of 9, engine varnish ratings of 47, and total engine sludge and varnish ratings of 93 out of a possible 100. Therefore, the additives did not contribute to any form of engine dirtiness.

ENGINE WEAR STUDIES

Chevrolet L-4 Tests. When the previously described L-4 tests were conducted, the individual piston rings were weighed before and after the tests in order to determine ring wear. These weight measurements revealed that AN-2 substantially reduced ring wear, in a linear relationship with additive concentration, and that AN-3 had no effect on this property, as shown in Figure 15. The rings from the base-oil and AN-3 tests were severely scuffed, while the rings from the tests using the higher AN-2 concentrations showed almost no wear, as evidenced by the original tool marks that can be seen in Figure 16.

The antiwear effect of AN-2 was quite unexpected, because its chemical structure does not conform with previous concepts of wear inhibitors. Since AN-2 was so effective in reducing wear under the L-4 test conditions, the author decided to investigate its antiwear properties further.

Chevrolet "Full Throttle" Tests. In order to increase the severity of the L-4 conditions, tests were performed in the Chevrolet engine using the L-4 operating conditions of speed, and sump and jacket temperatures, but substituting full-throttle operation for the L-4 part-throttle condition. This change doubled the fuel consumption of the engine and increased the brake horsepower from 30 to 70, thereby raising the temperatures in the ring zone. The base oil in these tests was the same as used in the L-4 tests; it was compared with a blend containing 1.5% of AN-2. The results are shown in Table I.

When the base oil was used, the rings were severely scuffed, and the wear rate was several times greater than in the L-4 test. AN-2 again demonstrated very effective wear inhibition as measured by ring-weight loss and ring-gap increase. Satisfactory inhibition of oxidation and

Table I. Effect of AN-2 in "Full Throttle" Chevrolet Test

	Base Oil	Oil + 1.5% AN-2
Piston-ring weight loss in grams—Average of 6 rings		
Top ring	0.48	0.15
Second ring	0.26	0.07
Oil ring	0.21	0.05
Piston-ring gap increase in inches—Average of 6 rings		
Top ring	0.017	0.008
Second ring	0.012	0.004
Oil ring	0.038	0.013
Copper-lead bearing corrosion, Average grams per bearing	0.584	0.199
Engine cleanliness		
Piston skirt varnish	8.4	8.9
Total varnish rating	45.2	46.9
Total engine rating	91.2	93.3
36-Hour used oil properties		
Acid number, mg. KOH/gram	3.3	1.0
Increase in viscosity at 100°F., %	29	13

bearing-corrosion and a measurable improvement in piston-skirt varnish rating were also observed for the oil containing AN-2.

Chevrolet FL-2 Tests. The Chevrolet FL-2 (7) procedure is a low jacket-temperature, high-load test which has been used to evaluate fuel cleanliness. In this 40-hour test, engine speed is 2500 r.p.m., brake horsepower output is 45, and the water-jacket inlet temperature is 90°F. Corrosive-type ring and bore wear is usually associated with such a low jacket temperature. Tests were conducted using the same fuel and base oil as in the Chevrolet L-4 test. Two concentrations of AN-2 were employed.

As shown in Figure 17, both additive concentrations of AN-2 showed a large reduction in ring wear when compared with the base oil. However, a lower wear rate was observed at the lower AN-2 concentration. The ring weight losses were considerably higher in the number one cylinder, and the wear here appeared to be due to corrosion. In the other five cylinders, the rings had undergone scuffing, and the antiwear effect of the AN-2 was evident. All of the engines had high piston-skirt and total-engine cleanliness ratings of 9.1 and 93–95, respectively, with the AN-2 causing a slight improvement in the sludge ratings.

"Hot-Ring" Engine Tests. In order to evaluate the antiwear properties of AN-2 under other conditions of engine design and operation and with the use of a different wear-measurement technique, a series of tests was undertaken in a single-cylinder engine fitted with a radioactive top piston ring. The engine was an overhead-valve prototype of the 1951 Oldsmobile engine. The radioactivity detection system was of the flow-monitored type.

The tests were conducted on an operating schedule conducive to ring scuffing:

2500 r.p.m.
Air flow (supercharger source), 95 lb./hour
0.080 F/A ratio (constant injection system)
Jacket water temperature, 180°F.
Air intake temperature, 100°F.
Oil sump temperature, 200°F.
Ignition cycle, 2.5 minutes at 30°BTC (max. power)
10 seconds at 100°BTC (60% power)
Test time, 20 hours
Tests per evaluation, three, preceded and followed by baseline tests

The fuel was technical-grade isooctane containing 3 ml. of tetraethyllead per gallon as 62 mix and 0.05 wt. % of sulfur as disulfide oil.

Because of the development of very high engine temperatures and the need to disperse wear debris for circulation through the detection system, it was necessary to use a detergent and an antioxidant in these tests. These requirements provided an opportunity to evaluate AN-2 in combination with detergents and in comparison with another antioxidant.

The oil in these tests was a blend of a solvent-refined neutral oil (95 VI and 200 SUS at 100°F.) with 6% of a commercial methacrylate-type VI improver. This formulation, which is typical of blends used in multiple-viscosity-grade oils, had a VI of 140 and a viscosity of 300 SUS at 100°F.

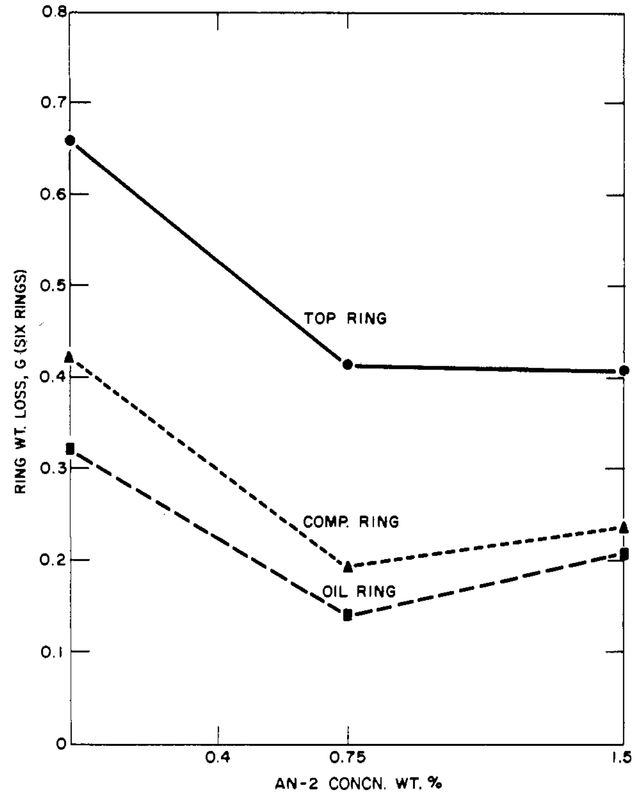


Figure 17. Effect of AN-2 on ring wear in Chevrolet FL-2 test

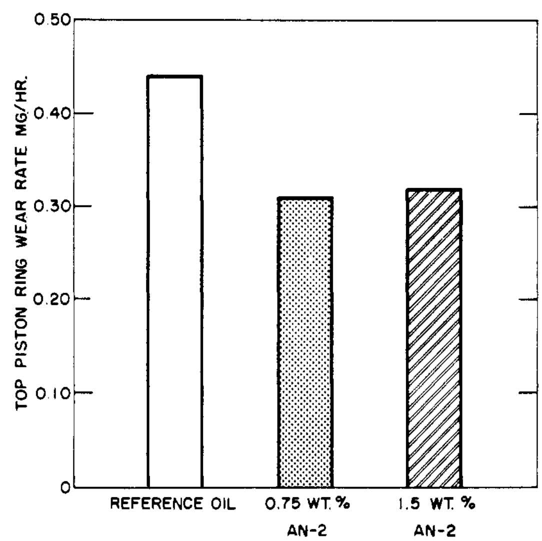


Figure 18. Effect of AN-2 and phenate detergent-antioxidant in radioactive ring engine test

Each oil contained 4% of barium phenate

In the first series of tests, the base oil contained 4% of a commercial barium phenol sulfide detergent-antioxidant. A comparison was made with two concentrations of AN-2 in the base oil-phenate blend. As shown in Figure 18, AN-2 concentrations of 0.75 and 1.50% caused an equal and significant reduction in the rate of ring wear.

In the second series of tests, shown in Figure 19, a typical commercial-oil formulation containing a balanced blend of 4% barium sulfonate and 1% zinc dithiophosphate was compared with the same base oil containing 4% barium sulfonate and 1.5% AN-2. In effect, the AN-2 was substituted for the zinc dithiophosphate. A significantly lower rate of ring wear was observed with the oil containing AN-2 than with the oil containing zinc dithiophosphate.

These results provide another example of engine conditions and wear measurement technique in which AN-2 effectively minimized abrasive ring wear. They also show that this antiwear effect was obtained in the presence of the two most widely used types of commercial motor-oil detergents.

PHYSICAL PROPERTIES OF AN-2 AND AN-3

Both AN-2 and AN-3 are white crystalline solids. A detailed description of the preparation of AN-2 and AN-3 was presented in a recent paper (*4*). The products used in

Table II. Certain Physical Properties of AN-2 and AN-3

Properties	AN-2	AN-3
Molecular weight	424.6	263.4
Melting point, °C.	154	94
Density at 20°C., grams/ml.	0.990	0.970
Boiling points, °C.		
at 40 mm.	289	179
at 30 mm.	280	172
at 20 mm.	269	163
at 10 mm.	250	147

the evaluation studies were of a technical grade having a purity of more than 98%. Certain physical properties of these compounds are listed in Table II.

Both AN-2 and AN-3 have a substantial solubility in all types of petroleum oils, even under the most severe conditions likely to be encountered in storage. During a 6-month storage test in which temperatures as low as 0°F. were encountered, the solubility of AN-2 and AN-3 in a light paraffinic oil did not fall below 1.5 weight %. This represented conditions of minimum solubility since both of these additives are more soluble in heavier and less paraffinic oils.

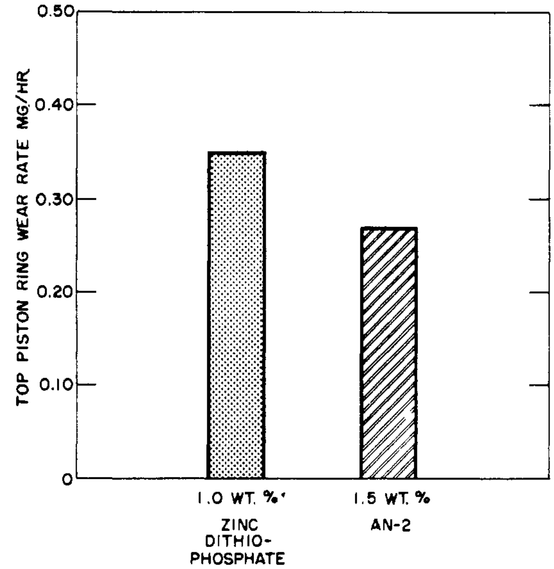


Figure 19. Effect of AN-2 and sulfonate detergent in radioactive ring engine test

Both oils contained 4% barium sulfonate

Acknowledgment

The author gratefully acknowledges the contributions of James O'Neill to the laboratory bench-scale testing, Tom Coffield to the identification of oil oxidation products and synthesis of AN-2 and AN-3, Harold Chalk and Richard Abowd, Jr., to the radioactive engine studies, and C. A. Hall and Tom Wilkinson to the transmission and multi-cylinder-engine studies.

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