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Study on Hydrocarbon Lubricating oil for Internal Combustion Engine, Synthesized from Fatty Oil as Crude Material, especially on Improvement of its Stability and on its Change in Engine. Part I.

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(Received Aug. 27, 1951)

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(Part II may appear in the Journal of the Fuel Society of Japan, XXXI, March, 1952).

Reserĉo pri hidrokarnona lubrikanta oleo por maŝino interne brulada, sintezita el grasa oleo kiel kruda materialo, speciale pri plibonigo de la firmeco kaj pri ĝia ŝanĝo en motoroj.

Resumo de Parto I.

Ĝis nun estis penita multaj reserĉoj pri sintezo de hidrokarbona lubrikanta oleo por maŝino interne brulada de pezaja servado. Speciale in Japanujo metodoj de sintezo de la oleo uzanta diversaj grasaj oleoj kiel krudaj materialoj estis konsiderita kiel plej grava kaj proponata. La unue sukcesata estis la metodo de Prof. J. Nagai kaj la aŭtoro de Tokio Imperiala Universitato, la unua de kiuj komencis la reserĉon tiel frue kiel 1932, kaj ilia studo (unua patento pri tio ĉi metodo : Japanuja patento Nr. 114, 485; kaj sekve multaj patentitaj) progresis al la rimarkinde granda industria fabriko, kio estis la unua de la multaj sintezantaj fabrikoj de aeromotor-oleo el grasaj oleoj.

Kial studo skribita tie ĉi uzis la produkton sintezita per la metodo, la aŭtoro volas citi la proceson de la sintezo. Kvankam patentita metodo uzis sajoleo, balenoleo, sardinoleo, kaj tiel plu kial krudaj materialoj, li reserĉis pri sinteza oleo el balenoleo. En la komenco, balenoleo estas hidrogenigita ĝis la iodonombro fariĝas al ĉirkaŭ 90. La duonhardita grasa oleo sekve hidroligita en grasa acido kaj glicerino, la unua de kioj estas distilita ĉe 40% per la efektiva kolono. kun alta vakuo La distilorestaĵo estas varmigita ĉe la temperaturo de 315°C en la daŭro de 25 horoj, resultante la varmpolimerigitan, viskozan kaj malpalan oleon. Oni aldonis la aktivan argilon en la kiamaniere obtenitan oleon, kio estas varmigit a laŭ la speciale determinita varmiganta kurbo ĝis la temperaturo de 400°C dum ĉ irkaŭ 150 aŭ plu minutoj. Tra la proceso de reakcio oni obtenas la hidrokarbonan oleon, kio estas la sintezita oleo uzita de la aŭtoro por la plia reserĉo. La aŭtora raporto estas tio, kio enhavas reserĉojn pri firmecoplibonigon de kiamaniere sintezita oleo kaj pri fizikoĥemika ŝanĝo de la firmecoplibonigita produkto en maŝino interne brulada de pezaja servado.

Studo pri sinteza oleo povus ne malkunigi el tio pri firmeco de la oleo. Oleo kio estis sintezita per ia metodo havas preskaŭ fiksitajn karakterojn. Se karakteroj estus sufiĉa iam por unu maŝino, gi iĝus malsufiĉa estonte laŭ la progreso de maŝino. Kvankam sinteza hidrocarbona oleo el balenoleo si mem havas viskec oindekson de 105~110, ĝia firmeco por varmo kaj oksigeno estas malsufiĉa al oleo de altrapida interne brulada maŝino. La aŭtoro penis plibonigi la oleon en la celo de uzo en aeromotoro, uzante diversajn metodojn. Tra en tuta raporto, la aŭtoro akceptis la

metodo de Brituja Ministraro de Aeronaŭto (British Air Ministry) por determino de lubrikanta oleo.

Unue, hidrogenigo de sinteza oleo estis tre efektiva. Grado de hidrogenigo estis simple konkludita per ĝia iodonombro. Firmecoj de hidrogenigitaj oleoj ĝis diversaj gradoj de satureco estis diversaj kaj ne simpla. Hidrogenigo sole ne povis produkti sufiĉe firmeca oleo (Viskecorilato VR<2.0, karbonpliiĝo KP<1.0%), ĉar por malaltigo de viskecorilato malpli ol 2.0, iod nombro de ohidrogenigita oleo devus esti 5～3, kaj ĉar por malaltiĝo de carbonpliĝo malpli ol 1.0%, tio devus esti malpli ol 3. Tiuj ĉi kondiĉoj resultis maleblecon obteni oleon. kio havis VR<2.0 kaj KP< 1.0% samtempe.

Sekve, la aŭtoro serĉis aliajn metodojn por plibonigi la firmeco. Tio estis serĉado de aldonaĵoj al la forthidrogenigita sinteza oleo kio estis pli firma kaj pli pala ol originala sinteza oleo. Estis penita ĉirkaŭ 30 aldonaĵoj, inter kioj organikaj kombinaĵoj de stano aŭ fosforo kaj mineralaj oleoj per specialan rafinadon havis bonegan efekton, kio estis, probable, utila.

Antaŭ ĉio la aŭtoro penis klarigi la efekton de rafinita kruda oleo, kio estis estimata kial la plej praktika, kaj li elelektis la oleo de Niicu de Niigata Prefektujo. Multaj diverse rafinitaj oleoj per la metodoj tia kiel sulfuracido-, alkalo-, argilo-, kaj Selektorafinadoj kaj distiladoj. Nombro de aldonaĵoj tiamaniere obtenitaj estis 20, kioj estis sekve aldonita al la baza oleo kun propreco skribita pli poste (de nun simple nomita NH-120) ĉe 5, 10 kaj 15% de pezo. 60 diversaj oksigenigprovoleoj, kioj recevos oksigenigon, estis obtenita. La baza oleo, al kio aldonaĵoleoj estis aldonita, havis sekvan preprecon : Specifa pezo ĉe 15°C : 0.8944, viskeco ĉe 100°F laŭ Saybolt-sekundoj : 1435, tio ĉe 210°F : 119.3, viskecoindekso laŭ Dean kaj Davis : 107.5, saponigonombro : 0.20, acidonombro : 0.02, Conradosona karbono : 0.084%, verŝopunkto -13.5～0.5°C, iodonombro : 5.3, anilinopunkto : 125.5°C, rifrakta indekso ĉe 20°C : 1.4920 : Post la oksigenigo — viskeco ĉe 100°F : 2712, viskeco-indekso : 103.9, Conradsona karbono 1.006%, acidonombro : 6.0, volatiligokvanto : 2.4%, viskecorilato ĉe 100°F : 1.70, karbonpliigo : 0.920%

Preskaŭ tutaj aldonaĵoleoj havis rimarkindan efekton, memkomprene kun diversaj gradoj. La plej efekta estis obtenita tra la plej simpla rafinado, t. e. per sulfuracido kaj argilo-rafinadoj sekvante de distiladoj. La plej granda efekto estis obtenita per rafinado uzanta 20～25% de forta sulfuracido. Tro profunda rafinado produktis plu malbone efektiva aldonaĵo. Efekto de aldonkvanto estis, ankaŭ, diversa. En mŭltaj okazoj, kvanto inter 5～10% donis plu fortan efekton kun kelkaj esceptoj. La plej bona resulto per aldonaĵo estis : VR 1.2～1.3, CI 0·5. Devas memori, ke oleo konsistanta el NH-120 kaj la aldonaĵoleo havas pro precon, kio estas plu bone ol ambaŭ komponantoj.

Ankaŭ la Seria kruda oleo estis provita kun sama ideo. Kvankam la rezultato estis plu malbone ol la supre, la rafinita oleo de Seria havis ebleco uzi kiel unu diluilo de altklasa lubrikanta oleo. Ideo de uzo de plu malbona oleo kial diluilo sen grave malboniganta efekto al la baza oleo havis rimarkindan ravecon, ĉar per tiu ĉi plu multe da altklasa oleo estus produktita uzante tie malaltklasan oleon kion devus, alie, uzi kial oleo de basa kvalito. Oleo, kia propreco estas nesufiĉa por uzi kiel altklasa lubrikanta oleo, sed malproksime plu bone ol, ekzemple, Seria oleo skribita supre, eble estus uzita kiel aldonaĵo, kio havas efektojn de diluilo kaj firmecoplibonigaĵo kaj povas esti aldonita en granda kvanto. En la celo de elfino de tiu ĉi ideo, la aŭtoro elelektis oleojn nomatajn City Services, Phillips kaj Gulf Pride, kaj penis klarigi ilia effektojn de diluilo kaj aldonaĵo. La miksitaj oleoj montris bonan firmecon en laŭlarga rango de mikskvanto de aldonaĵoleo. Devas esti notita, ke, kvankam la tri aldnaĵoleoj povas esti aldonita en grandan kvanto, la grado de plibonigo de firmeco estas plu malgranda ol la grado per Niicu oleo, kio estas plu malbona ol la tri en ĝia propreco kiel lubrikanta oleo kaj ne povas esti aldonita en granda kvanto.

Ankaŭ la baza oleo NH—120 povas esti efektita per sinteza aldonaĵo. La aŭtoro trovis, ke tetrafenilstano kaj tributilfosfito havas rimarkindan efekton, kaj reserĉis detale. La tetrafenilstano estas malfacile solvebla en la baza oleo, ĝia 0·01% aldonkvanto montrante grandan efekton. Ĝi mallevas rimarkinde viskecon, viskecorilaton, Conradsonan karbonon, karbonpliiĝon, acidnombron kaj elvaporiĝperdon post oksigenigo. Mallevo de viskecoindekso, kio estis observita dum oksigenigo de baza oleo, malgrandiĝas kaj acidnombro, kio estas tiel granda kiel 6 en originala baza oleo ankaŭ malleviĝas. Koeficiento de frotado havas rilaton kun acidnombro au firmeco de oleo. Preskaŭ samaj, kun kelkaj differencoj, estis montrita de oleo, kio enhavis la tributilfosfiton.

Observo, ke aldonaĵoleo rafinita el natura kruda oleo kaj sinteza aldonaĵo tia kiel tetrafenilstano havas grandan plibonigantan efekton al firmeco, alkondukas al unu ideo de kunhelpa uzo de ambaŭ aldonaĵoj. La aŭtoro aldonis al NH—120 aldonaĵoleon nomatan TK (rafinita per H_2SO_4 kaj argilo) ĉe 0, 2.5, 5, 10 kaj 15% kaj la tetrafenilstanon ĉe 0, 0.01, 0.05, kaj 0.10%. La resultato estis tre belega kial atendita. La plej firmeca miksita oleo, kio konsistas el 5% de aldonaĵoleo, 0.1% de tetrafenilstano kaj baza oleo NH—120, havas viskecoritaton de ĉirkaŭ 1.15 kaj karbonpliiĝon de ĉirkaŭ 0.21%, ambaŭ kiaj valoroj estas la plej bona iam obtenita de la aŭtoro. Observitaj resultatoj, kaj rilatoj inter aliaj estis detale deskutita.

CHAPTER I

Improvement of stability of synthetic oils.

In this chapter, a preliminary study on the improvement of stability of lubricating oils synthesized by the method which may be referred to later is described.

In order to determine stability of synthesized oils, the method of "The British Air Ministry" was employed throughout this work, because of its simplicity, good reproducibility and satisfactory correlation to engine performance. The apparatus and practice were slightly changed.

At first the stability of synthesized oils which were hydrogenated to various grades of unsaturation was determined. The hydrogenated oils were proven to be more stable. Improvement of carbon increase (CCI) and viscosity ratio were not always parallel to the decrease in unsaturation by hydrogenation. By means of hydrogenation, the properties of products approach to the specifications of aircraft lubricating oils (namely : CCI $<1.0\%$, VR <2).

But, hydrogenation only, could not produce oils which might completely satisfy the above specifications because the point of saturation of hydrogenated oil, where the smallest carbon increase was given, did not coincide with the point where the lowest viscosity ratio was obtained. Proper values of both factors could not be available at the same time.

By means of addition of various stability improvers, the author tried to improved hydrogenated oils of which unsaturation was made as small as possible. Some additive agents, especially, compounds of tin or phosphorus were proved to be powerful.

I — 1. Apparatus for determination of stability.

The reasons why the author accepted the method of the British Air Ministry for determination of stability of oils synthesized by him were based briefly, on the simplicity of its apparatus and practice, short period of determination, good reproducibility and reasonable correlation to engine performance. The essentials of the method may be found in:

Air Ministry General Specification for Mineral Lubricating Oils 1936. DTD 109.

and the details in:

The British Air Ministry Oxidation Test for Lubricationg Oils, F. M. Garner,

C. I. Kelley, J. L. Taylor ; World Petroleum Congress, London 1933, 2, 448—457.

The author used apparatus employing the same principles but with some modifications. The sketch is illustrated in Fig. I—1.

A. Gaede-pump for air blower almost without pulsation;

B. Air filter; C. Air washer with conc. NaOH;

D. Air washer with conc. H_2SO_4;

E. Air filter with soda lime and cotton fibers;

F. Flowmeter with accuracy better than 1% ;

G. Oil bath with large controllable heater (J) and small controlable one (L);

H. Test tube, 25.4 mm i. d., containing oil sample;

I. Thermometer; J. Gas burner:

K. Temperature regulator made of "Telex" glass, containing mercury, with the ability of regulation of temperature within 0.1°C at 200°C.;

L. Small electric heater with "Slidac" similar to "Variac"; and M. Relay.

The upper ground end of the Telex (similar to Pyrex) test tube is fitted with ground glass stopper with gas-inlet and outlet pipes of the dimension described in Air Ministry General Specification for Mineral Lubricating Oils (see Fig. I —1). Sample oil is taken into test tube by weight of 36.0 g. instead of volume, because of uncertainty of the latter in the case of viscous oils, such as aero oils. The temperature of bath is maintaind accurately at 200 ± 0.1°C. throughout the test. Volume of air for oxidation : 15 l /h. Test period : 6 h and 6 h., second 6 h. test on the next day. After oxidation, the test tube is cooled, its outside washed and the tube weighed. The weight difference before and after the oxidation, "Quantity of volatilization", a term which is not correct but accepted here for the sake of simplicty, is calculated and made a kind of measure of stability. For determining carbon residue, the author prefers Conradson's method to Ramsbottom's, though the latter is accepted in the original specification, and he neglects discordance between the two methods which may be found for the same sample oil. In this paper, the auther gives a name "Conradson Carbon Increase" (abbreviation : CCI) for the difference of Conradson carbons before and after the test, and another name "Viscosity Ratio" (Abbreviation : VR) for the ratio of viscosities ordinarily at 100°F. (also at another temperature) after and before the test. Acid numbers after the test were in some cases determined.

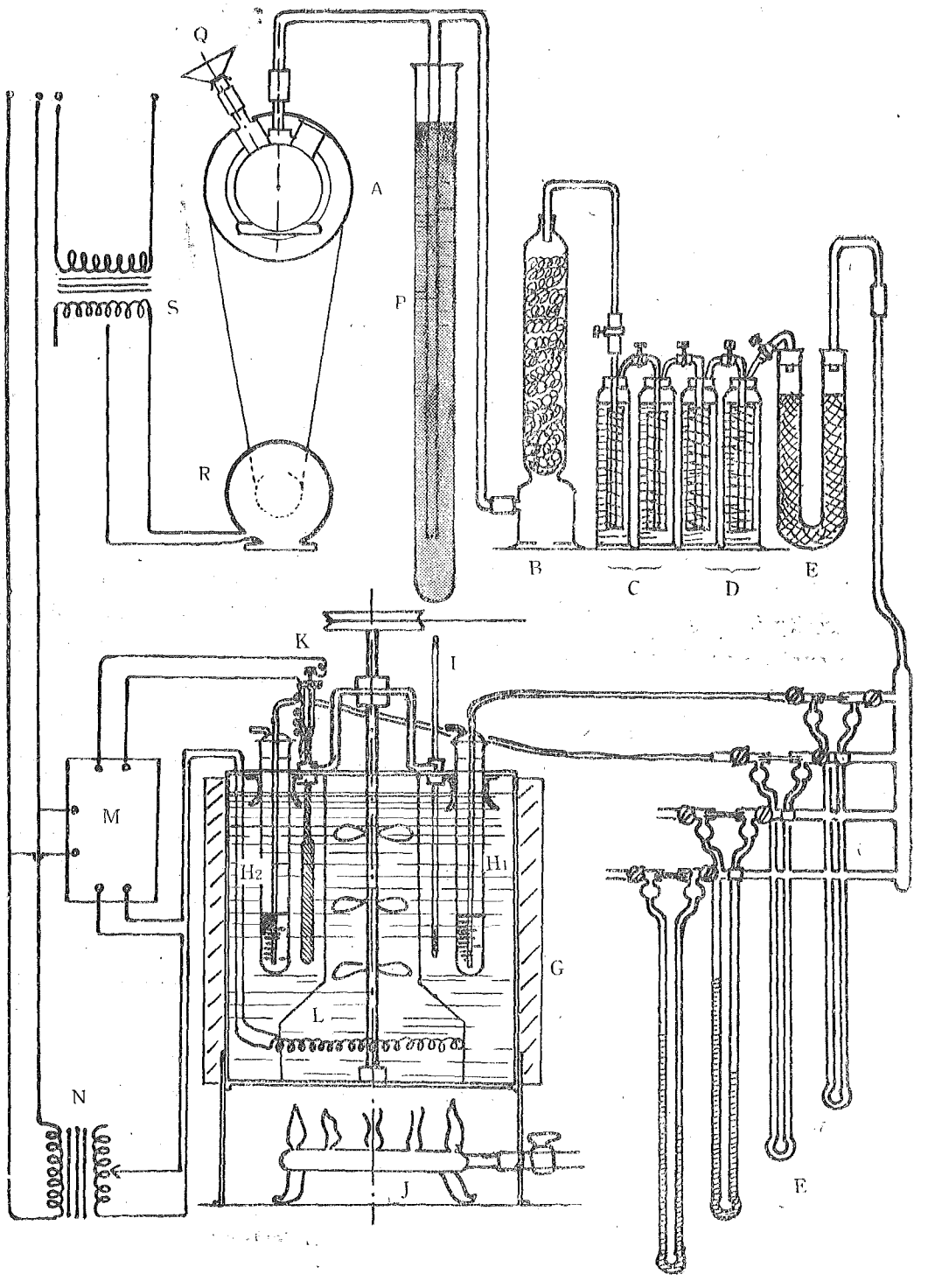


Fig 1—1 Apparatus for Determinaiton of Stability

I — 2. Improvement of stability by means of high-pressure hydrogenation.

The sample oil for this study is synthesized from whale oil. The synthesis is as follows. Whale oil, raffinated by NaOH solution and active clay, is hydrogenated or hardened by the usual method to iodine number of ca. 90. Then the semi-hardened oil is hydrolyzed into fatty acid and glycerine, the former being distilled to the point where distillate amounts to 40%. The residue is heated at a temperature of 315°C. for 25 hours in glass-lined iron vessel. To the polymerised and thickened oil, active clay is added in the quantity of 30% by weight and stirred vigorously. The mixture is heated rapidly to 250°C., then to 360～400°C. in ca. 90 min. Thus oxygen or radicals which contatin oxygen split out of the polymerized oil and hydrocarbon oil remains. The hydrocarbon is, then, extracted by suitable solvent, separated from the clay by filtration or centrifuging, and obtained in the state of viscous oil by means of vaporization of the solvent. The author denominates this as the "synthetic oil".

The lubricating oils synthesized by the method described above have viscosities and viscosity indices, which belong to high class oils for high speed internal combustion engines or aircaft motors. The stability against oxidation and high temperature, however, does not satisfy the requirements. Viscosity ratio being 3.5, carbon increase 3.5%, iodine number 30—50, the synthesized oil can not be used in high speed engines. The oil is brownish red or red in color and dark green or bluish green in fluorescence. The synthetic oil, when completely hydrogenated, changes color yellow to pale yellow or almost colorless and fluorescence green to weak violet. Of course various grades may exist between them according to the grade of hydrogenation. At about the point where iodine number of the oil is 20, it is red and transparent and has bluish green fluorescence. As iodine number decreases owing to hydrogenation, red color fades gradually. The oil becomes yellow, pale and then almost colorless. As the oil becomes colorless, its fluorescence gains color of weak bluish violet or weak violet. Here the iodine number is less than 5～7. With advance of hydrogenation, the oil gains faint fishy odor, which is quite different from natural petroleum oil.

Hydrogenation results in decrease in iodine number. The real quantity of hydrogen consumed, however, does not concord with the calculated quantity from the decrease in iodine number. This is natural, for unsaturation may exist in both hydrocarbon ring and side chain, the sole unsaturation of which the iodine number indicates. The author did not confirm whether the grade of saturation by hydrogenation proceeds in parallel or not.

The synthetic oil is hydrogenated under pressure at 50～200 kg/cm² and temperature at about 250～300°C. By various combinations, namely pressure, temperature and duration of the reaction, samples of various grades of unsaturation, in other words, samples of various iodine numbers were obtained. Iodine number of starting material is 33.6, that of samples thus obtained 15, 13, 12, ... 1, and so on. In progress of hydrogeneation, the viscosity of oil decreases acording to production of light hydrocarbon oil. As results of oxidation test may be disturbed by the random value of viscosity, the author fixed the value of viscosity as $S_{210} = 120$ (S_{210} means viscosity in Saybolt Universal Second at 210°F) by distilling hydrogenated crude sample to suitable extent.

The synthesized, hydrogenated and topped oil is the sample for the test of oxidation or stability. The method and apparatus have been already described in section I — 1. The detail of experiments is shown in Table 1 — 1, the feature of change in Fig. I — 2.

Table 1 — 1 Variation of stability by means of hydrogenation

No. of experiment			OT-181	OT-23	OT-1	OT-21	OT-55	OT-40	OT-77	OT-78	OT-91	OT-86	OT-83
Viscosity	before the test	S_{100}	1654	1430	1633	1717	1551	1562	1477	1408	1623	1550	1673
		S_{210}	121.2	116.0	127.0	130.5	121.4	—	—	—	—	—	—
		VI	105.1	105.3	106.0	105.4	104.0	—	—	—	—	—	—
	after 〃	S_{100}	5015	3060	3229	3550	2631	2499	2762	2773	3473	3131	4584
Viscosity ratio			3.03	2.14	1.98	2.08	1.70	1.60	1.87	1.97	2.14	2.02	2.74
Iodine value			33.6	15.4	13.0	12.4	8.15	7.73	6.43	5.93	2.25	1.49	1.04
CC%	before the test		4.16	0.61	0.45	0.52	--	0.22	0.28	0.25	0.23	0.07	0.06
	after 〃		8.02	2.71	2.20	2.31	2.07	—	1.41	1.15	1.00	0.76	0.56
	CCI		3.86	2.10	1.75	1.79	—	—	1.13	0.90	0.77	0.69	0.50
Acid number			11.7	6.21	6.84	5.29	—	—	3.7	4.0	3.5	5.6	5.7

1) Viscosity ratio (VR) ..... VR of original oil is 3.03, which is relatively low for usual synthetic oils of this sort. As iodine number decreases to the point of IN (Iodine number) 10, the curve simply goes lower. At IN = 7.8, minimum of VR may be found, where VR = 1.6. With further decrease in IN, VR steeply rises higher especially under IV = 2, the curve being almost vertical. The curve indicates that it consists of 3 parts, namely, first part, till IV = 7.8 ; second, IV = 2～8 ; third IV < 2. It is suggested that behavior of hydrogenation may be different at each region and optimal iodine number where VR is the best or the lowest may exist.

2) Conradson carbon (CC) ..... As IN lowers, CC simply decreases. At IV～

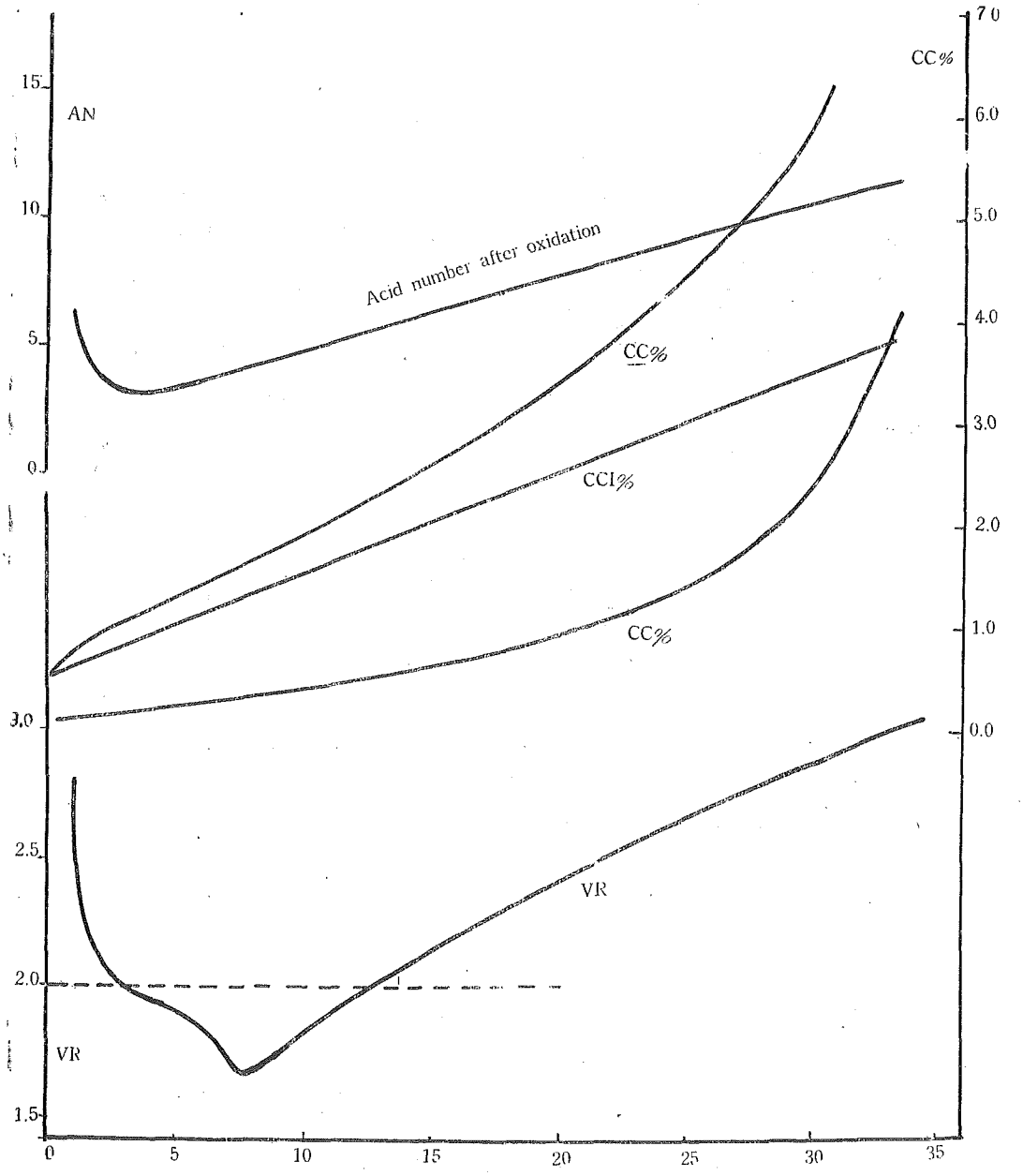


Fig. 1—2 Relation between grade of Saturation and Stability.

1, CC may be lower than 0.1%.

3) Conradson carbon after the test (CC)..... The value of non-hydrogenated oil is very high, i, e, higher than 8.0%. It cannot be used for high speed internal combustion engines. At about 7 of IN, CC approaches to ca. 1.5 %. The lower the IN, the lower the CC.

4) Conradson carbon increase (CCI)..... Almost straight line. As unsaturation decreases, CCI simply decreases.

5) Acid number (AN)..... As IN decreases, AN at first simply decreases. At IN ~ 5 the curve reaches to the lowest part then it rises higher.

6) The fact that non-hydrogenated original oil shows very high AN, and completely hydrogenated one also high AN, suggests that the cause of easiness of introduction of oxygen may be in correlation with that of growth of VR. But exactly speaking, IN where VR indicates minimum value, does not coincide with IN where AN indicates minimum.

The author believes that in this study viscosity ratio must receive most intensive interest and that it must be one of the most important factors which correlate with lacquer formation and ring-sticking in internal combution engines. If it be wished to obtain an oil, which has such properties as : VR < 2.0, CCI $< 1.0\%$, CC $< 2.0\%$, hydrogenation can not produce it. Because,

for VR < 2.0, IN must be between $5 \sim 3$,
for CCI $< 1.0\%$, IN must be lower than 3,
for CC $< 2.0\%$, IN must be lower than 7,

Accordingly, it is impossible to find a point where all the conditions may be satisfied at the same time. Further the fact that better oil such as VR < 1.5 and CCI < 0.5 in near future may be wanted, requires another method to improve it.

It is concluded in respect to hydrogenation of synthetic oil that:

1) VR, CCI, CC..... are highly improved.

2) An iodine number that satisfies every condition at the same time can not be found.

3) If VR < 1.5 and CCI < 0.5 are wanted, another way to improve must be searched for.

I—3. Preliminary study on effect of additives.

As it was concluded that highly stable oil can not be obtained by hydrogenation only, the author tried to use various additives which were supposed to have effect on improvement of stability. It has been learned by him that the effect of additives on original synthetic oil is very feeble and the blended oil can not be used

in high speed engines. In the present study, an attempt was made to find the effect of various additives to oil hydrogenated to a point where iodine number is under 5. Several of the additives tried exhibited excellent results.

The basic oil which was used for experiments on the addition of stability improvers was an oil which was synthesized by the method described above and hydrogenated at 100 kg/cm^2 on 300 ~ 310°C. for 5 h. Its properties and constants are:

viscosity at 100°F. (SUS) 1623, viscosity at 210°F. 127,
viscosity index (Dean & Davis) 106,
viscosity at 100°F. after the oxidation test 3229,
viscosity ratio (100°F.) 1.98, Conradson carbon 0.45%,
Conradson carbon after the oxidation test 2.68%,
Carbon increase 2.23%, acid number after the test 6.84, iodine number 12.

With this oil, about 30 additives were tried, among which several agents showed excellent effect, but others almost no effect. Two or three additives which were effective might be available for practical use. The quantity of additives was 0.1% throughout the tests. In Table I — 2 these results are shown.

Additives used may be classified as:

(1) inhibitor of rubber, (2) oil soluble dyestuff,
(3) compound which has -OH or $-NH_2$ group,
(4) organic compound of tin or phosphorus,
(5) mineral oil raffinated by peculiar way.

Organic tin compounds, phosphorus compound and specially refined mineral oils exhibited remarkable effect. The compounds and mineral oils were never used as additives for hydrogenated synthetic oil. Especially, it should be noted that, though TK_3 or Pn in themselves were not stable for oxygen and temperature, notable effect appeared when added in small quantity to hydrogenated oil.

The test conditions of British Air Ministry Method are very severe for usual oil and additive. At low test temperature as in the Indiana Method considerable effect may be found by a number of additives which nevertherless, can not exhibit favorable effect at such temperature as in the British Air Ministry test. For example, naphthol, though it may be an effective stability improver when tested by the Indiana method, has defective action when tested in another study.

In conclusion, among 30 additives which were tested in these preliminary experiments, several remarkably effective additives were found.

Table 1—2 Effect of additives

	additive	effcet		additive	effect
1	"VGB"	×	16	"Baygal C"	×
2	monobenzyl-p-aminophenol	—	17	"Stabilite"	+
3	p-hydroxyphenol-morpholine	+	18	"Oil Red G"	+
4	ethyl fluid	×	19	"Sudan Black"	—
5	dibenzyl aniline	×	20	"Spirit Fast Blue"	+
6	ethyl benzyl aniline	×	21	2-oxy lepidine	—
7	o-nitro anisole	—	22	anthraquinone	—
8	"Thermoflex"	—	23	pyrogallic acid	×
9	salicyl aldehyde	×	24	carbazole	—
10	phenyl hydrazine	—	25	2-anilino lepidine	+
11	α-naphthol	—	26	original synthetic oil	—
12	β-naphthol	—	27	indole	—
13	tetraphenyl tin	++	28	tributyl phosphite	++
14	tetranaphthyl tin	++	29	TK_3	++
15	tin naphthenate	++	30	Pn	++

Where × : no effect, — : lowering effect, + : positive effect,
++ : excellent effect, in " ": commercial name,
TK_3 : a commercial mineral oil followed by special raffination,
Pn : a residual oil of Nitsu crude raffinited.

CHAPTER II

Effect of refined Niitsu crude oil as an additive.

As reported in the previous section, it was found that specially refined and topped petroleum oil exhibited remarkable stabilizing effect on the hydrogenated synthetic oil. The author considered this way of improvement would be easier and more practical, and attempted to find details more clearly on the raffination of crude petroleum oil suitable for stabilizer. The crude oil of Niitsu, Niigata-Prefecture was selected for this purpose because of its abundance in lubricant fraction among Japanese oils and because of the absence of paraffin wax.

As the first step, suitable grades of raffination by means of sulfuric acid, alkali and clay were checked on the crude oil. It was found comparatively easy to refine. Twenty samples were prepared by various methods, combination of them and variation of degree of raffination. Refining was carried out by the use of sulfuric acid, alkali, clay, solvent and distillation. These samples were added to hydrogenated synthetic oil to concentrations of 5, 10 and 15% by weight. These oils with additive were tested as described above in Chapter I.

II—1. Preparation of additives from Niitsu crude oil.

Among Japanese crude oils, not only quantity but also quality of the crude oil of Niitsu, Niigata-Prefecture is known to be superior. From the crude oil it is possible to produce lubricating oil of comparatively high quality (of course the comparison is limited in Japan) and of low content of wax. A sample refined at

Table 2—1

	Niitsu oil	Toyokawa oil*
specific gravity	0.940	0.940
〃 after refining by 96%H_2SO_4	0.908	0.915
yield of refined oil, weight %	47%	30%
temperature rise during refining	20—38°C.	20—44°C.
filtrability of clay-treated oil, % of active clay: 5%	relatively easy	slow
10	more easy	easy
15	almost the same	easy
20	same	easy

* For comparison.

random (though of course by the usual way) gave remarkable effect on stability of hydrogenated synthetic oil as described in I — 3. These were reasons why the author undertook to prepare additives from Niitsu crude oil by means of various ways of refining and to find the best condition from among them. The properties of the crude oil received by him were as in Table 2 — 1.

Oils thus refined were treated by washing with warm water. Grade of separation of oil and water, and acid number after washing with water 3 times are listed in Table 2 — 2

Table 2 — 2

Niitsu oil		
percentage of clay separation		acid number
5	emulsifies, separates very slowly	0.09
10	emulsifies, separates relatively well	0.054
15	emulsifies, separates well	0.038
20	〃	0.022
Toyokawa oil		
5	emulsifies, poor separation	0.062
10	emulsifies, relatively poor separation	0.037
15	emulsifies, relstively good separation	0.27
20	〃	—

Through these data, it is clear that washing with water can be used after acid and clay refining, though the yield of refined oil may be extremely low. The influence of H_2SO_4 by quantity is as follows.

Table 2 — 3

crude oil	96% H_2SO_4 %, by vol.	loss %, by vol.	sludge	properties of oil
Niitsu	10	41	semi-solid, oily	low viscosity, fluorescent
	15	42	〃	〃
	20	47	〃	〃
Toyokawa	10	45	solid	〃
	20	48	semi-solid, movable	〃
	30	54	〃	〃

From these data, it is seen that the Niitsu crude oil raffinated by 10% of 96 % H_2SO_4 and followed by alkali washing produces emulsion and does not separate easily. The same crude oil refined by 10% of 96% H_2SO_4 and 10% of active clay is filtrable. But the same followed by alkali refining produces emulsion and does

not separate easily. It may not be practical to refine the crude oil by sulfuric acid followed by alkali treating. In acid oil produced by sulfuric acid refining, however, there may be suspended a small quantity of sludge which can not be forced to separate by means of gravity or centrifugal force, but can be separated through filter by means of raffination by active clay. Further it may be possible to refine the crude by solvent. The author refined the crude using the following raffination separately or in combination or in any succesion.

Table 2—4. Additives prepared by various methods.

		HN-4-1	HN-4-2	HN-5-1	HN-5-2	HN-6-1	HN-6-2	HN-7-1	HN-7-2	HN-8-1	HN-8-2	HN-10	HN-11	HN-12
H_2SO_4 refining	wt. % of H_2SO_4	10	10	15	15	20	20	25	25	—	—	10×2	10×2	10×2
	yield of acid oil	73	73	68	68	62	62	60	60	—	—	62.9	62.9	62.9
active-clay treat.	wt. % of clay	15	15	15	15	15	15	15	15	—	—	—	—	—
	yield of ref. oil	63	63	60	60	54	54	53	53	—	—	—	—	—
topping	vol. % of distillate	51.5	51.5	58.4	58.4	62.0	62.0	62.5	62.5	50	50	—	—	—
	yield of residue	32	32	26.2	26.2	22.6	22.6	21.6	21.6	50	50	—	—	—
H_2SO_4 refining	wt. % of H_2SO_4	—	10	—	10	—	10	—	10	20	20	—	—	—
	yield of acid oil	—	23.3	—	21.3	—	19.6		18.9	21.6	21.6	—	—	—
active clay treat.	wt. % of clay	—	20	—	20	—	20	—	20	—	—	—	—	—
	yield of ref. oil	—	20.7	—	17.4	—	15.8	—	15.8	—	—	—	—	—
H_2SO_4 refining	wt. % of H_2SO_4									20	—	—	—	—
	yield of acid oil									16.6	—	—	—	—
active clay treat.	wt. % of clay									20	20	—	—	—
	yield of ref. oil									13.4	17.7	—	—	—
alkali	yield of washed oil											43.7	43.7	43.7
topping	vol. % of olistillate											66.5	66.5	66.5
	yield of residue											15.3	15.3	15.3
active clay treat.	wt. % of clay												10	20
	yield of residue												14.2	13.0
Vis.	S_{210}	115.5	93.7	121.4	106.2	123.7	115.4	123.5	112.2	99.3	114.5	145.9	142.8	140.7
	VI	-22.6	-0.84	-6.9	5.4	-5.6	5.7	6.0	4.2	16.7	3.2	-5.3	-0.3	7

Table 2—5. Additives prepared by various methods

		HN-4-3	HN-5-3	HN-6-3	HN-7-3	HN-S-2	HN-S-5
H_2SO_4 refinig	wt. % of H_2SO_4	10	15	20	25	20	20
	yield of acid oil	73	68	62	60	8	68
clay treat.	wt. % of clay	15	15	15	15	20	20
	wt. %of ref. oil	63	60	54	53	54	54
topping	vol. % of distillate	66.5	66.5	66.5	66.5	66.5	66.5
	wt. % of residue	22.7	20.0	18.6	18.1	17.0	19.0
proper-ties	S_{210}	242.7	197.5	154.6	142.3	191.7	186.5
	VI	—	−9.0	−1.5	0.84	−11	−7
Slecto	yield after 1st sort*	7.0	7.6	8.8	9.3	7.95	—
〃	〃 after 2nd sort△	—	—	—	—	—	4.1
proper-ties	S_{210}	—	—	—	—	—	124.2
	VI	—	—	—	—	—	79.2
clay treat.	wt. % of clay	—	—	—	—	—	10
	wt. % of ref. oil	—	—	—	—	—	3.47
proper-ties	S_{210}	147.1	132.6	122.6	121.4	137.9	123.7
	VI	59.5	48.4	49.1	54.2	53.0	79.9

* "Selecto" refining of lst sort consists of extraction by the solvent (oil 1 : solvent 1) in 2 cycles followed by topping of the solvent.

△ "Selecto" refining of 2nd sort consists of extraction by the solvent (oil 1 : solvent 1) in 5 cycles followed by topping of the solvent.

Table 2—6. Preparation of additives from residual oil. (1)

		NK-1	NK-2
H_2SO_4 refining—(1)	wt. % of the acid	10	10
	yield of acid oil, %	48.7	48.7
H_2SO_4 refining—(2)	wt. % of the acid	10	10
	yield of acid oil, %	36.5	36.5
clay treatment	wt. % of clay	20	20
	yield of refined oil, %	30	30
topping	vol. % of distillate	—	5
	yield of residue, %	—	29
Viscosity	$S_{100°F}$	2,64	3,527
	$S_{210°F}$	105.4	122.0
	VI	18	19

Table 2—7. Preparation of additives from hesidual oil. (2)

		NK-5	NK-6	NK-3	NK-4
dilution	raw oil 1 : kerosene 1	+	+	+	+
H_2SO_4 ref.	wt. % H_2SO_4	20	20	20	20
alkali ref.	followed by water washing	+	+	+	+
topping of kerosene	steam distillation	+	+	—	—
	yield of residue, wt. %	53	53	—	—
topping under vacuum	vol. % of distillate	—	10	—	—
	yield of residue, wt. %	—	46.7	—	—
clay treat.	wt. % of clay			10	10
topping of kerosene	steam distillation			+	+
	yield of residue, wt. %			58	58
topping under vacuum	vol. % of distillate				12
	yield of residue, wt. %				50
Properties	S_{100}	2,084	3,716	1,987	3,466
	S_{210}	95.2	123.7	91.7	118.4
	VI	23	15.2	18	13
	Flash point (°C)	—	220	—	—

1. Sulfuric acid refining, quantity of the acid variable,
2. Active clay refining, quantity of clay variable,
3. "Selecto" refining, quantity of the solvent variable,
4. Alkali refining, definite quantity,
5. Distillation.

Through these processes, refined oil samples with viscosity of 120 SUS at 210°F. were obtained by means of proper topping.

Table 2—8

percentage of distillate	temp. of distillation	S_{210}
initial point	70°C	
10%	128	—
20	144	—
30	158	32.9
40	170	34.8
50	183	37.6
60	209	43.2

The crude oil used here really was from Kanatsu in the Niitsu oil field. That

is also a Niitsu crude oil. Thus 20 raffinates available for lubricant additives were obtained. Sample number of additive, detail of raffination for each and its yield are listed in Tables 2 — 4 and 2 — 5. Specific gravity of the Kanatsu oil was 17.85° Bé. Fractional distillation at 5.5 mm Hg showed the following features :

Further, a heavy oil obtained by means of steam distillation as residual oil from Kanatsu oil was used for the preparation of additive, the properties being as follows : specific gravity, 13° Bé ; flash point, 212° ; viscosity, 309 Redwood second at 100°C. The residual oil as it is and diluted kerosene were refined as above. Five samples were obtained (Table 2 — 6 and 2 — 7).

The base oil, to which additives prepared as above were added, was called NH-120, in which "N" meant first letter of the name of Dr. Nagai (inventor of the method of synthesis of hydrocarbon lubricating oil from fatty oils and the director of research for the author), H hydrogenated, and 120 Saybolt viscosity at 210°F. Its properties were as followes :

Table 2 — 9

specific gravity at 15°C, 0.8944 ; $S_{100°F}$, 1435 ;
$S_{210°F}$, 119.3 ; viscosity index, 107.5 ;
saponification number, 0.20 ; acid number, 0.02 ;
Conradson carbon, 0.084% ; pour point, -13.5°C ;
iodine number, 5.3 ; aniline point, 125.5°C ;
refractive index, n_D^{20} 1.4920 ;
after oxidation, $S_{100°F}$, 2,712 ; viscosity index, 103.9 ;
Conradson carbon, 1.006% ; acid number, 7.9 ;
volatility loss, 2.4% ;
viscosity ratio at 100°F 1.70 ; carbon increase 0.92%.

II— 2 Effect of additive.

In the tables 2 — 4 ~ 2 — 7 are listed samples used as additives which were treated by processes as follows :

1. Additives refined by means of sulfuric acid, clay and distillation, the quantity of the former only, varied.
   HN—4—1, HN—5—1, HN—9—1, HN—7—1.
2. Additives refined as above and once more by sulfuric acid and clay, quantities of both reagents being fixed.
   HN—4—2, HN—5—2, HN—6—2, HN—7—2.
3. Additives distilled and refined by sulfuric acid once, further by clay.
   HN—8—1, HN—8—2.
4. Additives refined by sulfuric acid twice, further by alkali, distillation or clay, etc.
   HN—10, HN—11, HN—12.

5. Some of additives in 1. further refined by Selecto.
   HN—4—3, HN—6—5, HN—7—3.
6. Other additive refined by Selecto.
   HN—S—2.
7. Residual oil of steam distillation, further refined by sulfuric acid, active clay and distillation.
   NK—1, NK—2.
8. Residual oil of steam distillation, further diluted and refined as in 7.
   NK—3, NK—4, NK—5, NK—6.

To the base oil, i. e., NH — 120, each additive described above was added to the amount of 5, 10 and 15% by weight. Mixtures thus obtained were oxidized by the method of the British Air Ministry somewhat modified by the author. After oxidation, test tubes containing test oils were cooled and various constants and numbers taken, together with those of unoxidized starting samples, as follows :

S_{210}, S_{100}, both before and after the test, viscosity indices, viscosity ratio, pour point, Conradson carbon before and after the test, carbon increase, volatility loss, acid number after the test.

The results thus obtained are listed in Table 2 — 10.

II—3. Relation between refining treatment and effect of addition. (1)

It is natural that there may be variations to some extent in viscosity of additives prepared from Niitsu oil, though an effort was made to secure uniformity of viscosity. As a reasonable result, viscosity of blended oil is not definite. Because of low viscosity index of additive, that of blended oil falls accordingly.

As will be seen in Table 2—10, the effect on stability is remarkable. Almost every additive exhibits improving effect, though the optimal point of action may vary. Effect of addition is shown for each additive in Fig. 2 — 1 ~ 4. Abbreviations mean as follows : VI, viscosity index ; VR, viscosity ratio ; CC, Conradson carbon before the test ; CC ; that after the test ; CCI, Conradson carbon increase, that is, CCI =CC—CC. Indices which must be noticed seriously are VR, CC and CCI.

In reference to Table 2 — 10 and figures 2 — 1 ~ 4, the effect of additives on CCI and VR and courses of refining for them are graphed in Fig. 2 — 5 for the purpose of clear understanding.

1) CCI for blended oils is for the most part lower than non-blended NH-120. When we classify Class A as additives able to lower CCI to 0.5%, Class

Table 2—10. Effect of additives

			OT-HN-4	OT-HN-15	OT-HN-18	OT-HN-19	OT-HN-11	OT-HN-17	OT-HN-14	OT-HN-21	OT-HN-22	OT-HN-23	OT-HN-24	OT-HN-26	OT-HN-27	OT-HN-28
base oil			N-120-P	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃
additive	name		—	HN-4-1	〃	〃	HN-4-2	〃	〃	HN-5-1	〃	〃	HN-5-2	〃	〃	HN-6-1
	addn. %		—	5.0	10.0	15.0	5.0	10.0	15.0	5.0	10.0	15.0	5.0	10.0	15.0	5.0
viscosity	before test	S_{100}	1,435	1,493	1,515	1,566	1,456	1,473	1,488	1,485	1,527	1,561	1,466	1,502	1,520	1,485
		S_{210}	119.3	121.1	118.4	118.4	118.4	118.0	115.8	119.3	119.3	119.3	118.8	118.8	118.4	118.4
		VI	107.5	106.6	102.9	100.5	105.6	104.8	102.1	105.2	103.3	101.7	106.1	104.4	102.6	104.3
	after test	S_{100}	2,712	1,916	1,947	2,039	1,965	1,903	1,812	1,892	1,915	1,979	2,015	1,969	1,967	1,945
VR			1.89	1.283	1.285	1.302	1.350	1.292	1.218	1.274	1.254	1.268	1.375	1.311	1.293	1.310
PP (°C)			−13.5	−13	−13.0	−14.5	−19.5	−13.5	−14.5	−16.5	—	—	−17.0	−13.5	−16.5	−19.5
CC %	before t.		0.111	0.216	0.268	0.369	0.172	0.179	0.210	0.164	0.235	0.322	0.158	0.205	0.224	0.154
	after t.		0.920	0.765	1.064	1.319	0.715	0.755	0.800	0.665	0.796	1.011	0.711	0.747	0.778	0.632
	CCI		0.809	0.549	0.796	0.950	0.543	0.576	0.590	0.501	0.561	0.689	0.553	0.542	0.554	0.478
volatility loss			2.42	0.06	1.25	1.14	0.89	0.47	—	—	—	—	—	0.64	0.62	0.60
AV after test			7.89	2.34	3.09	3.84	3.14	2.27	2.15	2.96	3.15	3.02	4.32	3.24	3.51	3.95

Table 2—10. Effect of additives, continued.

			OT-HN-29	OT-HN-30	OT-HN-31	OT-HN-32	OT-HN-34	OT-HN-35	OT-HN-36	OT-HN-37	OT-HN-38	OT-HN-39	OT-HN-40	OT-HN-41	OT-HN-42	OT-HN-43
base oil			N-120-P	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃
addi-tive	name		HN-6-1	〃	HN-6-2	〃	〃	HN-7-1	〃	〃	HN-7-2	〃	〃	HN-8-1	〃	〃
	addn. %		10.0	15.0	5.0	10.0	15.0	5.0	10.0	15.0	5.0	10.0	15.0	5.0	10.0	15.0
viscosity	before test	S_{100}	1,542	1,589	1,489	1,509	1,551	1,481	1,509	1,555	1,486	1,497	1,542	1,466	1,480	1,503
		S_{210}	119.7	120.4	119.7	118.4	118.4	118.4	118.4	118.4	119.3	118.4	118.4	118.4	117.6	117.6
		VI	103.5	101.4	105.9	103.1	101.2	104.5	103.1	101.0	105.1	103.7	101.6	105.2	104.5	103.4
	after test	S_{100}	1,942	1,984	2,299	2,426	2,539	1,937	1,864	1,859	2,268	2,399	2,529	1,914	2,503	2,527
VR			1.259	1.249	1.544	1.608	1.637	1.307	1.235	1.195	1.526	1.603	1.640	1.306	1.691	1.681
PP (°C)			−15.5	−17.5	−16.5	−16.5	−17.5	+1.5	−15.5	−13.5	−13.5	+1.5	−15.5	−14.5	—	—
CC %	before t.		0.235	0.248	0.138	0.176	0.219	0.163	0.190	0.273	0.199	0.202	0.246	0.174	0.159	0.197
	after t.		0.702	0.849	0.966	1.248	1.388	0.645	0.689	0.766	1.002	1.221	1.442	0.809	1.265	1.390
	CCI		0.467	0.601	0.828	1.072	1.169	0.482	0.499	0.493	0.803	1.019	1.196	0.635	1.106	1.193
volatility loss			—	—	—	—	1.74	1.28	1.22	3.58	1.92	1.69	2.08	0.64	2.14	2.00
AV after test			4.62	5.33	6.96	6.07	6.30	4.32	3.92	3.17	6.2	6.91	6.86	1.85	5.86	5.46

Table 2—10. Effect of additives, continued.

			OT-HN-62	OT-HN-64	OT-HN-65	OT-HN-66	OT-HN-67	OT-HN-68	OT-HN-69	OT-HN-70	OT-HN-71	OT-HN-72	OT-HN-103	OT-HN-104	OT-HN-105	OT-HN-106
base oil			N-120-P	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃
addi-tive	name		HN-4-3	HN-6-3	〃	〃	HN-7-3	〃	〃	HN-S-2	〃	〃	NK-1	〃	〃	NK-2
			15.0	5.0	10.0	15.0	5.0	10.0	15.0	5.0	10.0	15.0	5.0	10.0	15.0	5.0
viscosity	before test	S_{100}	1,601	1,484	1,537	1,554	1,495	1,525	1,544	1,525	1,543	1,600	1,482	1,496	1,533	1,498
		S_{210}	122.4	119.3	120.6	120.6	120.6	120.6	120.6	121.5	122.4	122.4	119.3	119.3	119.3	120.6
		VI	102.8	105.2	104.7	103.9	106.6	105.2	104.4	106.1	105.3	102.8	105.6	104.9	103.2	106.0
	after test	S_{100}	1,995	2,080	1,936	1,854	2,116	1,954	2,075	2,043	2,028	2,001	1,984	1,953	2,033	1,911
VR			1.246	1.402	1.260	1.193	1.415	1.281	1.344	1.340	1.314	1.250	1.339	1.306	1.326	1.276
PP (°C)			−15.5	—	16.5	−17.5	−16.5	−17.5	−15.5	−14.5	−17.5	−16.5	−14.5	−16.5	−13.5	−17.5
CC %	before test		0.319	0.128	0.201	0.214	0.153	0.166	0.214	0.133	0.206	0.262	0.164	0.203	0.249	0.201
	after test		0.933	0.710	0.655	0.676	0.768	0.646	0.867	0.755	0.754	0.809	0.730	0.738	0.885	0.729
	CCI		0.614	0.582	0.454	0.462	0.615	0.480	0.653	0.622	0.548	0.547	0.566	0.535	0.636	0.528
volatility loss			1.12	0.83	—	1.39	1.39	1.66	1.12	1.12	1.12	1.39	2.22	1.94	4.17	3.06
AV after test.			7.72	6.72	4.43	3.86	6.47	4.58	2.25	4.50	3.82	2.93	3.21	2.60	2.79	4.28

Table 2—10. Effect of additives, continued.

			OT-HN-44	OT-HN-45	OT-HN-46	OT-HN-47	OT-HN-48	OT-HN-49	OT-HN-50	OT-HN-51	OT-HN-52	OT-HN-53	OT-HN-54	OT-HN-55	OT-HN-56	TO-HN-61
base oil			N-120-P	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃
addi-tive	name		NH-8-2	〃	〃	NH-10	〃	〃	NH-11	〃	〃	HN-12	〃	〃	HN-4-3	〃
	addn. %		5.0	10.0	15.0	5.0	10.0	15.0	5.0	10.0	15.0	5.0	10.0	15.0	5.0	10.0
viscosity	before test	S_{100}	1,476	1,517	1,551	1,502	1,572	1,631	1,533	1,575	1,617	1,507	1,567	1,621	1,512	1,545
		S_{210}	118.4	119.3	119.3	119.3	121.5	122.0	121.5	121.5	121.5	120.6	120.6	120.6	120.6	121.5
		VI	104.7	103.7	102.2	104.4	104.0	101.5	105.7	103.9	102.1	105.0	103.4	101.0	105.7	105.2
	after test	S_{100}	2,015	1,842	2,001	1,899	1,882	1,920	1,762	1,975	2,039	2,027	1,998	2,013	1,996	1,974
VR			1.365	1.214	1.290	1.264	1.197	1.177	1.149	1.254	1.255	1.275	1.242	1.320	1.320	1.278
PP (°C)			—	−18.0	+9.5	−13.0	−9.5	−14.5	−12.5	—	−15.5	−16.5	−16.5	−15.5	−15.5	−15.5
CC %	before test		0.173	0.305	0.341	0.221	0·242	0.302	0.173	0.251	0.272	0.197	0.297	0.390	0.176	0.222
	after test		0.788	0.783	1.161	0.594	0.650	0.739	0.455	0.747	0.812	0.733	0.850	0.953	0.739	0.774
	CCI		0.615	0.478	0.820	0.373	0.408	0.437	0.282	0.496	0.540	0.536	0.553	0.563	0.563	0.552
volatility loss			1.64	0.89	0.56	1.14	—	1.27	0.84	0.33	1.08	1.39	1.12	1.12	1.12	1.39
AV after test			2.48	4.98	3.83	6.88	4.75	4.33	3.50	4.74	3.76	5.07	5.96	6.13	6.13	8.30

Teble 2—10. Effect of additives, continued.

			OT-HN-107	OT-HN-108	OT-HN-111	OT-HN-112	OT-HN-129	OT-HN-130	OT-HN-131	OT-HN-128	OT-HN-132
base oil			N-120-P	〃	〃	〃	〃	〃	〃	〃	〃
addi-tive	name		NK-2	〃	NK-3	〃	NK-4	〃	NK-5	NK-6	〃
	addn. %		10.0	15.0	5.0	10.0	10.0	15.0	15.0	10.0	15.0
viscosi-ty	before test	S_{100}	1,537	1,556	1,447	1,466	1,510	1,556	1,472	1,519	1,577
		S_{210}	120.9	120.6	118.3	117.6	118.3	119.8	116.8	119.4	119.8
		VI	105.1	103.4	106.3	104.8	103.4	102.7	103.4	104.0	101.7
	after test	S_{100}	1,970	2,095	1,962	1,927	1,927	1,995	1,885	1,895	1,958
VR			1.282	1.346	1.356	1.315	1.276	1.282	1.281	1.247	1.242
PP (℃)			−14.5	−16.5	−11.5	−15.5	−14.5	−10.5	−13.5	−11.5	—
CC %	before test		0.233	0.299	0.143	0.240	0.233	0.267	0.277	0.250	0.304
	after test		0.751	0.916	0.729	0.718	0.777	0.884	0.894	0.752	0.905
	CCI		0.518	0.617	0.586	0.478	0.564	0.617	0.617	0.502	0.601
volatility loss			2.50	3.06	2.50	3.34	—	3.09	2.22	0.83	3.09
AV after test			2.70	3.99	5.59	3.58	3.92	2.30	2.21	2.82	2.69

B as those able to lower it to 0.6 ~ 0.7% and Class C as those which give CCI higher than base oil, the following list can be arranged :

Class A : HN—4—2 (H_2SO_4 10%, clay 15%, topping, H_2SO_4 10%, ciay 20%)
HN—7—1 (H_2SO_4 25%, clay 15%, topping)
HN—10 (H_2SO_4 20% 2, alkali, topping)
HN—11 (H_2SO_4 20% 2, alkali, topping, clay 10%)
HN—12 (H_2SO_4 20% 2, alkali, topping, clay 20%)

Class B : HN—5—1 (H_2SO_4 15, clay 15%, topping)
HN—5—2 (H_2SO_4 15%, clay 15%, topping, H_2SO_4 10%, clay 20%)
HN—6—1 (H_2SO_4 20%, clay 15%, topping)

Class C : HN—4—1 (H_2SO_4 10%, clay 15%, topping)
HN—6—2 (H_2SO_4 20%, clay 15%, topping, H_2SO_4 10%, clay 20%)
HN—7—2 (H_2SO_4 25%, clay 15%, topping, H_2SO_4 10%)
HN—8—1 (topping, H_2SO_4 20% 2, clay 20%).

It is clear that sulfuric acid has remarkable influence on the stabilizing effect of additive. The problem may be discussed later in detail.

2) On VR the effect of additives is recognized more remarkably. Additives which have excellent effect give VR 1.2～1.3, the larger part of them between 1.2～1.4. Under 15% of addition, the blended oil does not show lower VR than base oil. The fact indicates great influences of additives on VR of blended oils. If we divide these additives under Class A' whose blended oil has VR 1.4, Class B' those which give VR 1.4～1.5 and Class C' over 1.5, they may be classified as :

Class C'……includes only Class C for CCI.

Class B'……HN—7—2.

Class A'……all other additives.

Among those of Class A', HN—7—1, HN—10～12 (all class A of CCI), HN—5—1, HN—6—1 (Class B) are superior.

Variation of quantity of each additive produces variation of CCI, VR or other indices with special feature of curve. As for VR, for example, the curve changes with quantity of additive (up to 15% of additives) :

a. Curve of VR simply declines and has no minimum point.
b. Curve of VR initially declines sharply, then it runs almost horizontally.
c. Curve of VR has minimum point.
d. Curve of VR has minimum point then rises and runs almost horizontally.

Four types as above may be observed not only in curves of VR but also in that of CCI, though types c and d may be found in the latter for the most part and consequently the curves of VR and of CCI do not always exhibit the same type. If a curve has type a, large quantity of additives may be allowed so far as other properties do not make the blend inferior. In such cases as these, additives are generally inferior in quality, as, for example, in aircraft lubricating oil, they may be regarded as blending materials or extenders instead of stability agents.

In Table 2—11, are included all the additives used, their process of refining, their yields, types of curves of VR, lowest VR, percentage of addition for minimum value of VR, CCI for minimum value of VR, types of curves of CCI, lowest CCI, percentage of addition for minimum values of CCI, VR for minimum value of CCI, and CC for minimum value of CCI, obtained from the curves of Fig. 2—1～4. Line under certain Figures means that they belong to class VR = 1.5 and CCI = 0.5 Among these, the following values must be noticed.

Additive	% of additive	VR	CCI
HN—7—1	15	1.20	0.49
HN—10	15	1.18	0.44
HN—6—3	15	1.19	0.46

II — 4. Relation between refining treatment and effect of addition. (2)

Influences of individual refining processes must be more clearly understood. Quantity of sulfuric acid, number of times of treatment, and other points will be discussed here.

Influence of quantity of sulfuric acid ————————

1. Sulfuric acid treatment one time.

The process of refining is as follows :

sulfuric acid treatment→clay refining→topping.

In the clay refining, the amount of clay is always 15%, temperature of treatment, 150°C. and its period 30 min. Only the quantity of sulfuric acid is variable. The results are shown in Table 2 — 11. The yield of refined oil amounts to 21 ~ 22% by increasing the quantity of sulfuric acid to 25%. Viscosity indices are all under zero except HN — 7 — 1 where sulfuric acid has been used to 25%. Results of oxidation test for blended oils with those additives are listed once more in Table 2 — 12.

Effects of quantity of refined oil are illustrated in Fig. 2 — 1. Curves of VR decline at first sharply, with quantity of sulfuric acid, then at over 15% of addition, become almost horizontal and near one another, VR being under 1.3. Curves of CCI exhibit distinctly the characteristics of sulfuric acid refining. Curve for oil blended with the additive refined by sulfuric acid of 25% is in lowest position among 4 curves, showing largest influence on CCI and that a large amount of addition has no deleterious effect. Oils with additives refined by a smaller amount of sulfuric acid are inferior as to their action.

Table 2 — 12. Influence of quantity of H_2SO_4

		HN-4-1	HN-5-1	HN-6-1	HN-7-1
acid refining	wt. % of H_2SO_4	10	15	20	25
	yield of refined oil, %	73	68	62	60
clay treatment	wt. % of clay	15	15	15	15
	yield of refined oil, %	63	60	54	53
topping	vol. % of distillate	51.5	58.4	62.0	62.5
	yield of residue	32	26.2	22.6	21.6
viscosity	S_{210}	115.5	121.4	123.7	123.5
	VI	−22.6	− 6.9	− 5.6	+ 6.0

Table 2—11. Course of preparation & effect of additives.

Process for preparation of additives	HN-4-1	HN-4-2	HN-5-1	HN-5-2	HN-6-1	HN-6-2	HN-7-1	HN-7-2	HN-8-1	HN-8-2	HN-10	HN-11	HN-12	HN-4-3	HN-6-3	HN-7-3	HN-S-2	HK-1	HK-2	HK-3	HK-4	HK-5
H_2SO_4 refining	⑩	⑩	⑮	⑮	⑳	⑳	㉕	㉕			⑩× 2	⑩× 2	⑩× 2	⑩	⑳	㉕	⑳					
clay treat.	⑮	⑮	⑮	⑮	⑮	⑮	⑮	⑮			×	×	×	⑮	⑮	⑮	⑳					
topping	○	○	○	○	○	○	○	○	○	○	×	×	×	○	○	○	○	○	○	dilution 1:1		
H_2SO_4 refining		⑩		⑩		⑩		⑩	⑳	⑳	×	×	×	×	×	×	×	⑩	⑩	⑳	⑳	⑳
clay treat.		⑳		⑳		⑳		⑳	×	×	×	×	×	×	×	×	×	×	×	×	×	×
H_2SO_4 refining									⑳	×	×	×	×	×	×	×	×	⑩	⑩	×	×	×
clay treat.									⑳	⑳	×	×	×	×	×	×	×	⑳	⑳	×	×	×
alkali refining											○	○	○	×	×	×	×	×	×	○	○	○
topping											○	○	○	×	×	×	×	×	○	×	×	○
clay treat.												⑩	⑳	×	×	×	×			⑩	⑩	×
Selecto refining														㊿× 2	㊿× 2	㊿× 2	㊿× 2			×	×	×
topping														○	○	○	○			○	○	
yield of additive	32	20.7	26.2	17.4	22.6	15.8	21.6	15.8	13.4	17.7	15.3	14.2	13.0	7.0	8.8	9.3	8.0	30	29	58	50	53
VR type of curve	C	a	C	b	a	d	a	d	b	C	b	d	C	a	a	C	a	C	C			
VR lowest VR	1.28	1.22	1.25	1.27	1.25	1.50	1.20	1.49	1.31	1.21	1.18	1.15	1.24	1.25	1.19	1.28	1.25	1.31	1.28			
VR addition % for lowest VR	5	15 →	10	15 →	15 →	2	15 →	3	5	10	15 →	3.5	8.5	15 →	15 →	10	15 →	10	8			
VR CCI for lowest VR	0.55	0.59	0.56	0.55	0.60	0.73	0.49	0.78	0.64	0.48	0.44	0.28	0.54	0.61	0.46	0.48	0.55	0.54	0.50			
CCI type of curve	d	C	C	b	C	d	C	C	d	C	d	C	C	C	C	C	C	C	C			
CCI lowest CCI	0.44	0.54	0.50	0.54	0.45	0.73	0.48	0.78	0.60	0.48	0.36	0.28	0.54	0.54	0.45	0.48	0.50	0.53	0.50			
CCI addition % for lowest CCI	3	4	4	10	5	2	4	3	4	10	3.5	5	5	9	13.5	11	12.5	8	8			
CCI VR for lowest CCI	1.33	1.38	1.28	1.31	1.31	1.50	1.34	1.49	~1.4	1.21	1.31	1.15	1.28	1.28	1.20	1.28	1.28	1.32	1.28			
CCI CC for lowest CCI	0.72	0.72	0.66	0.75	0.62	0.90	0.66	0.93	0.75	0.78	0.52	0.45	0.73	0.75	0.66	0.64	0.77	0.72	0.72			

Effects of quantity of sulfuric acid are illustrated in Fig. 2—1. Curves for VR are somewhat complicated. Substantially, the more the quantity of the acid, the lower the curves with points of inflection, which are found between 15~20% of H_2SO_4 quantity. Position of curves under 15% of the acid are irregular. Curves for CCI go lower with increase in quantity of the acid. CCI for the blend which contains larger quantity of additive is higher the curve showing larger inclination for the acid quantity.

Table 2—13 Influence of sulfuric acid

			N-120-P	HN-4-1	HN-5-1	HN-6-1	HN-7-1
wt. % of H_2SO_4			—	10	15	20	25
yield of raffinate, wt. %			—	32	26.2	22.6	21.6
Properties		S_{210}	119.3	115.5	121.4	123.7	123.5
		VI	107.5	−22.6	− 6.9	− 5.6	6.0
addition percentage of additive	5%	S_{210}	*119.3	121.1	119.3	118.4	118.4
		VI	*107.5	106.6	105.2	104.3	104.5
		VR	* 1.89	1.28	1.27	1.31	1.31
		CCI	* 0.81	0.55	0.50	0.48	0.48
	10%	S_{210}	—	118.4	119.3	119.7	118.4
		VI	—	102.9	103.3	103.5	103.1
		VR	—	1.29	1.25	1.26	1.24
		CCI	—	0.70	0.56	0.47	0.50
	15%	S_{210}	—	118.4	119.3	120.4	118.4
		VI	—	100.5	101.7	101.4	101.0
		VR	—	1.30	1.27	1.25	1.20
		CCI	—	0.95	0.69	0.60	0.49

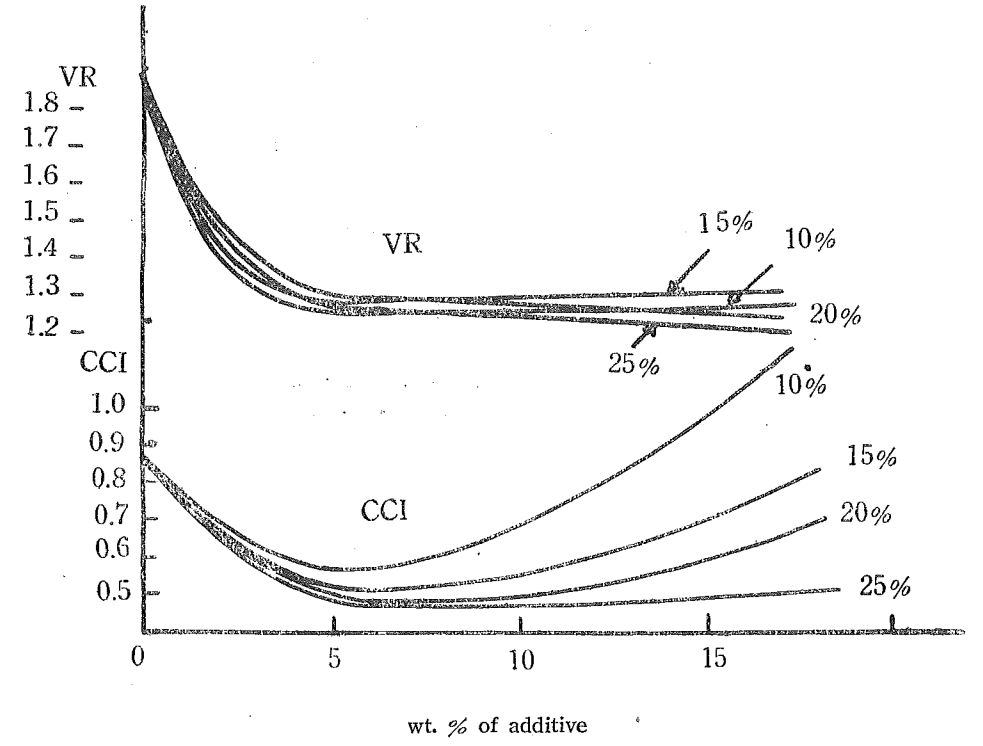
* : the base oil NH—120 without additives.

2. Double treatment by sulfuric acid.

The process of refining is as follows :

sulfuric acid treatment→clay treatment→topping→
sulfuric acid treatment→clay treatment.

In this case, amount of sulfuric acid was varied only for the first treatment, that for the second treatment being constant, viz., 10%. For the first treatment clay was used to the amount of 15% and that for the second was 20%. Yield of refined oils and their properties are listed in Table 2—14 and behaviors of their blended oils in Table 2—15. CCI and VR plotted by quantity of additive and those plotted by quantity of sulfuric acid are illusrated in Fig 2—3 and 2—4 respectively. It must be noted that curves of CCI plotted by quantity of addition of improvers



Fgi. 2—1 Effect of quantity of additives

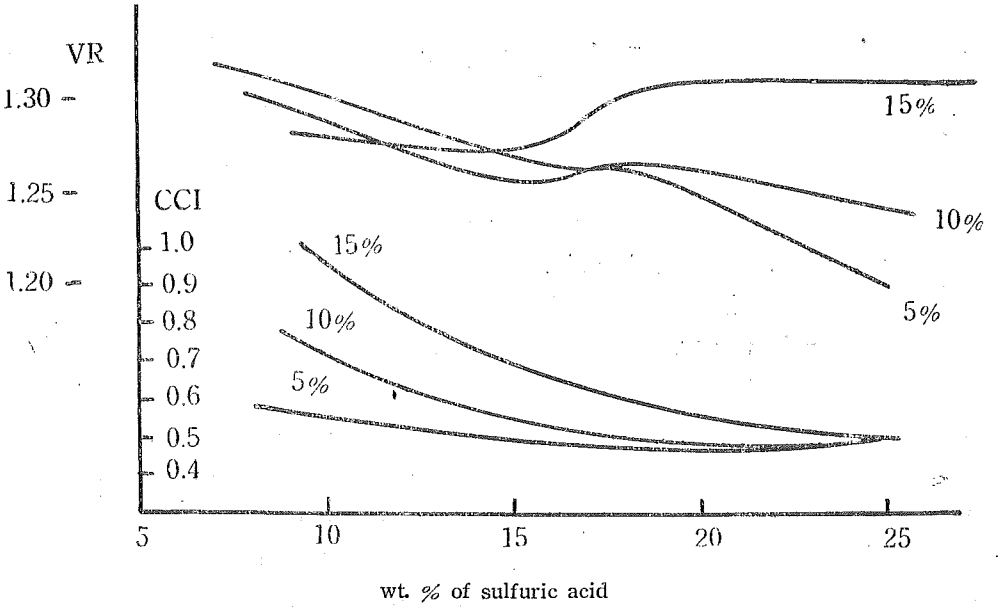


Fig. 2—2 Effect of quantity of sulfuric acid for refining mineral oil.

are grouped into two types, that is, curves for blended oil of additives treated by 20 and 25% of sulfuric acid for the first treatment are far apart from the others, being in far higher position. In other words, additives treated by a large amount of sulfuric acid (for the first treatment over 20%, for the second 10%, that is together over 30%.) are very inferior in action as improvers. They even cause deterioration when added over 10% to the base oil. On the other hand additives treated by sulfuric acid by 10~15% for the first treatment (in toto 20~25%) behave profitably, that is, decrease CCI distinctly. Curves for VR behave similarly to these for CCI. These facts suggest that a kind of inhibitors or essential part of additives naturally contained in crude oil may be removed by excess treatment of sulfuric acid and a boundary may exist in the effects of an amounts between 25 and 30% of total sulfuric acid. Curves plotted by sulfuric acid quantity sharply rise between 15 and 20% (or totally 25 and 30%) of sulfuric acid. Curves for VR and CCI are similar. Additives refined by 10 and 15% of sulfuric acid give VR 1.3 ~ 1.4 when added to the amount of 5%, and lower than 1.3 when added in larger quantity. Also they provide oils of CCI of 0.5 ~ 0.6. Contrary to these, additives refined by 20 to 25% of sulfuric acid (or in toto 25 ~ 30%) give VR over 1.54 and CCI over 0.8.

Table 2 — 14. Preparation of additives

			HN-4-2	HN-5-2	HN-6-2	HN-72-
wt. % of H_2SO_4 for the lst treatment			10	15	20	25
yield of raffinate, wt. %			73	68	62	60
yield of clay treated raffinate, wt. %			63	60	54	53
wt. % of residue by topping			32.0	26.2	22.6	21.6
wt. % of H_2SO_4 for the 2nd treatment			10	10	10	10
yield of raffinate, wt. %			26.3	21.3	19.6	18.9
total quantity of H_2SO_4 used, wt. %			20	25	30	35
yield of clay treated raffinate, wt. %			20.7	17.4	15.8	15.8
comparison of yield	simple treatment		32.0	26.2	22.6	21.6
	double treatment		20.7	17.4	15.8	15.8
	difference		11.3	8.8	6.8	4.8
properties	product by simple treatment	S_{210}	115.5	121.4	123.7	123.5
		VI	−22.6	− 6.9	− 5.6	+ 6.0
	product by double treatment	S_{210}	93.7	106.2	115.2	112.2
		VI	−0.84	5.4	5.7	4.2

3. Comparison of simple treatment and double treatment by sulfuric acid.

Table 2—15. Effect of additives

			HN-4-2	HN-5-2	HN-6-2	HN-7-2
percentage of addition of raffinate prepared by double treatment of sulfuric acid	5%	S_{210}	118.4	118.8	119.7	119.3
		VI	105.6	106.1	105.9	105.1
		VR	1.35	1.38	1.54	1.53
		CCI	0.54	0.55	0.83	0.80
	10%	S_{210}	118.0	118.8	118.4	118.4
		VI	104.8	104.4	103.1	103.7
		VR	1.29	1.31	1.61	1.60
		CCI	0.58	0.54	1.07	1.02
	15%	S_{210}	115.8	118.4	118.4	118.4
		VI	102.1	102.6	101.2	101.6
		VR	1.22	1.29	1.64	1.64
		CCI	0.47	0.55	1.17	1.20

Table 2—16. Comparison of H_2SO_4 refining.

			HN-3-1	HN-4-2	HN-7-1	HN-5-2
wt. % of H_2SO_4 for 1st. treatment			20	10	25	15
wt. % of H_2SO_4 for 2nd treatment			—	10	—	10
yield of raffinate, wt. %			22.6	20.7	21.6	17.4
properties		S_{210}	121.7	93.7	123.5	106.2
		VI	− 5.6	−0.84	+ 6.0	+ 5.4
Percentage of addition of raffinate prepared by simple and double treatment of H_2SO_4	5%	S_{210}	118.4	118.4	118.4	118.8
		VI	104.3	105.6	104.5	106.1
		VR	1.31	1.35	1.31	1.36
		CCI	0.48	0.54	0.48	0.55
	10%	S_{210}	119.7	118.0	118.4	118.8
		VI	103.5	104.8	103.1	104.4
		VR	1.26	1.29	1.24	1.31
		CCI	0.47	0.58	0.50	0.54
	15%	S_{210}	120.4	115.8	118.4	118.4
		VI	101.4	102.1	101.0	102.6
		VR	1.25	1.22	1.20	1.29
		CCI	0.60	0.47	0.49	0.55

As for simple treatment by sulfuric acid, the effect upon blened oil by additives as expressed by VR and CCI was most excellent in the case of refining by 25% of the acid, next by 20%. As for double treatment by the acid, the most excellent result was obtained in the case of refining by 20 and 25%, the former

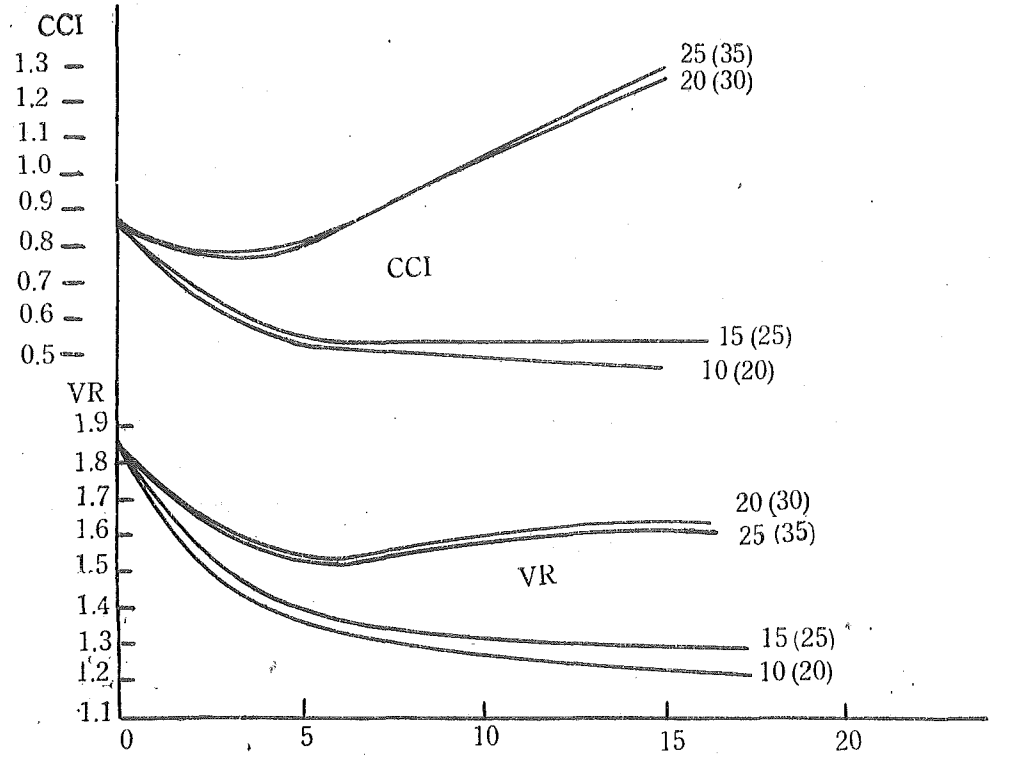


Fig. 2—3 Effect of treatment by sulfuric acid.

Figures at the end of curve means percentage of the acid used for the first time, that in the bracket total amount used.

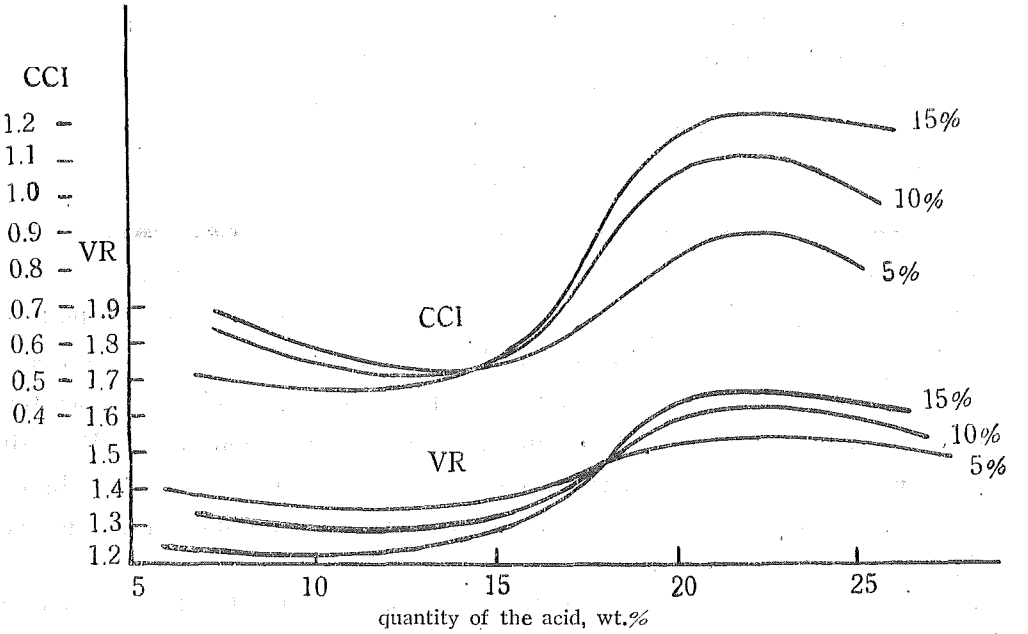


Fig. 2—4 Effect of treatment by sulfuric acid.

being somewhat superior. Additive refined once by 20% of the acid was a little superior compared with that refined twice by 10% and 10%. In Table 2—16 as directly comparable cases, additives refined simply and separately by 20 and 25% of the acid are shown, yield of additives by simple treatment of the acid are better than that of double treatment, total quantity of the acid being the same, thus 22.6% for the former, 20.7% for the latter, in the case of 20% of sulfuric acid. As simpler treatment results in higher yield and excellency in action, there's no question which method should be adopted.

4. Effect of sulfuric acid quantity and of extraction by "Selecto".

Process of preparation is as follows:

sulfuric acid refining→clay treatment→topping→extraction.

Quantities at all stages are definite except that of sulfuric acid refining, in which the amount of the acid is varied from 10 to 25%. Yield by each step and properties of additives thus obtained are listed in Table 2—17.

Table 2—17. Yield and properties of raffinate.

			HN-4-3	HN-5-3	HN-6-3	HN-7-3
sulfuric acid	wt. % of H_2SO_4		10	15	20	25
treatment	yield (for crude oil)		73	68	62	60
clay treat-	wt. % of clay		15	15	15	15
ment	yield (for crude oil)		63	60	54	53
topping	% of topping		66.5	66.5	66.5	66.5
	residue (for crude oil)		22.7	20.0	18.6	18.1
yield of raffinate by Selecto %			7.0	7.6	8.8	9.0
properties	topped oil	S	242.7	197.5	154.6	142.3
of oils		VI	—	− 9.0	− 1.5	0.84
	raffinate	S	147.1	132.6	122.6	121.4
	by Selecto	VI	59.5	48.4	49.1	54.2

Several characters may be recognized from the table. 1) Yield of residue falls as quantity of the acid increases, 2) Yields of oils extracted by Selecto increase as amount of the acid increases, 3) Viscosity indices of extracted oils are high, but a generalization regarding the amount of the acid can not be drawn. Actions of additives thus obtained are summarized in Table 2—18. Though no obvious functional relation can be deduced, VR declines as amount of addition grows. By adding to the amount of 10%, VR is in the range of 1.25～1.3, 10% addition exhibiting largest effect. Also in CCI, the features of the effect are roughly similar to those in VR.

From these results, it may be concluded that oil extracted by the solvent would be able to be added in larger quantity, though the upper limit of quantity of the

acid would be 20%, and that the yield of extracted oils would not be over 10%, though it would be 22～30% when the acid is used once followed by no more extraction. Further it is pointed out that additives produced by extraction as is described here do not always exhibit higher performance than additives obtained by simple treatment of sulfuric acid followed by no more extraction. It is natural that one would select the latter course of refining in practical utilisation.

5. Additives produced from heavy oil.

The heavy oil was a bottom of a Niitsu oil, the gravity being 13° Bé, flash point 212°C, viscosity 309 R (100°C). The course of refining, yield, properties of additive thus obtained and effect of addition are shown in Table 2—19.

Table 2—18. Action of additives

			HN-4-3	HN-6-3	HN-7-3
percent of addition of additive	5%	S_{210}	120.6	119.3	120.6
		VI	105.7	105.2	106.6
	10%	VR	1.320	1.402	1.415
		CCI%	0.563	0.582	0.615
		S_{210}	121.5	120.6	120.6
		VI	105.2	104.7	105.2
		VR	1.278	1.260	1.281
		CCI%	0.552	0.553	0.480
	15%	S_{210}	122.4	120.6	120.6
		VI	102.8	103.9	104.4
		VR	1.246	1.180	1.334
		CCI%	0.614	0.281	0.653

Two additives by the direct sulfuric acid refining of the heavy oil, 4 additives by dilution with kerosene followed by the acid refining were obtained. Their effects of their action are comparatively large. At 5～10% of addition optimum points are generally found. It is likely that additives treated after dilution by kerosene are more active than those withont dilution, for example, in a case of addition of 10%, VR of the former was 1.32, 1.28, 1.25 and of the latter 1.31, 1.35.

Conclusion.

What is the best for practical use may be deduced from the results described above. The additive which is capable of producing a blended oil having lowest VR, CCI and CC, and producible by the simplest course of refining and with highest yield is the most desirable. Results obtained hitherto show that some of the additives refined by the course——sulfuric acid refining, clay treating and topping——

Table 2—19. Additives prepared by petroleum residue.

			HK-1	HK-2	HK-3	HK-4	HK-5	HK-6
course of refining	dilution by kerosene		×	×	1 : 1	1 : 1	1 : 1	1 : 1
	H_2SO_4 refining, wt. %		10	10	20	20	20	20
	alkali washing		×	×	×	×	0	0
	topping of diluent		×	×	×	×	0	0
	topping under vacuum		×	×	×	×	×	0
	H_2SO_4 refining		10	10	×	×	×	×
	clay treatment		20	20	10	10	×	×
	topping of diluent		×	×	0	0	×	×
	topping under vacuum		×	0	×	0	×	×
	yield *		30	29	58	50	53	46.7
properties of resultant oil		S	105.4	122.0	95.2	123.7	91.7	118.4
		VI	18	19	23	15.2	18	13
weight percent of addition	5 %	S	119.3	120.9	118.3	—	—	—
		VI	105.6	105.1	106.3	—	—	—
		VR	1.34	1.28	1.36	—	—	—
		CCI	0.57	0.52	0.59	—	—	—
	10%	S	119.3	120.6	117.6	118.3	—	119.4
		VI	104.9	103.4	104.8	103.4	—	104.0
		VR	1.31	1.35	1.32	1.28	—	1.25
		CCI	0.54	0.62	0.48	0.56	—	0.50
	15%	S	119.3	118.3	—	119.8	116.8	119.8
		VI	103.2	106.3	—	102.7	103.4	101.7
		VR	1.33	1.36	—	1.28	1.28	1.24
		CCI	0.64	0.59	—	0.62	0.62	0.60

and that those refined by the course——sulfuric acid refining, alkali refining, clay treatment and topping—— are comparable in performance and the most powerful. The latter is more effective than the former, whose course of treatment is distinctly simpler. In the course of alkali refining persistent emulsion is likely to be produced, and the yield of oil naturally declines. Overall yield of additives by the simpler way may amount to 19～23%, though that by the course including alkali refining comes to about 13～15%.

In conclusion, it is possible to obtain powerful additives for the synthetic oil NH—120 by means of relatively simple course, such as sulfuric acid refining whose quantity is within the range of 20～25%, treating by 20% of clay and topping to the viscosity of $S_{210} \simeq 120$. These additives may produce blended oils whose VR $\simeq$ 1.3 and CCI 0.5.

CHAPTER III

Effect of additives of refined Seria oil and several commercial oils.

In the previous chapter, the behavior of Niitsu oil refined by means of a relatively simple process was observed in respect to its stabilising action upon the synthetic lubricating oil NH—120. The most part of the additives refined by various means behaved as powerful improvers. As they were further recognized as diluents of the synthetic oil, it might be deduced that the amount of production of viscous oil of high quality could be increased by the amount of addition of the refined oil. But from another point of view, the Niitsu crude oil is the most important source of lubricating oil, whose shortage would seriously disturb home supply. This required a substitute for Niitsu oil as additive. That is one reason why the author undertook to study Seria and other commercial oils.

Treatment of Seria crude oil was almost the same as that of Niitsu oil. Effects of addition were tested on blended oils which contained additives to the same amount, that is, 10%. Generally speaking, the effects of them were far inferior to the effect of Niitsu oil, sometimes even causing deterioration. If it was permitted that VR and CCI of blended oil might be large enough within the limits of a specification (that is VR < 2.0, CCI $< 1.0\%$), the refined oil could be used in relatively large amount, being recognized rather as a diluent. Lowest VR attained in this study was about 1.4 at the best and lowest CCI about 0.7%.

The idea that improving the properties of synthetic oil and increasing its quantity by means of dilution with refined crude or commercial oils which are not of high performance, may be reasonable from the standpoint of enhancing production of home supply of high quantity lube and of reclaiming low quality lubes. For the purpose of utilizing Niitsu oil and commercial oils as extenders for high quality oils, several experiments were carried out with satisfactory results to a certain extent.

III—1. Refined oil from Seria crude.

It is well known that Borneo crude oil has been used as raw material for lubricating oil because of its poor content of light fraction, though it is not suitable for manufacturing good lubricating oil on account of its extremely low viscosity index. It may be unfavorable for use as a lubricant for high speed internal com-

bustion engines. In order to produce oil of high quality out of the oil, the following means may be considered :

1. Reforming the chemical structure of the oil in order that it might be made suitable for high duty purpose.
2. Blending it with oil of high performance.
3. Blending it with fatty oil of high viscosity index.

No's 1 and 3 are out of consideration in the author's researches, only 2 coming to the front. The aim is to see whether Seria oil (a sort of Borneo oil) might be used as a substitute for Niitsu oil as studied in the preceding chapter.

Preparation of additives.

Seria crude oil topped or not was refined by means of treatments such as sulfuric acid, active clay or alkali or their combinations, being topped to the viscosity of $S_{210}\simeq 120$ at the end.

Crude oil—(received on 9 May, 1943 from the Toa Petroleum Co.)

distillation test (sample II.)

initial	5%	10	15	20	25	30
81°C	226	239	251	263	274	278

The following points were observed :

1) In the case of treating the crude by conc. sulfuric acid.—Most part of sludge settled relatively easily, leaving small amount of it finely and persistently dispersed in acid oil. Black acid oil followed by clay treating revealed difficulty of filtration. Finished oil was dark. Increasing sulfuric acid quantity made oil darker.
2) In the case of treating the crude by dil. sulfuric acid.—Settling of sludge produced was slower than in 1. Sludge dispersed in acid oil was in small quantity. Coloring of finished oil was a little better.
3) Alkali treatment of acid oil from the crude oil was comparatively easier than that of acid oil from heavy oil of the crude, the latter forming persistent emulsion.

Samples prepared were classified into 4 groups, from the standpoint of :

a. effect of amount of sulfuric acid (10, 15, 20%)
b. effect of amount of clay when quantity of the acid was held constant, (10, 15, 20%)
c. effect of alkali treatment when quantity of the acid varied, and
d. effect of concentration of sulfuric acid (80, 85, 90, 98%).

Preparative method and yield for these groups are shown in Table 3—1~3. Yield of oil refined by sulfuric acid amounts to 89~91%, that of final product successively refined and topped to $S_{210}\simeq 120$ to about 30~40% bottom, the yield being higher

than that of Niitsu oil. Owing to its high yield it is sufficient to refine a smaller quantity of the crude for a definite amount of the base oil. Together with eleven samples thus prepared, two more samples, viz., HSe — 120 and HSe — 160 were blended to the base oil in a definite amount, that is, 10%. These HSe — 120 and HSe—160 mean #120 and #160 oils respectively, both of which are obtained by topping HSe — 2 to a suitable grade. HSe—R means residual oil of HSe — 10 topped under vacuum of 1.0 mmHg as far as possible.

Table 3 — 1. Rafining of Seria crude oil

		HSe-2	HSe-5	HSe-7	HSe-8	HSe-9
acid refining	amount of addn. of acid, wt. %	10	15	20	20	20
	yield of acid oil wt. %	91.3	89.5	88.9	88.9	88.9
clay treatment	amount of addn. of clay, wt. %	15	15	10	15	20
	yield of filtered oil wt. %	86.7	84.7	88.0	84.0	81.3
	its yield to raw oil wt. %	79.2	75.8	78.2	74.7	72.3
topping to 275°C topping under vac.	vol. % of distillate	30.0	32.7	27.6	28.1	30.4
	vol. % of distillate	20.7	20.0	26.8	26.1	24.4
	overall vol. %	50.7	52.7	54.4	54.2	54.8
bottom	yield to clay-treated oil vol. %	48.4	47.3	45.6	45.8	45.2
	yield to clay-treated oil wt. %	50.9	49.7	47.9	48.1	47.6
	yield to raw oil wt. %	40.3	37.7	37.5	35.9	34.3

Table 3 — 2. Refining of Seria crude oil.

		HSe-10	HSe-11	HSe-12
acid refining	amount of addn. of acid, wt. %	10	15	20
	yield of acid oil wt. %	91.3	89.5	88.9
alkali washing	amount of alkali (4% sol. vol. %)	10	10	10
	yield of washed oil wt. %	66	56	62
	〃 to raw oil wt. %	60.3	50.0	55.1
topping to 275°C toping under vac.	vol. % of distillate	20.5	22.5	20.0
	vol. % of distillate	27.8	27.0	27.7
	overall vol. %	48.3	49.5	47.7
bottom	yield to clay-treated oil, vol. %	51·7	50.5	52.3
	yield to clay-treated oil, vol. %	54.0	52.8	54.7
	yield to raw oil	32.6	26.5	30.1

Table 3—3. Refining of Seria crude oil.

		HSe-8	HSe-23	HSe-24	HSe-25
acid refining	concentration of H_2SO_4, %	98	90	85	80
	amount ofacid wt. %	20	20	20	20
	yield of acid oil wt. %	88.9	92.8	93.8	93.2
clay treatment	amount of clay wt. %	15	15	15	15
	yield of filtered oil wt. %	84.0	84.1	83.2	82.8
	its yield to raw oil wt. %	74.7	78.0	78.0	77.2
top. to 275°C	vol. % of distillate	28.1	26.7	26.4	25.8
〃 under vac.	vol. % of distillate	26.1	25.1	25.4	26.3
	overall vol. %	54.2	51.8	51.8	52.1
bottom	yield to clay-treated oil, vol. %	45.8	48.2	48.2	47.9
	yield to clay-treated oil, wt. %	48.1	50.6	50.6	50.3
	yield to raw oil, wt. %	35.9	39.5	39.5	38.8

III—2. Effect of additives from Seria oil.

Additives prepared from Seria oil as described in the preceding section were blended to NH—120, a hydrogenated synthetic oil, to which some detailed reference was made in Chapter I. 10% of the additives was used throughout tests. Results obtained are shown in Table 3—4 and in Fig 3—1～2.

(1) Effect of amount of sulfuric acid.——The course was as follows:

sulfuric acid refining→clay treatment→topping.

Amount of clay used here was definitely 15%, while that of the acid was varied. The behavior is as shown in Fig 3—1—(I). In proportion as amount of acid increased, VR decreased, as 1.65, 1.63 and 1.60; CCI also decreased as 0.83, 0.77 and 0.78.

(2) Effect of amount of clay.——The course of refining is the same as above. Amount of clay was varied as 10, 15 and 20%, while that of sulfuric acid was kept constant. The behavior is shown in Fig 3—1—(II), in which both VR and CCI are at the lowest for 15% clay, otherwise they increase.

(3) Effect of alkali treatment.——The course of refining is as follows:

sulfuric acid refining→alkali refining→topping.

Four percent caustic soda concentration was used in 10%, after refining by sulfuric acid, amount of which varied as 10, 15, and 20%. This course may be compared to (I). The behavior is shown in Fig 3—1—(III). The smallest amount, viz., 10%, of sulfuric acid produces the lowest VR and CCI, that is VR=1.47,

Table 3—4. Effect of additives prepared from Seria oil.

			OT-Se 50	OT-Se 51	OT-Se 52	OT-Se 53	OT-Se 54	OT-Se 55	OT-Se 1	OS-Se 56	OT-Se 57	OT-Se 58	OT-Se 59	OT-Se 60	OT-Se 61
base oil			N-120-P	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃
additive	name		HSe-2	HSe-5	HSe-8	HSe-23	HSe-24	HSe-25	—	HSe-10	HSe-11	HSe-12	HSe-7	HSe-8	HSe-9
	addn. %		10	〃	〃	〃	〃	〃	—	10	〃	〃	〃	〃	〃
viscosity (cst)	before oxidn.	V_{100}	326.7	328.1	329.9	330.8	335.9	330.0	310.8	334.7	327.3	330.0	339.3	329.9	329.6
		V_{210}	24.70	24.73	24.82	24.79	25.03	24.76	24.89	25.08	24.80	24.90	25.27	24.82	24.83
		KVI	104.0	103.9	103.8	103.5	103.4	103.6	108.4	103.9	104.3	104.1	103.7	103.8	104.0
	after oxidn.	V_{100}	538.6	536.0	529.1	513.4	506.5	497.4	586.8	490.4	500.8	507.0	655.7	529.1	577.0
		V_{210}	34.00	33.70	33.49	32.98	32.68	32.49	36.68	32.30	32.79	33.07	38.93	33.49	35.51
		KVI	102.1	97.3	98.9	102.3	102.3	103.0	103.4	103.3	103.4	103.4	102.4	98.9	101.9
VR (100°F)			1.65	1.63	1.60	1.55	1.51	1.51	1.89	1.47	1.53	1.54	1.93	1.60	1.75
CC %	before oxidn.		0.148	0.156	0.146	0.164	0.184	0.200	0.076	0.172	0.192	0.182	0.198	0.146	0.138
	after oxidn.		0.980	0.930	0.924	0.934	0.941	0.884	0.878	0.852	0.864	0.940	1.392	0.924	1.140
	CCI		0.832	0.774	0.778	0.770	0.757	0.684	0.802	0.682	0.672	0.758	1.194	0.778	1.002
volatility loss			—	3.1	3.1	3.3	2.8	3.3	2.2	3.6	3.9	3.9	3.9	3.1	3.6

Table 3—4. Effect of additives prepared from Seriaoil, continued.

			OT-Se-62	OT-Se-63	OT-Se-64	OT-Se-65	OT-Se-66	OT-Se-67	OT-Se-68	OT-Se-69	OT-Se-70	OT-Se-71	OT-Se-72
baseoil			N-120-P	〃	〃	〃	〃	〃	〃	〃	〃	〃	〃
addtivie	name		HSe-120	〃	〃	〃	HSe-160	〃	〃	Seria bottom	〃	〃	〃
	addn. %		2.5	5.0	10.0	15.0	2.5	5.0	10.0	1.0	3.0	5.0	10.0
viscosity (cst)	before oxidn.	V_{100}	317.0	323.9	326.0	339.5	516.7	530.2	548.0	322.2	346.8	375.6	459.2
		V_{210}	24.82	24.82	24.73	24.64	34.47	34.39	34.21	25.74	26.88	28.14	31.57
		KVI	106.7	105.7	104.1	100.9	105.9	104.2	101.6	109.2	108.4	107.5	105.4
	after oxidn.	V_{100}	562.2	563.6	566.3	603.0	843.1	825.2	879.9	570.0	548.8	561.2	648.1
		V_{210}	35.49	35.34	34.71	35.67	46.67	45.57	46.37	36.53	35.82	36.38	39.77
		KVI	103.4	102.9	100.9	99.5	103.3	102.6	100.4	105.1	105.7	105.7	104.9
VR (100°F)			1.77	1.74	1.74	1.78	1.63	1.56	1.61	1.77	1.58	1.49	1.41
CC %	before oxidn		0.100	0.116	0.138	0.152	0.128	0.138	0.154	0.132	0.250	0.386	0.710
	after oxidn.		1.060	1.068	1.070	1.146	0.942	0.936	1.052	0.996	1.110	1.200	1.428
	CCI		0.960	0.952	0.932	0.994	0.814	0.798	0.898	0.864	0.860	0.814	0.718
volatility loss			2.4	2.8	3.5	3.9	—	—	—	1.4	1.7	1.9	1.9

CCI = 0.68.

(4) Effect of concentration of sulfuric acid.——The course of refining is the same as in (I). Here was used sulfuric acid of various concentrations as 80, 85, 90 and 98%, the amount added being 20% throughout.

The behavior is illustrated in Fig 3—1—(IV). Both VR and CCI are the lowest in the case of concentration of 80%, that is VR = 1.51, CCI = 0.68. It may be concluded that concentrated acid would produce less effective additive.

From (1), (2) and (4), it may be deduced that when the amount of clay is fixed constant at 15%, over 10% of 98% sulfuric acid and the acid of 80% in concentration might be the most suitable, and that when sulfuric acid used is 15% in amount 15% of clay is suitable. In conclusion, treatment by 20% of 80% H_2SO_4 and 15% clay produced the best additive, the blend of which gave VR = 1.51, CCI = 0.68 and CC = 0.88. The data might not be called as excellent, though there might be some allowance for VR < 2.0 and CCI < 1.0. In case of another way of raffination including alkali treatment better results were gained, such as VR = 1.47, CCI = 0.68 and CC = 0.85.

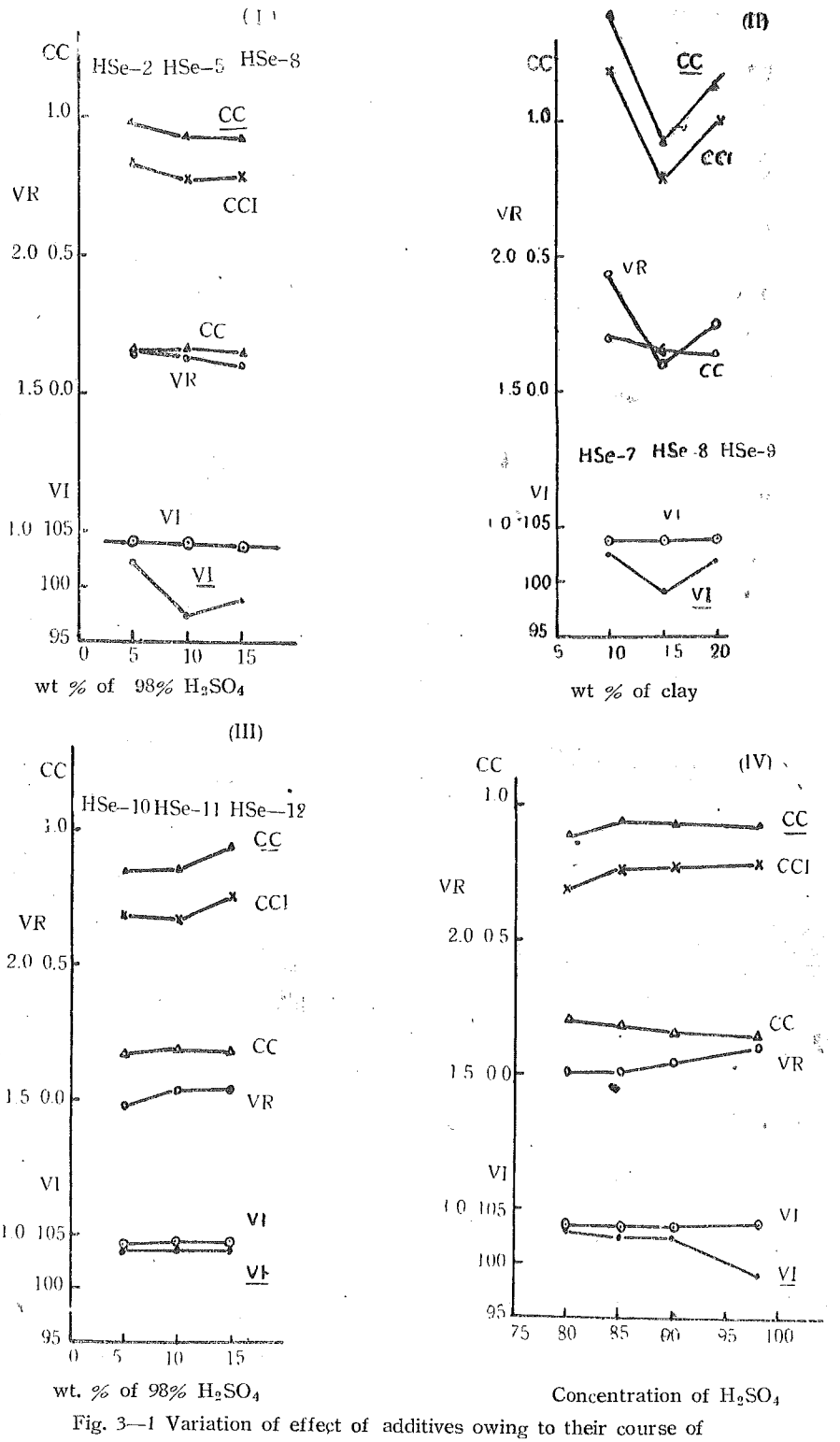


Fig. 3—1 Variation of effect of additives owing to their course of refining. (wt. % of additives are fixed as 10%)

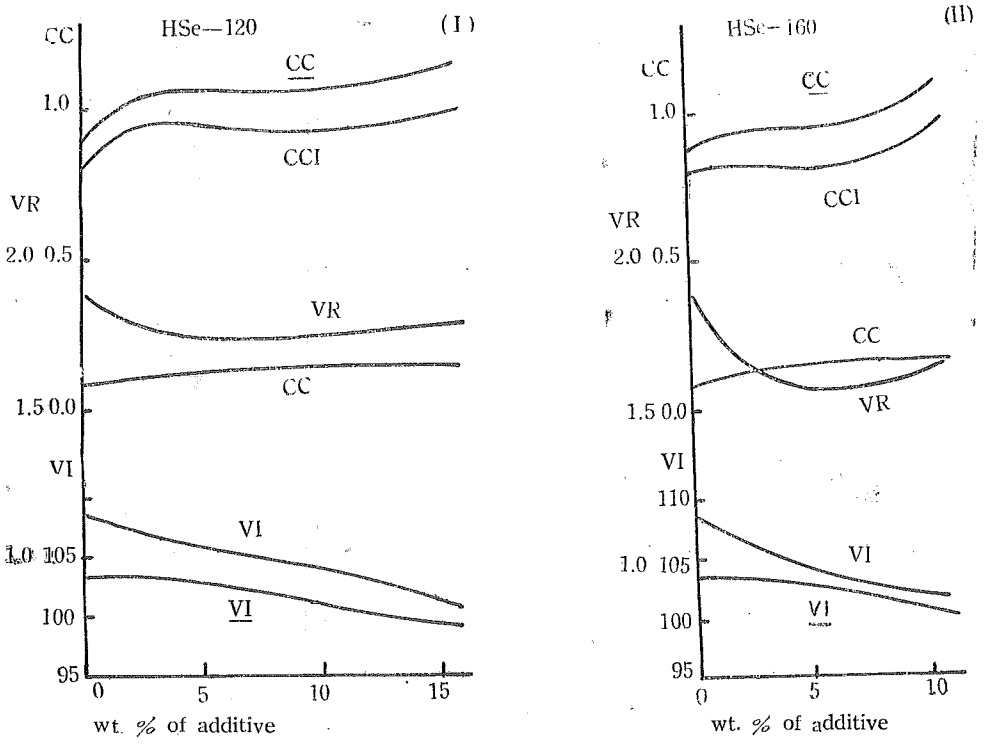


Fig. 3—2 Effect of concentration of additives

Further additives HSe—120, HSe—160 and HSe—R were added to NH—120 in various quantities, and tested to see how the stability of blends was influenced according to quantity of addition.

Results are shown in Table 3—4 and Fig 3—2—(I), (II) and (III).

III—3. Effect of addition of commercial mineral oils.

In I—3 a commercial mineral oil (TK) was found to have remarkable effect to improve stability of NH—120. In the preceeding Chapter and III—2 some mineral oil fraction which may be regarded as lubricating oil with suitable viscosity were used as effective addition agent to improve stability with satisfactory results in many cases. Here the author reached a point in his studies where he had to see if other commercial lubricating oils easily available were effective as above.

He selected several oils such as Gulf-Pride, City Services and Phillips which were of comparatively high quality but out of specification (VI > 100, CCI < 1.0, CC < 2.0), and PNHC, a #120 lube from Niitsu oil which was inferior in various points. Their properties are shown in Table 3—5, including that of base oil NH—120. The reasons why the former 3 oils were selected are that at the beginning of the Great War II the Army and Navy of Japan stocked large amounts of the oils for the purpose of use in high-duty air craft engines, without satisfactory results because of their slight inferiority in viscosity index and stability as might be seen in the Table. The author also believed them to be available for additives or more strictly speaking, diluents for hydrogenated synthetic oil NH—120 in order to produce larger amounts of aero oil with sufficiently high performance.

These lubricants were added to base oil to the amount of 0.5, 10, 15, 25, 50 and 100%, with subsequent tests for stability. The larger range of addition was to see not only the effect to improve stability but also the effect as the diluent.

Results obtained including that of PNHC are shown in Table 3—6~3—7, and illustrated in Fig 3—3~3—6.

Three oils except PNHC and NH—120 had similar properties, such as viscosity at 210°F (ca. 26 cst), viscosity index (ca. 80), CC (0.47~0.86%), VR (1.54~1.60) and CCI (1.63~1.95). These were inferior in viscosity index and carbon increase, frequently producing deterioration and ring-sticking in engine service.

(1) City Services——Adding 37% and 73% of it produces blended oil of 100 VI and 90 VI respectively. Permitting VI up to 90, blending ratio may be thus : NH—120 1 to City Services 3. VR is the lowest (that is 1.40) at 35% addition, CCI being the lowest at 15% addition.

Table 3—5. Properties of base oil and additives.

		N-120-P	City Service	Phillips	Gulf Pride	P_{NHC}
S_{100}	before oxidn.	323.4	454.8	460.0	493.6	829.7
S_{210}	〃	25.31	26.06	26.03	25.84	27.27
VI	〃	107.4	83.5	82.2	80.4	20.4
S_{100}	after oxidn.	551.2	717.5	708.3	743.8	497.0
S_{210}	〃	35.20	35.40	35.08	36.06	72.34
$\underline{VI}$	after oxidn.	103·9	86.2	86.1	85.7	10.3
VR		1.70	1.58	1.54	1.60	2.82
VR		1.39	1.35	1.35	1.40	5.99
CC%		0.09	0.86	0.65	0.47	2.06
$\underline{CC}$%		0.97	2.49	2.60	2.19	6.99
CCI%		0.88	1.63	1.95	1.72	4.93

(2) Phillips——Almost similar to (I). For VI 100 and 90 of blended oil 36% and 74% may be sufficient. The lowest VR (1.43) and CCI are obtained by 30% addition.

(3) Gulf-Pride——Resembles closely (1) and (2). The lowest VR (1.34) and CCI (0.6) are obtained by 30% and 15% additions respectively.

(4) Niitsu oil, P_{NHC}——Effect of addition differs remarkably from oils above described. CC increases approximately linearly with increasing in addition. By addition of 50% and 100% CC values are ca. 1% and 2.1% respectively. The lowest $\underline{CC}$ (0.77%) and CCI (0.6%) are observed at 5% addition, 3.5% $\underline{CC}$ (very large) at 50% addition, the lowest VR (1.26) at 5~10% addition. Contrary to the case with other commercial oils used previously, the range of effective addition is far narrower, but with distinct influences.

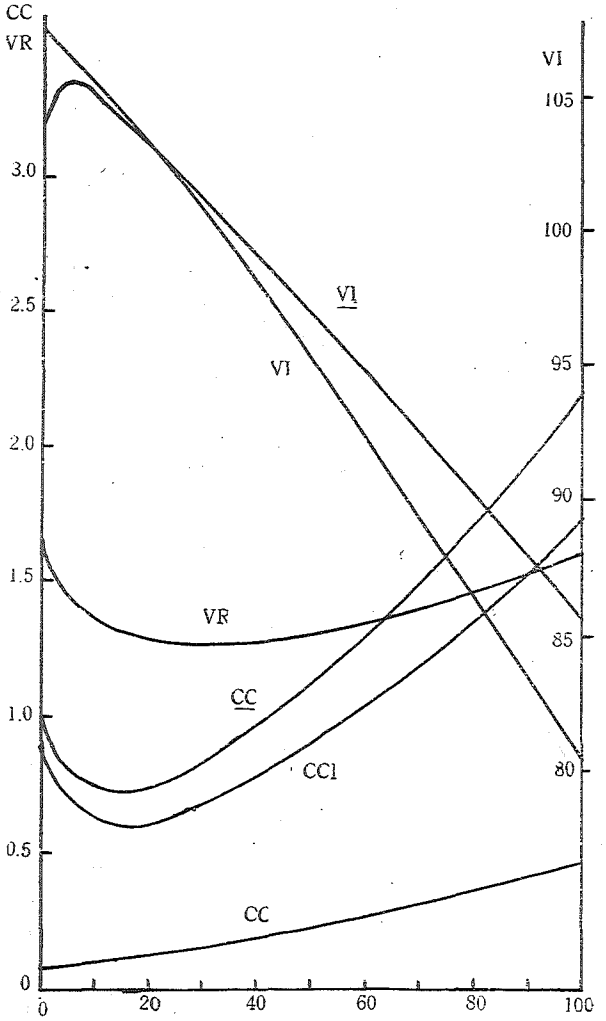
These four oils may be recognized as stability improvers and diluents. In Table 3—8 are shown limits of addition to NH—120 oil within various supposed specifications, for instance, VI=90 and VI=100. In order to obtain 100 VI blended oil, City Services may be added to the amount of 37%, Phillips 36%, Gulf Pride 36%. and P_{NHC} 19%, for 90 VI blended oil, the former three to the amount ranging 71~77%, the latter 37%. P_{NHC}, when added to the extent of maximum quantity to obtain 90 VI or 100 VI blended oil, produces oil inferior in stability and out of specification for stability. With correct addition, however, P_{NHC} may give blended oil of the lowest VR among all additives discussed here.

Table 3—6. Effect of City Service and Phillips.

			OT-300	OT-301	OT-302	OT-303	OT-304	OT-305	OT-306	OT-307	OT-308	OT-309	OT-310	OT-311	OT-312
base oil			NH-120	〃	〃	〃	〃	〃	City Service	NH-120	〃	〃	〃	〃	Phillips
additive	name		—	City Service	〃	〃	〃	〃	—	Phillips	〃	〃	〃	〃	—
	addn. %		—	5	10	15	25	50	(100)	5	10	15	25	50	(100)
viscosity (cst)	before oxidn.	V_{100}	323.4	327.5	332.7	337.3	347.3	377.3	454.8	328.7	333.6	338.7	349.3	379.1	460.1
		V_{210}	25.31	25.34	25.37	25.37	25.43	25.56	26.06	25.34	25.37	25.43	25.43	25.56	26.03
		KVI	107.4	106.5	105.6	104.6	102.7	96.9	83.5	106.3	105.4	104.5	102.3	96.5	82.2
	after oxidn.	V_{100}	551.2	497.0	489.0	485.7	493.3	533.6	717.5	493.6	482.8	490.1	475.2	520.9	708.3
		V_{210}	35.20	33.12	32.48	32.17	31.95	32.17	35.4	33.18	32.39	32.55	31.55	31.79	35.68
		KVI	103.9	104.8	104.0	103.5	101.9	97.2	86.2	105.4	104.6	104.1	102.5	97.6	86.1
VR (100°F)			1.70	1.52	1.47	1.44	1.42	1.41	1.58	1.50	1.45	1.45	1.36	1.37	1.54
CC %	before oxidn		0.090	0.110	0.128	0.152	0.210	0.354	0.856	0.118	0.126	0.154	0.218	0.436	0.650
	after oxidn.		0.968	0.894	0.912	0.924	0.980	1.260	2.490	0.944	0.865	0.912	0.946	1.234	2.602
	CCI		0.878	0.784	0.784	0.772	0.778	0.906	1.634	0.826	0.739	0.758	0.728	0.798	1.952
volatility loss			1.9	1.9	1.9	1.9	1.9	1.9	1.1	1.4	1.7	1.7	1.7	1.7	1.9

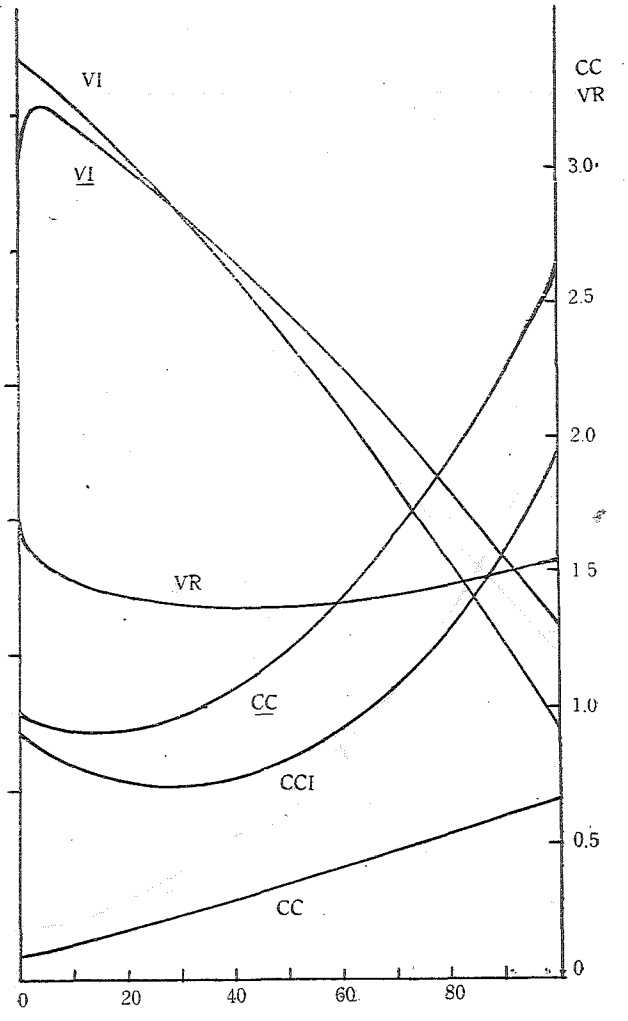
Table 3—7. Effect of Gulf Pride and P_{NHC}.

			OT-300	OT-313	OT-314	OT-315	OT-316	OT-317	OT-318	OT-319	OT-320	OT-321	OT-322	OT-323	OT-324
base oil			NH-120	〃	〃	〃	〃	〃	Gulf Pride	NH-120	〃	〃	〃	〃	P_{NHC}
additive	name		—	Gulf Pride	〃	〃	〃	〃	—	P_{NHC}	〃	〃	〃	〃	—
	addn. %		—	5	10	15	25	50	(100)	5	10	15	25	50	(100)
viscosity (cst)	before oxidn.	V_{100}	323.4	328.8	332.8	338.3	348.9	381.9	463.6	333.4	342.4	353.2	378.8	457.5	829.7
		V_{210}	25.31	25.40	25.40	25.43	25.49	25.62	25.84	25.34	25.37	25.43	25.46	25.65	27.27
		KVI	107.4	106.5	105.6	104.6	102.6	96.3	80.4	105.3	103.5	101.4	96.1	80.5	20.4
	after oxidn	V_{100}	551.2	464.3	448.8	441.6	445.6	501.5	743.8	421.8	432.9	459.5	526.3	920.0	4970
		V_{210}	35.20	31.85	31.00	30.24	22.99	31.03	36.06	29.68	29.80	30.65	32.67	44.95	72.34
		KVI	103.9	105.5	105.1	103.8	102.5	97.7	85.7	105.0	103.7	102.4	99.8	98.8	10.3
VR (100°F)			1.70	1.41	1.35	1.31	1.28	1.31	1.60	1.26	1.26	1.30	1.39	2.01	5.99
CC %	before oxidn.		0.086	0.082	0.102	0.114	0.134	0.218	0.468	0.175	0.212	0.308	0.470	1.024	2.062
	after oxidn.[5]		1.006	0.780	0.760	0.696	0.780	1.116	2.190	0.772	0.920	1.070	1.552	3.468	6.992
	CCI		0.920	0.698	0.658	0.582	0.646	0.898	1.722	0.597	0.708	0.762	1.082	2.444	4.930
volatility loss			1.9	1.7	1.7	1.7	1.7	1.7	1.7	1.1	1.1	1.7	1.9	2.50	3.1



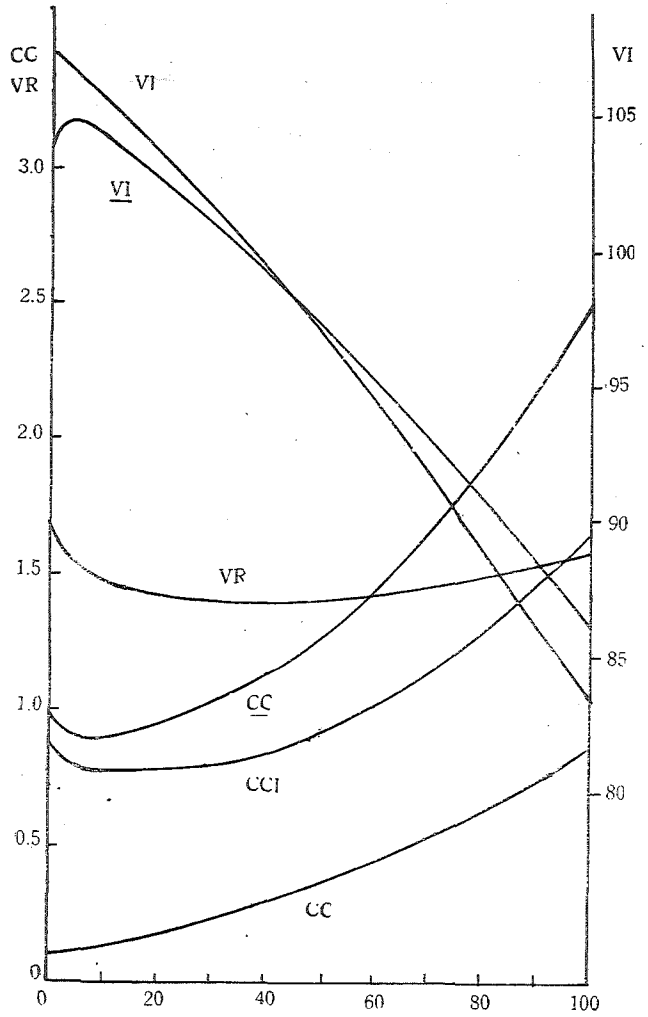
Concentration of additive (%)

Fig. 3—3 Effect of City Service



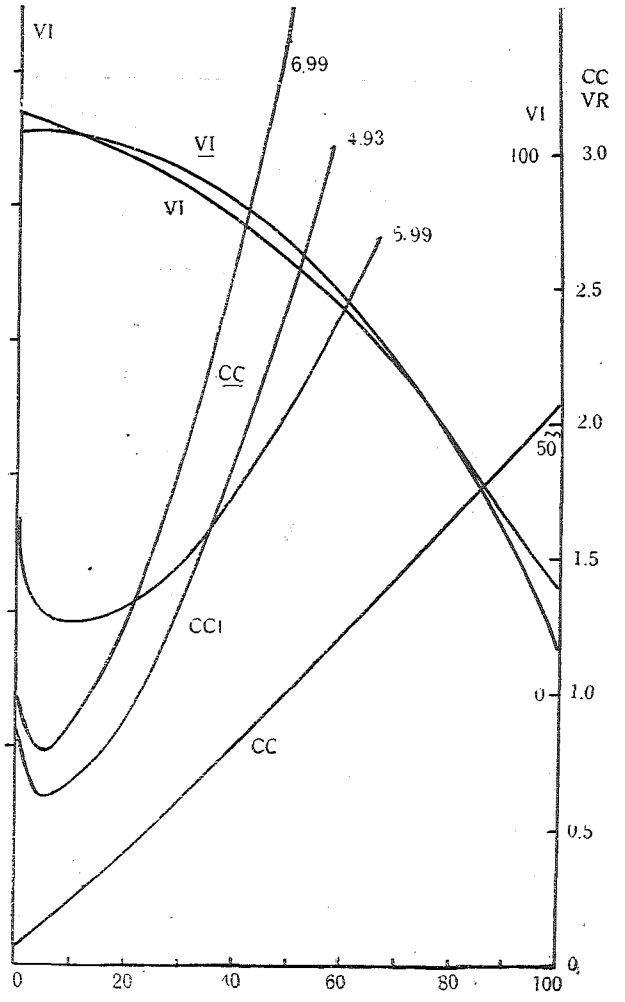
Cocentration of additive (%)

Fig. 3—4 Effect of Philips



Concentration of additive (%)

Fig. 3—5 Effect of Gulf Pride



Concentration of additive (%)

Fig. 3—6 Effect of P_{NHC}

Table 3—8. Effect of blending of commercial mineral oils.

in order to give		City service	Phillips	Gulf Pride	P_{NHC}
	amount of addn. %	37	36	36	19
	amt. of NH—120	63	64	64	81
V I 100	V R	1.40	1.36	1.28	1.45
	C C %	1.08	1.04	0.91	1.23
	C C I %	0.82	0.73	0.74	0.90
	amount of addn. %	77	74	71	37
	amt. of NH—120	23	26	29	63
V I 90	V R	1.47	1.44	1.40	1.64
	C C %	1.81	1.75	1.53	2.24
	C C I %	1.23	1.15	1.20	1.65
	amount of addn. %	37	33	32	10
	amt. of NH—120	63	67	68	70
lowest V R	V R	1.40	1.36	1.28	1.26
	C C %	1.08	1.01	0.86	0.90
	C C I %	0.82	0.72	0.70	0.66
	amount of addn. %	10	13	15	5
	amt. of NH—120 %	90	87	85	95
lowest CC	V R	1.47	1.42	1.31	1.28
	C C %	0.91	0.89	0.71	0.77
	C C I %	0.78	0.77	0.59	0.61
	amount of addn. %	15	30	15	5
	amt. of NH—120 %	85	70	85	95
lowest C C I	V R	1.44	1.36	1.31	1.28
	C C %	0.92	0.98	0.71	0.77
	C C I %	0.77	0.72	0.59	0.61

CHAPTER IV

Effect of synthetic stability improvers.

There are many published reports upon a great many additives of all sorts of chemical structure to improve stability of various oils. But it is in many cases not entirely clear whether they might be effective, why they should have effect on stabilty, for what lubricants they might be available with greatest effect or under what conditions they might act. The present author found a few agents suitable for stabilizer of NH—120 after almost groping his way through his studies with slight confidence. They were mineral oil refined by some way, organic tin and organic phosphorus compounds, which offer leads for studies on various aspects of action.

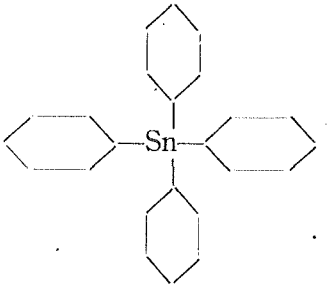
Among organic tin compounds, tetraphenyl tin obtainable with ease by synthesis was selected for the purpose of further detailed research. The additive exhibited remarkable effect, which was somewhat different in comparison with additive obtained from mineral oil. Imagining that the tin compound might fill up a gap left by mineral oil additive, the author attempted by cooperation of both agents with considerable success. Cooperation of both additives resulted in larger effect than separate use.

Among organic phosphorus compound, as one of the simplest, tributyl phosphite was tried with success to some extent.

On every blend before and after oxidation test the friction coefficient was determined. More oxidation-resistant oil gave higher coefficient.

IV — 1. Effect of tetraphenyl tin

Patents which claim tetraphenyl tin as a stability improver for lubricating oil and studies on its effect are found. For instance Dr. B. Yamaguchi stated that it has remarkable influence on some commercial lubricating oils. No observation on synthetic hydrocarbon oil has been reported.

Tetraphenyl tin 

〔228.6—229.6 C〕 MW 427.1

exhibited great effect on NH—120 as already mentioned in preliminary study. We must distinguish between the significances in a case when an additive decreased VR which was originally large, for instance 5 to 2.5, and that in another case when an additive decreased VR which was originally small, for instance 2 to 1.3, though apparent effect of the former might be larger than that of the latter, if indicated in VR difference. For oil which is superior in quality, a smaller difference in VR, has greater significance for practical purpose. Tetraphenyl tin has remarkable influence on high quality oil.

The additive is an organic tin compound, which may produce ash when burned in internal cumbustion engine. The amount of ash derived from it may be as follows. Molecular weight of the additive is 427.1 and that of tin 118.7, whose cotent in the compound is 27.9%. When an engine of 1000HP is used and its consumption of lublicating oil is supposed to be 5g/HP. h., 5kg of oil may be consumed per one hour. If the additive is added to amount of 0.02%, it may be 1 g in weight for 5kg lube, whose Sn content is only 0.28g. If the engine is 7-cylindered, Sn weight per cylinder is only 0.04g. Eight g. tin or 10.2g of the oxide for one cylinder may be deposited after 200 hr. service. The amount of deposit, supposing that all of it may appear in engine, is about 10g which may be comparable to the usual amount of engine deposit. It may be concluded that the additive would have practical significance.

As tetraphenyl tin is with difficulty soluble in mineral oil, specially in NH—120, its crystal is pulverized extremely finely in an agate mortar, and added to the base oil on agitating vigorously and heating at about 50°C. More than 0.1% may be scarcely soluble. In an experiment where 0.20% of the compound was added, white turbidity was observed. Results in a series of experiments are shown in Table 4 — 1 and illustrated in Fig. 4 — 1, various properties being plotted by quantity of addition of the improver.

After oxidation test, no sludge formation and no considerable change of odor were observed. Addition of the additive resulted in insignificant variation of viscosity and slight decrease in viscosity index. For instance, base oil which had 108.4 VI, exhibited 103.4 VI after test, difference being as large as 5.0 and blended oil which contained 0.01% of the additive and had 108.6 VI showed 107.8 VI after test, difference being as small as 0.8. Difference in viscosity index (abbreviated as VI dif. in Fig 4 — 1) dropped sharply by addition of the additive as little in quantity as 0.01 %, then continued almost without change by further addition. Though Conradson carbon before test tended to increase slightly owing to increase in addition amount of the additive, carbon of oxidized oil decreased sharply by addition of 0.01% additive, being minimum in the neighborhood of the addition quantity, then increasing

considerably. That is, by addition of 0.01 %, carbon fell to 0.58 % from 0.88 % which belonged to base oil. then rose to 0.79 % for 0.2 % addition. Curve for CCI behaved as that of CC. Lowest CCI was as small as 0.5 %. It must be noticed that the additive was able to decrease VR considerably. By addition of only 0.01 % VR fell as much as to 1.31 from 1.89 which belonged to the base oil. By further addition the decrease continued slightly. Feature of variation of curve of VR differed remarkably from that of CCI. It is interesting to observe the acid number variation. Acid numbers for base oil and blended oils before test were 6.0 from which AN decreased to 4.74 by 0.01 % addition, then continued to decrease considerably with increase of addition.

Table 4—1. Effect of tetraphenyltin.

exper. no.			OT-1001	OT-1002	OT-1003	OT-1004	OT-1005
base oil			NH—120	〃	〃	〃	〃
additive	name		—	TPT*	〃	〃	〃
	wt. %		—	0.01	0.05	0.10	0.20
vis. cst	before test	V_{100}	310.8	308.8	308.8	308.6	313.8
		V_{210}	24.89	24.82	24.89	24.95	24.79
		VI	108.4	108.6	108.8	109.1	107.3
	after test	V_{100}	586.8	404.4	389.5	388.5	387.2
		V_{210}	36.68	26.69	29.26	29.23	29.29
		VI	103.4	107.8	108.8	108.9	109.3
VR	210°F		1.47	1.20	1.18	1.17	1.18
	100°F		1.89	1.31	1.26	1.26	1.23
carbon	CC		0.076	0.072	0.112	0.148	0.128
	$\underline{CC}$		0.876	0.582	0.620	0.708	0.788
	CCI		0.802	0.512	0.508	0.560	0.660
vol. loss	wt. g		0.8	0.8	0.6	0.6	0.7
	%		2.2	2.2	1.7	1.7	1.9
AN	before oxidn.		0.065	—	—	—	0.066
	after oxidn.		6.0	4.74	3.38	2.63	2.10
n_D^{20}			1.4832	1.4810	1.4802	1.4790	1.4791

* TPT is an abbreviation of tetraphenyltin.

Addition of an improver able to make oxidation-resistance revealed many-sided effects, that is, decreasing CCI, VR, VI difference or acid number which did not always behave similarly, displaying peculiar features, by which the inner mechanism

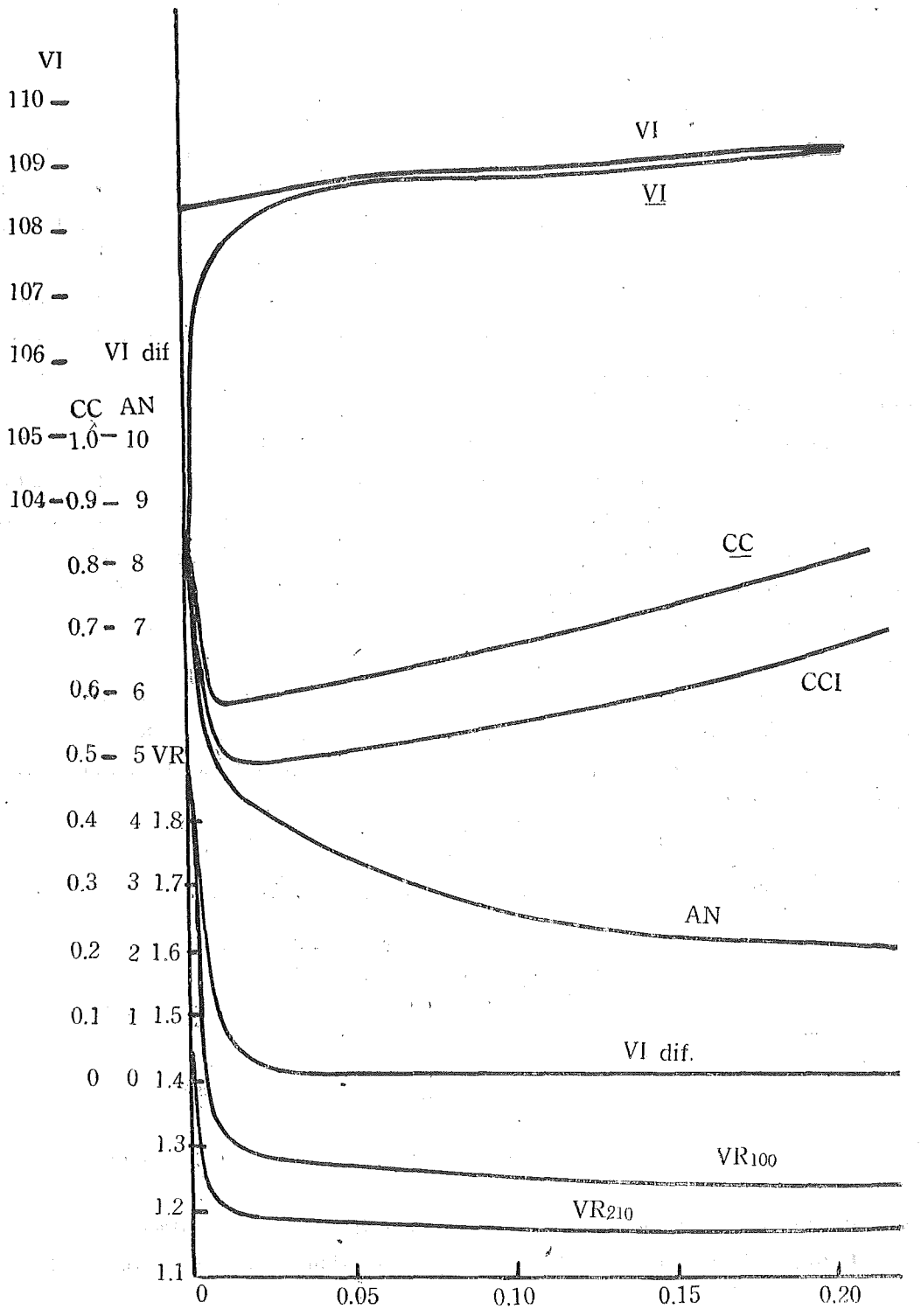


Fig. 4—1 Effect of tetraphenyltin.

of the inhibiting action of the additive might be suggested.

The author thought that VR might have intimate correlation to engine performance of lubricating oil, particularly to deterioration, lacquer or varnish formation and ring-sticking. Then he tried in Fig 4 — 2 to plot VR to other factors, such as CCI, VI and AN after the test. Blended oil of high VR exhibited low VI and high AV after test, though the latter behaved in some what different feature, that is, it decreased very slightly with decreasing VR, from about 2 to 1.3 and then distinctly decreased with slight decrease in VR. CCI also decreased with decrease in VR , increasing, however, with decrease in VR from 1.3 to lower value, that is, CCI had a minimum point after which it rose. These facts suggest that the causes of CCI and VR might be different.

Oiliness of oxidized oil.

In engine, a lubricating oil which has used for a rather long period is said to behave more favorably for bearings than fresh one. Though it may be doubtful to what extent its favorability might be expressed quantitatively, it should be considered as natural. Bacause, it is reasonable that a polar substance such as oxide, ketone, aldehyde or acid might be produced during service and that they might act as oiliness agent. It is interesting to ascertain what influence on friction coefficient might exist in the oxidation of oil containing stability improver.

Friction coefficients were determined by means of an apparatus named "T-Pendulum type oiliness tester"* improved by assistant professor N. Soda of the Aeronautical Research Institute of Tokyo Imp. University (now Research Institute of Science and Technology).

Results obtained are shown in Table 4 — 2 and Fig. 4 — 4 ~ 5.

Table 4 — 2. Coefficient of friction of oxidized oils.

		OT-1001	OT-1002	OT-1003	OT-1004	OT-1005
additive, wt. %		0	0.01	0.05	0.10	0.20
friction coeff.	before test	0.183	0.177	0.154	0.152	0.152
	after test	0.110	0.121	0.129	0.135	0.141
difference		0.073	0.056	0.025	0.017	0.011

As indicated by the table and figures, the following facts are deduced :

(1) Before oxidation test, as the amount of the additive increases, the coefficient

* Report No. 27 of 7th Special Committee of Association for Promotion of Science of Japan, August 1941).

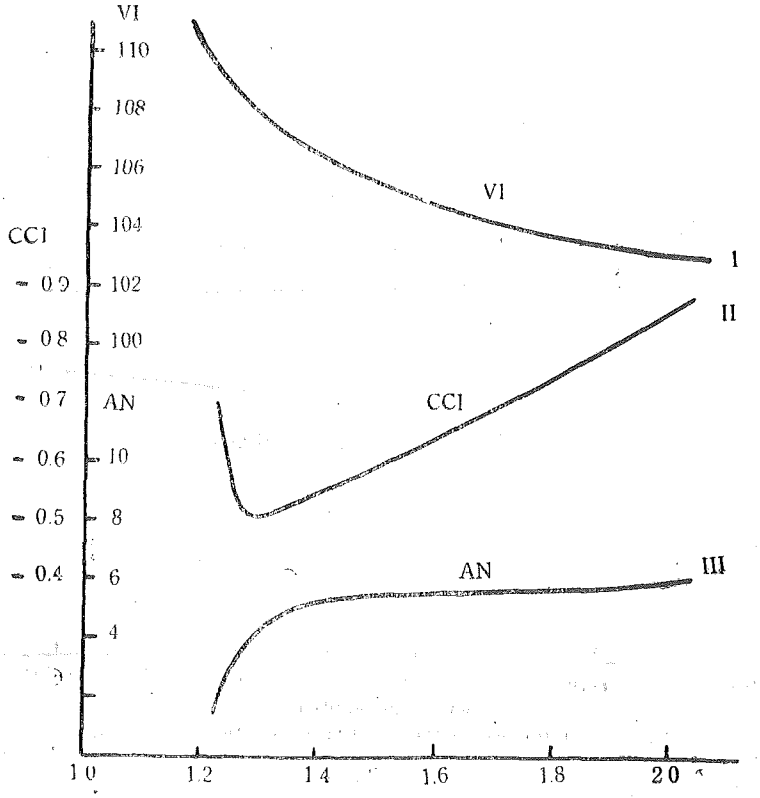
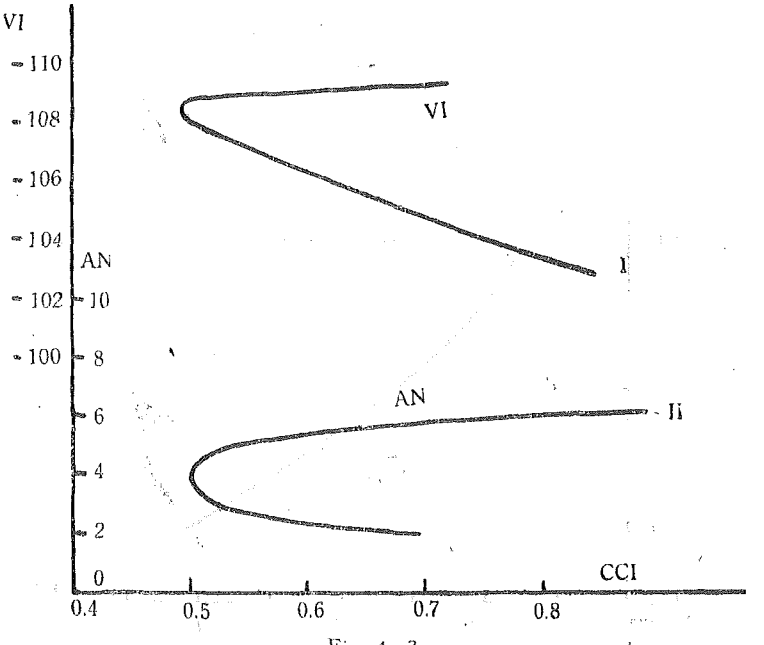

VI
110
108
106
104
102
100
CCI
0.9
0.8
0.7
0.6
0.5
0.4
AN
10
8
6
4
VI
I
II
CCI
AN
III
1.0
1.2
1.4
1.6
1.8
2.0

Fig. 4—2


VI
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VI
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0.4
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0.8

Fig. 4—3

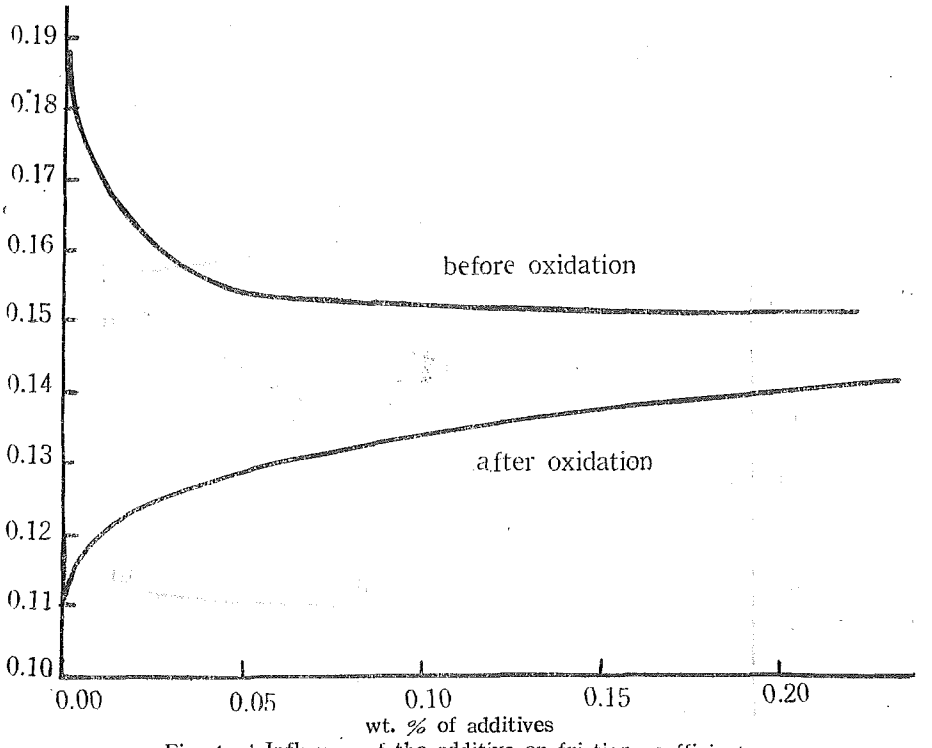


Fig. 4—4 Influence of the additive on friction coefficient.

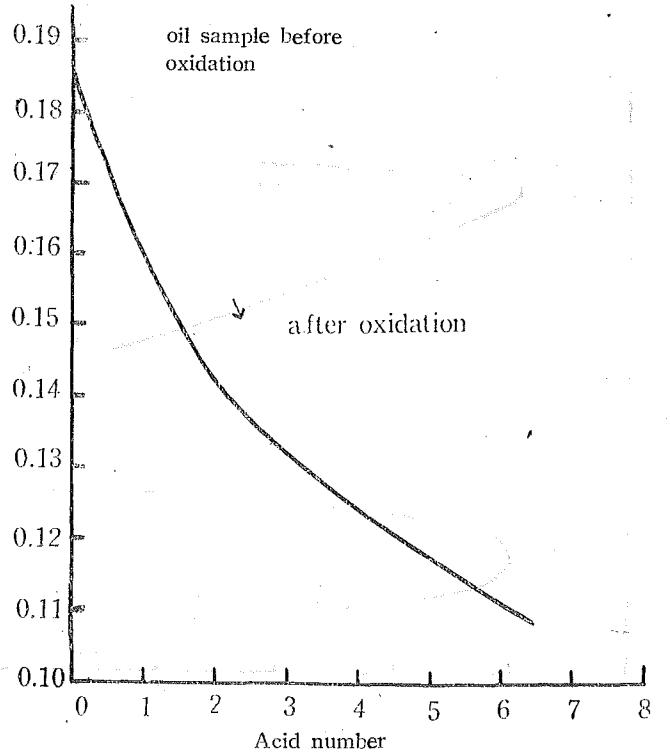


Fig. 4—5 Relation befween acid number and coefficient of oil

of friction f decreases slightly, its change for over 0.05% addition being very feeble. Tetraphenyl tin acts as an oiliness agent with weak effect.

(2) After oxidation test, as the amount of the additive increases, the coefficient f becomes larger. In other words, oil which is stable, that is, which has low VR and CCI, owing to higher content of the additive exhibits higher f ; oil which is more unstable showing lower f. Base oil whose coefficient f is 0.183 possesses f of 0.11 after oxidation test. Sample oil which contains 0.1% of the additive and having f of 0.152 gives oxidized oil of f 0.135 which is higher than that of oxidized base oil.

(3) The fact that more difficultly oxidizable oil has higher coefficient of friction means that such oil has less oiliness. One of the factors which are concerned in such phenomenon is thought to be the acid number or active group -COOH of oil molecule. Figure 4 — 3 illustrates this characteristic to some extent. It is evident that oxidized oil of larger acid number exhibits lower f, that is, larger content of active carboxyl group results in higher degree of oiliness. It must be noticed that f-AN curve, if extrapolated to small acid number region, for example that of base oil, hits nearly the point of f which belongs to fresh base oil.

IV— 2. Effect of tributyl phosphite.

A patent on phosphites as lubricant stabilizer was first claimed by Moran, Evers anb Fuller in 1936. Some of important literatures on this subject is as follows :

1. Moran, Evers, Fuller ; Socony Vac. Oil Co., U.S.P. 2,058, 343
   Triphenyl phosphite and other aryl phosphites
2. Weinrich, Gulf Res. & Dev. Co., U.S.P., 2,101, 632.
   Tributyl phosphite
3. Standard Oil Dev. Co., E.P., 465, 825.
4. Fenske, Stevenson, Larson, Herbolsheimers, Kock : Industrial and Engineering Chemistry, 1941, 33, 516,

The author also found one of these phosphites to be excellently active as stated in Chap. I. Tributyl phosphite tested in detail as a stability agent was presented by the Kyowa Chemical Laboratry. It is a colorless oily liquid. So far as this additive was concerned, it produced oxidized oil which was superior in physical propertis but separated a small amount of sludge. Separation of sludge might depend upon whether the additive itself would create sludge or would produce oxidized which could dissolve no more sludge. The author could not distinguish which it is, without further study, but supposed the latter to be right because of pale color

of oxidized oil.

The agent, easily soluble in base oil clearly, was added to the amount of 0.1 ~2.0%. Results of determination are tabulated in Table 4 — 3.

Table. 4 — 3. Stabilizing effect of tributyl phosphite.

			OT-1001	OT-1006	OT-1007	OT-1008	OT-1009	OT-1010
base oil			NH-120	〃	〃	〃	〃	〃
additives	name		—	TBP	〃	〃	〃	〃
	wt. %		—	0.1	0.2	0.5	1.0	2.0
vis. cst.	before oxidn.	V_{100}	310.8	304.5	302.5	293.7	271.6	243.1
		V_{210}	24.89	24.73	24.70	24.17	23.16	21.80
		VI	108.4	109.1	109.5	109.5	110.6	112.5
	after oxidn.	V_{100}	586.8	441.0	424.2	377.7	365.6	360.5
		V_{210}	36.68	31.23	30.74	28.74	28.18	27.97
		VI	103.4	106.9	107.9	109.1	109.4	109.6
VR	210°F		1.47	1.26	1.24	1.19	1.22	1.28
	100°F		1.89	1.45	1.40	1.29	1.35	1.48
Carbon %	CC		0.076	0.112	0.110	0.202	0.262	0.462
	$\underline{CC}$		0.878	0.674	0.756	0.800	0.832	0.796
	CCI		0.802	0.562	0.646	0.598	0.570	0.334
Volatitily loss, %			2.2	1.7	2.2	1.9	2.2	3.3
AN	before oxidn.		0.065	—	—	—	—	0.15
	after 〃		6.0	4.2	3.6	2.2	1.8	1.2
n_D^{20}			1.4832	1.4810	1.4789	1.4770	1.4758	1.4751

Change in properties.

Tributyl phosphite depresses viscosity of blended oil linearly with amount of addition owing to its low viscosity. On the contrary the viscosity index increases, because of its apparent elevation in case of mixing high viscosity liquid and far lower viscosity liquid.

The viscosity of oxidized oil is lower for lower content of the additive as in the case of tetraphenyl tin, although at over 0.5% content the curve of VI level off. Difference in VI is the smallest for ca. 0.5% content of the additive. Larger difference for larger content of the additive suggets, that the additive might evaporate partially in the course of oxidation test. Viscosity ratio decreases steeply with increase in amount of additive until about 0.5% addition where it is 1.29, then

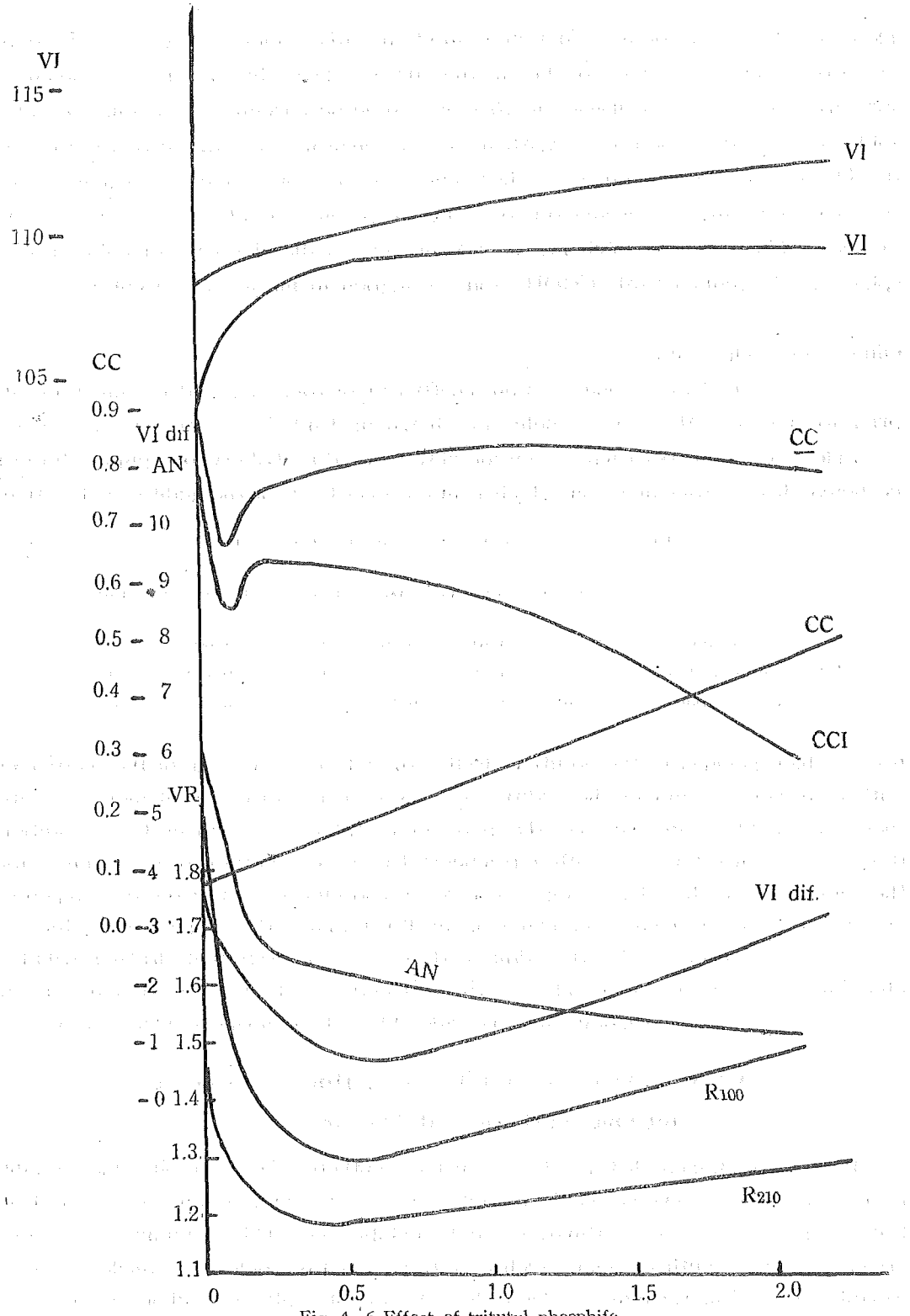


Fig. 4—6 Effect of trityl phosphite.
wt. % of theadditive.

increases slowly. Prior to oxidation Conradson carbon increases with increase of quantity of additive. After oxidation, the curve is somewhat irregular. The curve for carbon increase is analogous to that of Conradson carbon, yet it falls considerably for over 0.2% addition. With increasing quantity of additive there is considerable decrease in acid number, whose curve consists of two almost straight parts. As compared with tetraphenyl tin, the additive produces oxidized oil of lower acid number. This fact may probably be attributable to the character of tributyl phosphite which would retard -COOH-group-formation in lubricant molecule.

Oiliness of oxidized oil

As was stated in previous section, coefficient of friction was determined for oils prior to and after the test. Results are shown in Table 4—4, Figs 4—7 (Ⅰ) and 4—7 (Ⅱ). Friction coefficient is considerably reduced by tributyl phosphite. It must be noted that coefficient of oil which contains over 0.5% of the additive is less than

Table 4—4. Friction coefficient of blended oils

	OT-1001	OT-1006	OT-1007	OT-1008	OT-1009	OT-1010
wt. % of additive	0	0.10	0.20	0.50	1.00	2.00
f prior to oxidation	0.183	0.149	0.143	0.122	0.119	0.106
f post oxidation	0.110	0.119	0.117	0.122	0.127	0.132

0.122, which belongs to the additive itself. In spite of decreasing of the coefficient with increasing amount of the additive in case of nonoxidized oil, it increases with increasing additive amount and the two curves intersect at about 0.5% addition (Fig 4—7). In comparing with tetraphenyl tin, lower coefficient is obtained for the same acid number, for example in case of acid number 2, f of the tin compound and the phosphorus compound being about 0.141 and 0.124 respectively. Intersection of the two curves for the additive (Fig 4—7) suggests that although tributyl phosphite would have remarkable lowering effect for coefficient of friction of fresh oil, it might probably evaporate to a considerable extent during oxidation test.

IV—3. Cooperative effect of raffinated mineral oil and synthetic stability improver.

It was ascertained that for hydrogenated synthetic 120 SSU oil which might be used for aircraft engine oil, Niitsu oil or other natural mineral oils which had been subjected to special raffination would exhibit remarkable stability-improving effect and some synthetic agent such as tetraphenyl tin would have analogous powerful effect. But speaking in detail, lowest viscosity ratio was about 1.3 in case of mineral oil refined by easy way and about 1.2 in case of tetraphenyl tin, lowest

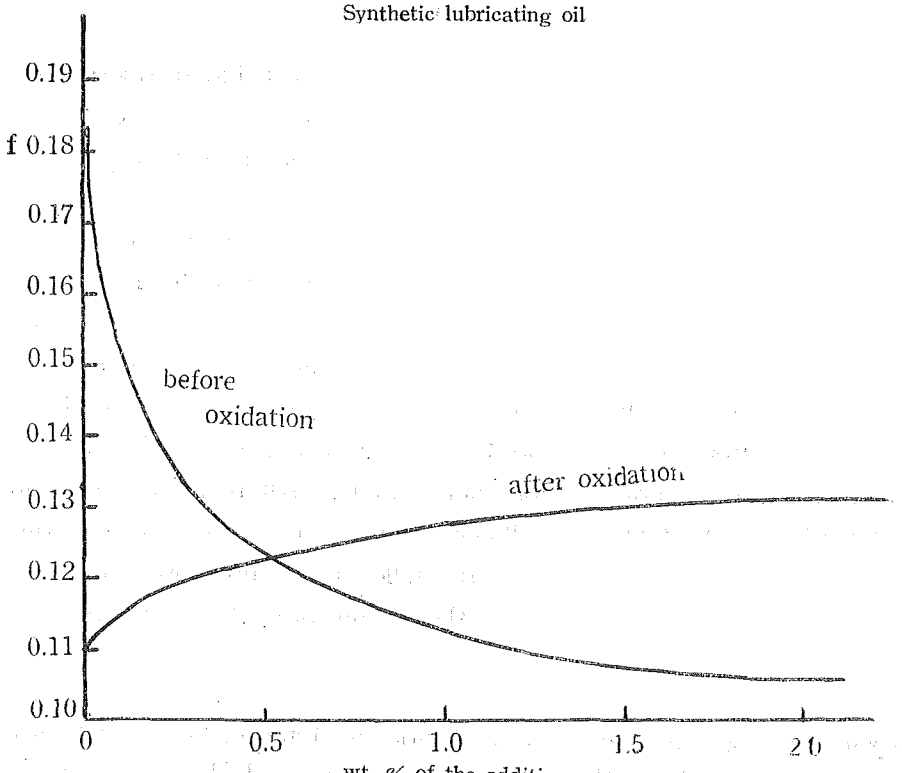


Fig 4—7 (I) Effect of tributyl phosphite.

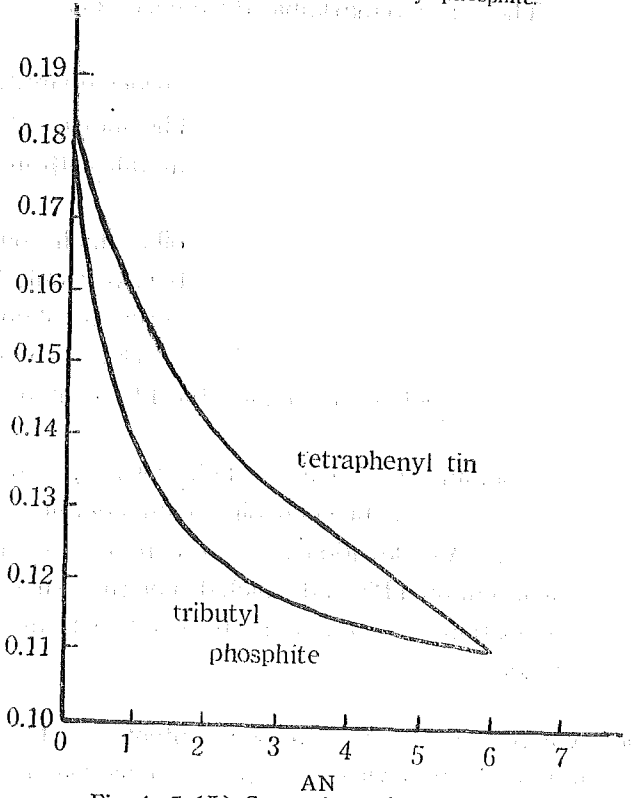


Fig. 4—7 (II) Comparison of two additives.

CCI being also an analogous feature. There is remarkable distinction of effect between the two additives, which suggests that they might act in different manners or protect different parts of the oil molecule. These observations led to an attempt to acertain the cooperative utilisation of both additives.

To the base oil NH-120, mineral oil named TK_3 was added to the amount of 2.5～15% and at the same time tetraphenyl tin, abbreviated TPT, was added to the amout of 0.01～0.1%. Properties of NH—120 and TK_3 are given in the following table. These blended oils were tested in the same way as described above. Viscosity in centistokes at 100°F, kinematic viscosity index, and Conradson carbon both before and after the test, acid number after oxidation, viscosity ratio and carbon increase were determined for each sample. All data are given in Table 4—5. Referring to the table and following figures, characters of cooperating action of both additives will be discussed. In the following figures, M_0, $M_{2.5}$, ……, M_{15} mean blended oils which contain TK_3 to the amount of 0, 2.5, ……, 15% respectively.

1) Viscosity and viscosity index. Viscosities at 100°F of blended oils differ considerably one from another. Viscosities after oxidation which vary to a large extent will be discussed later. There are remarkable differences befween oils before and after oxidation and among variously blended oils.

Viscosity indices of blended oil which contain various quantities of TK_3 appear to rise slightly with increase in quantity of TPT. The indices of added oils which contain various quantities of TPT reveal almost linear fall with increase in quantity of TK_3 (Fig 4—8).

Curves of viscosity indices of oxidized blended oils which contain various quantities of TK_3, when plotted by quantity of TPT, behave similarly, that is, gathering in narrow range and falling from about 108～109 to about 103～104 with increase of amount of TK_3, except that of oxidized oils which contain no TPT, rising from about 103 to 106 which is maximum for TK_3 content of 5～6%, then falling to about 103.

Although oils which contain TK_3 solely or TPT solely, certainly exhibit viscosity index depression after oxidaton, blended oil which contains over 5% of TK_3 and cooperatively TPT shows VI elevation to some extent. Remarkable distinction between blended oils, which contain TPT and which do not, may suggest that these two additives would inhibit oxidation of different parts in oil molecules, or act to cause different grades of oxidation.

2) Viscosity ratio. Curves of VR for various contents of TK_3 plotted by TPT quantity are shown in Fig 4—9. All curves are of analogous type, sharply falling by small addition of TPT, for example for addition of 0.1% TPT, then going almost

Table 4—5. Cooperation of two additives of different types.

			OT-1037	OT-1038	OT-1039	OT-1040	OT-1012	OT-1013	OT-1014	OT-1015	OT-1019	OT-1020	OT-1021
signature			$M_{2.5}$	$M_{2.5}TPT_1$	$M_{2.5}TPT_2$	$M_{2.5}TPT_3$	M_5	M_5TPT_1	M_5TPT_2	M_5TPT_3	M_{10}	$M_{10}TPT_1$	$M_{10}TPT_2$
base oil			NH-120	NH-120-$M_{2.5}$	〃	〃	NH-120	NH-120-M_5	〃	〃	NH-120	NH-120-M_{10}	〃
additive	name		TK_3	TPT	〃	〃	TK_3	TPT	〃	〃	TK_3	TPT	〃
	wt. %		2.5	0.01	0.05	0.10	5	0.01	0.05	0.10	10	0.01	0.05
viscosity in cst.	before oxidation	V_{100}	332.3	315.0	312.9	313.6	317.9	317.5	317.9	317.9	—	324.1	323.7
		V_{210}	24.82	24.85	24.82	24.85	24.88	24.82	24.88	24.82	—	24.76	24.76
		VI	103.3	107.3	107.9	107.6	106.6	106.6	106.8	106.6	104.8	104.9	105.0
	nafter oxidation	V_{100}	444.1	381.2	373.6	367.9	446.8	389.4	368.9	367.0	—	400.9	379.9
		V_{210}	31.06	28.94	27.81	27.63	31.23	28.55	27.69	27.57	—	28.77	27.81
		VI	105.9	109.1	107.2	107.1	106.1	106.5	107.2	107.1	105.1	105.3	105.6
viscosity ratio		VR_{100}	1.34	1.21	1.19	1.17	1.41	1.23	1.16	1.16	1.36	1.24	1.17
Conradson carbon	before oxidation		0.108	0.120	0.120	0.114	0.186	0.274	0.246	0.256	0.230	0.198	0.190
	after oxidation		0.785	0.540	0.496	0.472	0.820	0.532	0.470	0.472	0.870	0.598	0.524
	CCI		0.677	0.420	0.376	0.358	0.634	0.258	0.224	0.216	0.640	0.400	0.334
volatiliy loss, wt. %			2.1	1.1	0.8	0.8	1.7	1.7	1.4	1.4	—	1.7	1.4
AN after oxidation			2.63	1.79	1.15	0.90	4.85	2.80	1.78	1.40	5.00	3.00	2.18

Table 4—5. Cooperation of two additives of different type, continued.

			OT-1022	OT-1026	OT-1027	OT-1028	OT-1029	OT-1001	OT-1002	OT-1003	OT-1004	OT-1017
signature			$M_{10}TPT_3$	M_{15}	$M_{15}TPT_1$	$M_{15}TPT_2$	$M_{15}TPT_3$	NH-120	TPT_1	TPT_2	TPT_3	TK_3
base oil			NH-120-M_{10}	NH-120	NH-120-M_{15}	〃	〃	NH-120	〃	〃	〃	TK_3
additive	name		TPT	TK_3	TPT	〃	〃	—	TPT	〃	〃	—
	wt. %		0.10	15	0.01	0.05	0.10	—	0.01	0.05	0.10	—
viscosity in cst.	before oxidation	V_{100}	323.7	330.6	330.2	330.1	330.4	310.8	308.8	308.8	308.6	565.6
		V_{210}	24.76	24.73	24.73	24.74	24.82	24.89	24.82	24.89	24.95	24.64
		VI	104.9	103.3	103.4	103.7	103.7	108.4	108.6	108.8	109.1	49.4
	after oxidation	V_{100}	376.2	447.4	411.1	394.6	390.5	586.8	404.4	389.5	388.5	1196.6
		V_{210}	27.59	30.38	28.79	27.87	27.75	36.68	26.69	29.26	29.23	39.71
		VI	105.5	103.3	103.7	103.3	103.5	103.4	107.8	108.8	108.9	109.3
viscosity ratio		VR_{100}	1.16	1.35	1.25	1.19	1.18	1.89	1.31	1.26	1.26	2.12
Conradson carbon	before oxidation		0.190	0.208	0.202	0.201	0.182	0.076	0.072	0.112	0.148	—
	after oxidation		0.536	0.926	0.705	0.600	0.588	0.878	0.584	0.620	0.708	3.484
	CCI		0.346	0.718	0.504	0.399	0.406	0.802	0.512	0.508	0.560	—
volatility loss, wt. %			1.1	1.1	1.7	1.1	1.4	2.2	2.2	1.7	1.7	1.4
AN after oxidation			1.65	5.09	3.55	2.42	2.04	6.00	4.74	3.38	2.63	—

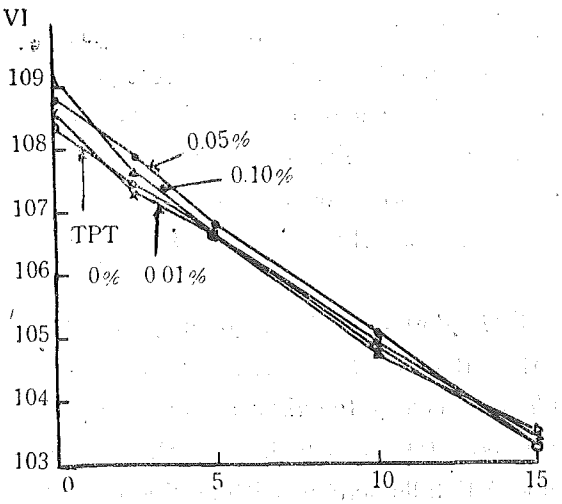


Fig. 4—8 (I) Viscosity indices before oxidation.

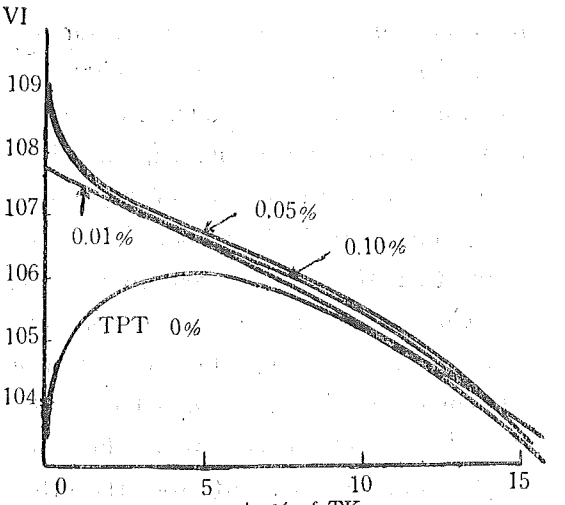


Fig. 4—8 (II) Viscosity indices after oxidation

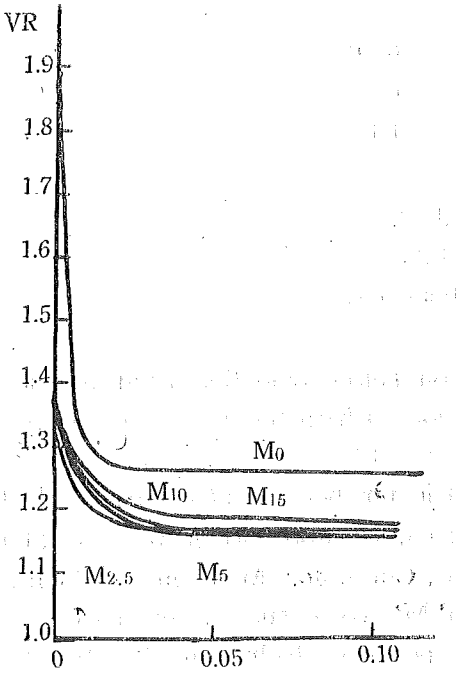


Fig. 4—9 Viscosity raito.

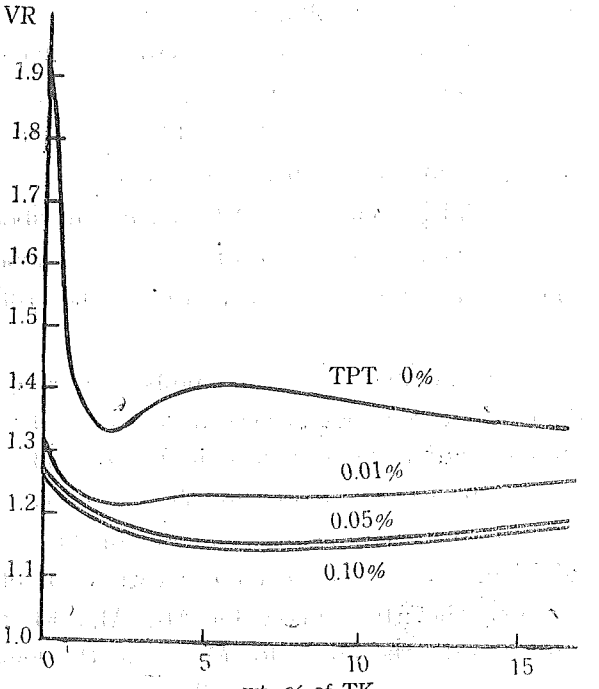


Fig. 4—10 Viscosity ratio.

parallelly, that is, with slightest effect of addition. Curve for M_0 is in highest position, which means that the limit of action of TPT only is inferior to blended oil which contains some TK_3. Curves of $M_{2.5}$, M_5, and M_{10} are in the lowest position and far apart from the curves of M_0, which means excellent cooperative action of both additives. Curve for M_{15}, which contains 15% of TK_3 is in higher position compared with the curves of $M_{5.5}$, M_5 and M_{10}. In other words, in the case of the same content of TPT, blended oils which contain more than 10% of TK_3 are less stable than those which contain less TK_3.

Curves for VR for various contents of TPT plotted by TK_3 quantity are illustrated in Fig 4—10, which reveal clearly the effect of TK_3. VR-curves of added oil which contains more than 0.01% of TPT plot nearly together and are side by side suceessively, except that which contains no TPT, in which case the position of the curve is far apart from the others and VR falls acutely with addition of TK_3 until 2.5% of the additive, then rises slightly and decreases gradually. An astonishing cooperative effect may be recognized from the figure, in which blended oils which contain about 0.10% of TPT and 5～10% of TK_3 exhibit the most remarkable result. Summarising excellent data, the optimal quantity of TK_3 for various amount of TPT is as follows :

TPT %	0	0.01	0.05	0.10
TK_3 %	2.0	2.5	5	6
VR	1.33	1.21	1·16	1.15

or, expressing it in other way, when

TK_3 only, VR reaches to about 1.34
TPT only, VR about 1.26
and TK_3+TPT together, VR reaches till about 1.15.

3) Acid number. As acid number of sample oil before oxidation is always less than 0.1, it does not become a subject of discussion. Characteristic rise is observed after oxidation, being shown in Fig 4—11 and 4—12.

In the former figure, are shown curves of acid number for blended oils which contain variously fixed percentages of TK_3. All curves drop with increase in TPT addition, and they do not cross with each other Curve for M_0 is in the highest position, then the curves for M_{15}, M_{10}, M_5 and $M_{2.5}$ come successively lower. In other words, the curve for $M_{2.5}$ is in the lowest position which means that blended oils which contain 2.5% of TK_3 and have some added TPT are inhibited to the largest extent. Curves of blended oils of higher content of TK_3 are between those of $M_{2.5}$ and M_0. In Fig. 4—12 are indicated curves for acid number plotted by TK_3 content for added oils which contain variously fixed percentages of TPT. Features of curves are considerably complicated. The most characteristic is the

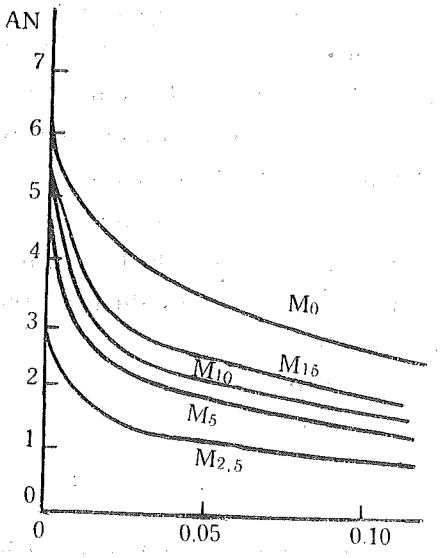


Fig. 4—11 Acid number after oxidation.

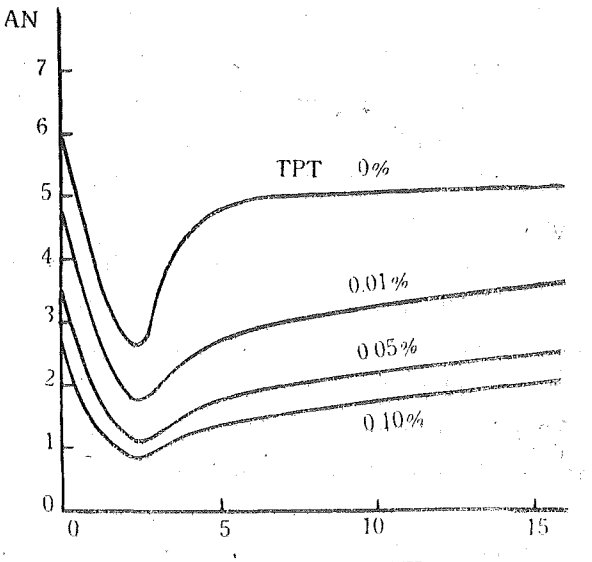


Fig. 4—12 Acid number after oxidation.

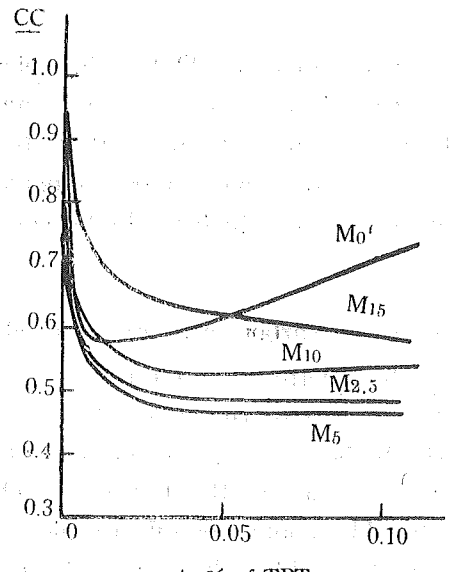


Fig. 4—13 Conradson carbon after oxidation.

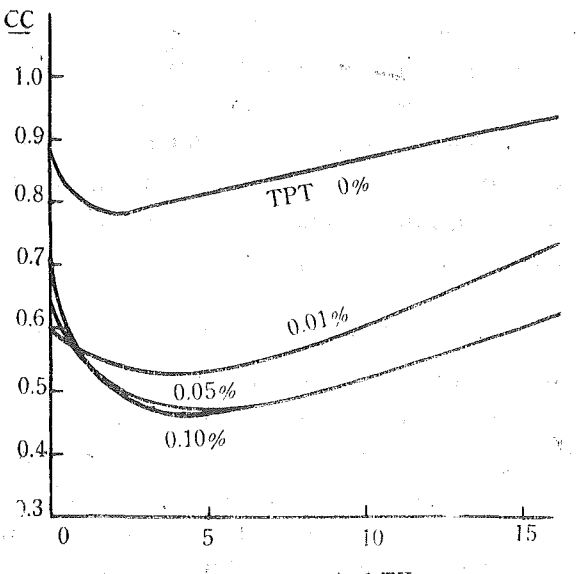


Fig. 4—14 Conradson carbon after oxidation.

curve for added oils which contain no TPT. Owing to addition of TK_3 the curve falls steeply until about 2.5% content of TK_3 (acid number being from 6 to 3.6), with increase in its content rising up to about 5%, then with its further increase going almost flat (acid number from 4.8 to 5.1). Curves for added oils which contain over 0.01% of TPT are to some extent, analogous with the curve just mentioned with the lowest parts of curves of lesser depths. Curve for oil of 0.10 % of TPT is in the lowest level, which means inhibition of the highest degree. Considering that acid number might be a measure for oxidation of oil and oil of lower acid number might mean higher inhibited oil, improved oil which contains 0.10% of TPT and 2.5% of TK_3 is the most inhibited and is a product of the highest agreement with the author's puprose. Acid number for $M_{2.5}$:

TPT %	0.00	0.01	0.05	0.10
acid number	2.6	1.8	1.2	0.9

that of base oil being as high as 6.

4) Conradson's carbon after oxidation. Carbons after oxidation for oils which con tain variously fixed percentages of TK_3 decrease in general with increase in TPT content, except that for M_0, which falls at first to about 0.58% of carbon with 0.01% of TPT, then rises with its increase. Curve for M_5 is in the lowest level. In case of acid number the most inhibited condition is found for 2.5% of TK_3 content ; here in case of Conradson's carbon the most excellent condition is observed for 5% of TK_3 content (Fig 4—13).

Carbons for oils which contain variously fixed percentages of TPT, when plot ted by TK_3 percentage, have minimum points, which are located between 2 and 5% of TK_3. Curve for 0% TPT is in the highest level and far apart from the other three curves, two of which are in the lowest position and almost coincide with each other. The lowest value of them is about 0.47%, which might be considered said as very excellent (Fig 4—14).

5) Conradson's carbon increase. A group of curves of carbon increases for oils which contain variously fixed perentages of TK_3, when plotted by TPT percentage, is analogous to curves of Conradson's carbons after oxdation, the order, however, being some what changed, that is, M_0 being in the highest level and considerably apart from the others, then M_{15}, $M_{2.5}$, M_{10} and M_{15} successively, the last of which is remarkably far under the other three. Curves for TK_3-containing oils are almost parallel to the abscissa for TPT-content over ca. 0.01%. This character indicates very slight effect of further addition. Most excellent value for CCI is as low as about 0.22%, while CCI for the base oil is about 0.8% (Fig 4—15).

An extremely peculiar feature of the group of curves of CCI for added oils plotted by TK_3 percentage may be observed, as indicated in Fig. 4—16. The curve

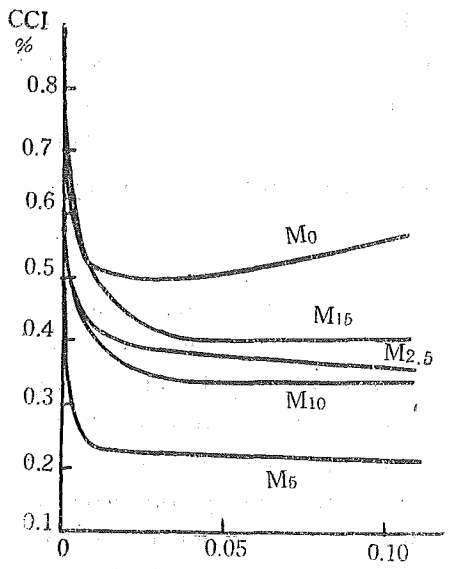


Fig. 4—15 Carbon increase after oxidation.

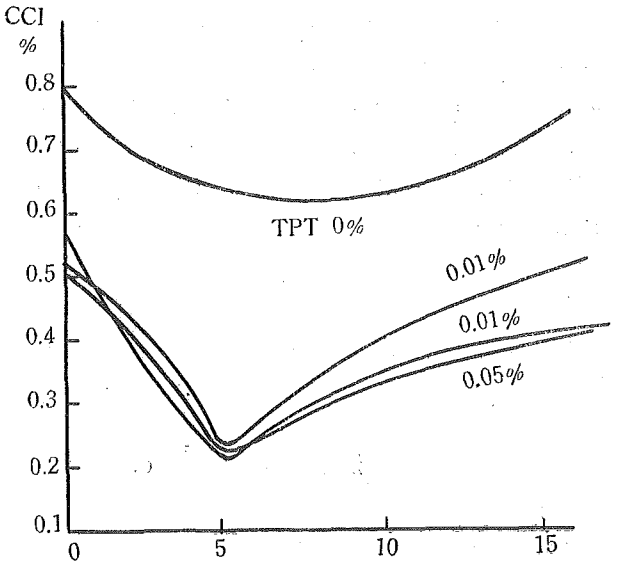
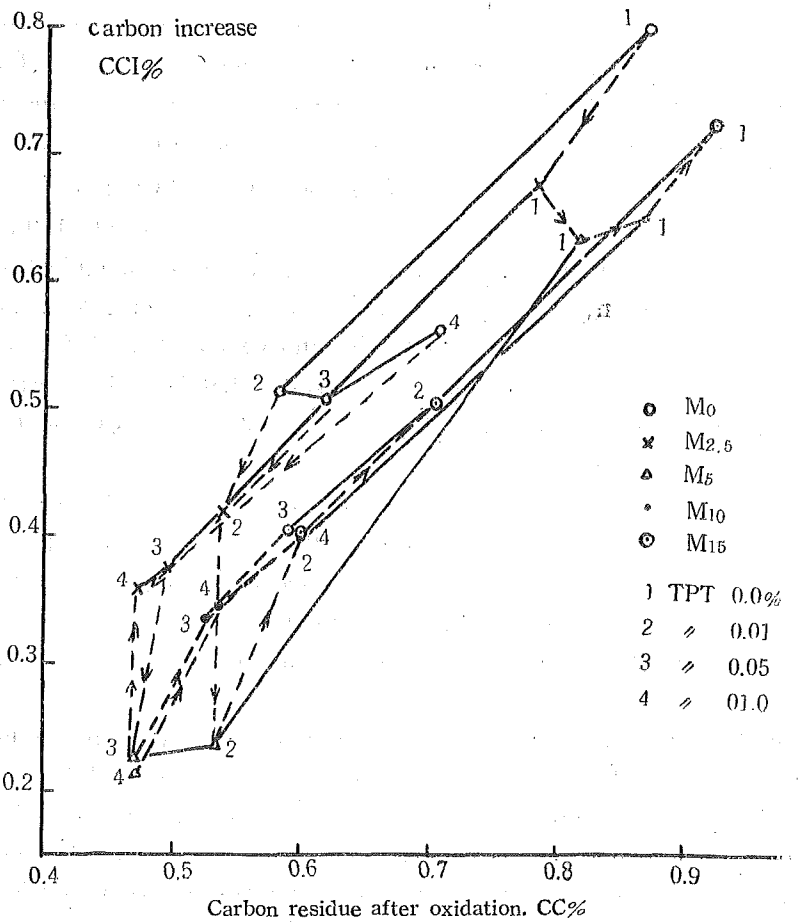


Fig. 4—16 Carbon increase after oxidation.



Carbon residue after oxidation. CC%

Fig. 4—17 Relation botween Carbon after oxidation and Carbon increase.

for blended oils containing no TPT is in far higher level than the other three, its form being considerably different. Its lowest value of CCI is about 0.62% for addition of about 6 ~ 8% of TK_3, while that of base oil is about 0.8%.
Carbon increases for oils containing TPT are far lower, their curves being V-shaped and gathering within a narrow range. Minimum values are found around 5 % addition of TK_3.

6) Relation between Conradson's carbon after oxidation and its increase. Generally speaking, oils of high Conradson's carbon content after test exhibit also high increase in carbon almost parallely. But low carbon increase may be observed in either case that some kind of sample oils would have low carbons after and before oxidation resulting in low CCI and others would have relatively higher carbons after and before oxidation resulting also in low CCI, the former being preferred in practice. Such a state of affairs may be observed in Fig 4 — 17, where all CCI and CC obtained in experiments described in this chapter are plotted. Addition of improvers generally brings the location of CCI and CC nearer to the origin of axis, except several points which move backward with further addition. In the upper right corner, is located a group of M_0, $M_{2.5}$---------- and M_{15}, whose character tells us that by means of simple addition of TK_3, CCI falls at first, leaving CC without remarkable change and that then CC increases, leaving CCI without remarkable change. In every case, addition of TPT decreases CCI and CC approximately along 45° line to a large extent. Some of them (for instance, M_0 to which TPT is added) change their directions backward. M_5 with further addition of 0.05% of TPT and $M_{2.5}$ with further addition of 0.10% of TPT are in the lowest left corner, which means most desirable feature of inhibition, CC and CCI of both being around 0.47 and around 0.23 respectively. It must be noticed that M_5 with further addition of 0.10% of TPT would give considerably higher CCI leaving CC unchanged.

7) Relation between viscosity ratio and carbon increase. Considering behavior of lubricating oil in internal combustion engine, there are preferred lower viscosity ratio, lower carbon increase and lower carbon, especially lower value of the former two. It is very convenient to plot VR on ordinate and CCI on abscissa for the purpose of prediction of performance of lube oil in engine. Such is given in Fig 4 — 18.

In the highest right corner is located a point denoted as 1 and a line denoted as M_0 (or M_0, 1 as an abbreviation), which is a measure of stability of the base oil. As points are connected with full line in case of addition of TPT for TK_3-containing base oil, the line makes us appreciate the effect of the amount of TPT on stability. Such five lines represent effective addition of TPT for M_0, $M_{2.5}$, M_5, M_{10} and M_{15} respectively. Out of the five lines that of M_0 reveals a peculiar fea-

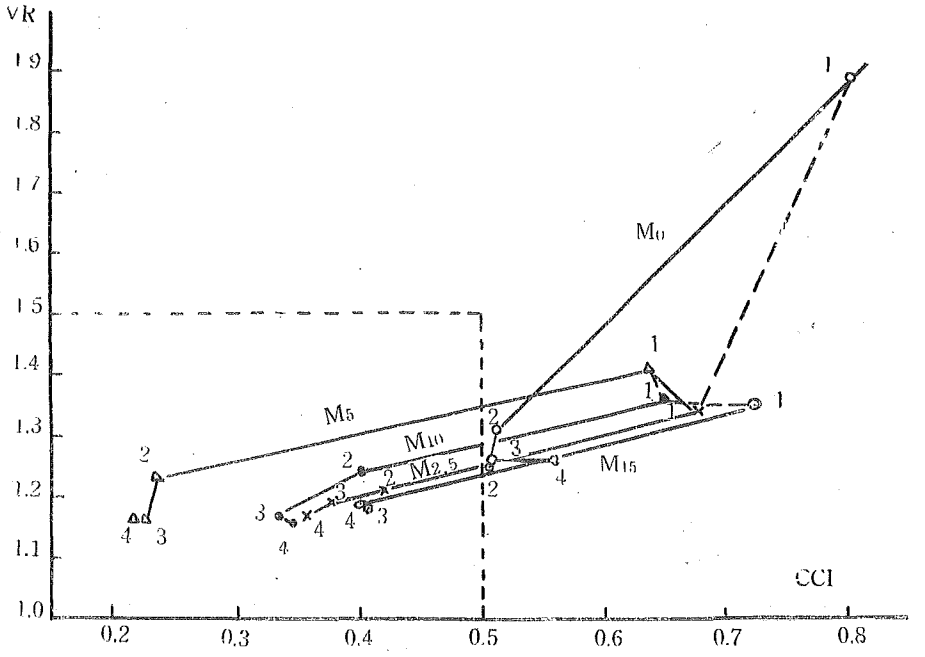


Fig. 4—18 Relation between VR and CCI

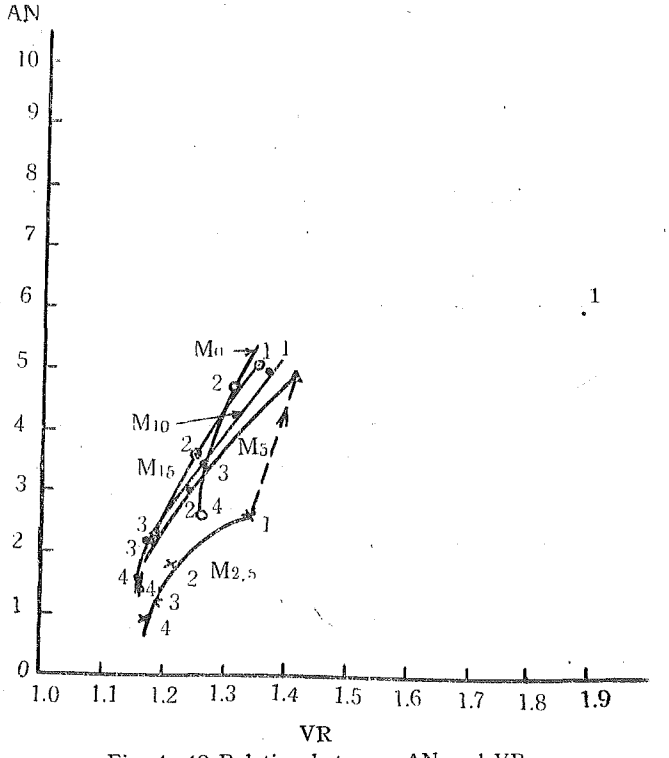


Fig. 4—19 Relation between AN and VR.

ture in comparison with the other four curves, the former standing acutely and the others rather parallel to the axis of CCI. Line of M_0, i. e. that of the base oil indicates that 0.01% addition of TPT would depress either VR or CCI to large extent, and further addition would yield rather small effect. Moreover, addition over 0.05% results in larger CCI. All the points belonging to M_0 are outside of a rectangular area confined by the line (CCI=0.5) and the line (VR=1.5), values of both of which are recognized to have to be characters of superior quality lube and to be adopted as a specification in near future. Four points belonging to M_0 are all out of the area, while all the points belonging to other than M_0 are within it, except their starting samples, i.e $M_{2.5}$, M_5, M_{10} and M_{15}. All the TK_3—blended oils are prolongedly subjected to the effect of TPT resulting in highly inhibited oil whose CCI and VR are thrown deeply within the area. Moreover it is extraordinarily interesting that by means of first addition of 0.01% TPT, with extreme clearness, and by its further addition, with less distinctness, all the four starting oils (TK_3—blended oil) produce lines almost parallel to each other, which incline far less than that of M_0. This condition means that addition of TPT results chiefly in larger depression of CCI than that of VR.

With the addition of TPT, points for M_5 run to far left corner, considerably apart from the other three series. Although VR of TPT—added M_5 have similar value with other series, CCI values are far distant, showing far less values. With 0.1% of TPT, M_5 produces inhibited oil whose CCI is as small as 0.23 and VR as small as 1.16, the values being the most striking data the author ever obtained. Its CC is as small as 0.47 and AN is 1.5.

From these data, it may be stated that the base oil by the addition of TPT only or TK_3 only, could not produce, or might with great difficulty produce oil with CCI less than 0.5% and VR less than 1.5, and optimum amount of TK_3 might be around 5% and that of TPT 0.1% or more.

8) Relation between acid number and viscosity ratio.

There may be close relation between VR and acid component of oxidized product. The base oil has the largest VR (1.89) and the largest AN (6.0). Similarly as was shown in previous paragraphs, only a series belonging to M_0 exhibits a curve quite different from others, which crowd, into a comparatively small region (Fig. 4—19).

Generally speaking, AN decreases with decrease in VR. Although addition of TPT decreases AN acutely, blended oil with less amount of refined mineral oil exhibits lower AN. Points belonging to $M_{2.5}$ make a curve far lower than the others. Curves for M_5, M_{10} and M_{15} are located in higher positions successively. This means, for a fixed value of VR, AN for $M_{2.5}$ is lower than that for M_{15}. For instance, if value for VR be taken as 1.3, then AN for a series of $M_{2.5}$ is 2.5, that

for a series of M_{15} is 4.5. These facts may suggest some of the mechanisms of inhibition of each sort of improvers.

Conclusions

The present paper describes results of research on the improvement of stability of synthetic hydrocarbon lubricating oil from whale oil.

(1) It was possible to improve stablity of the synthetic oil to a remarkable extent by means of hydrogenation, but that process only was insufficient to produce high performance aircraft lubricating oil.

(2) Addition of a few kinds of stability improvers to the hydrogenated synthetic oil proved to produce highly stable oil. One of the most effective improvers was a specially raffinated petroleum oil, others being some organo-tin and organo-phosphorus compounds.

(3) Niitsu crude oil, which was relatively abundant in Japan, was raffinated in various ways ; it was added in various amounts to the hydrogenated synthetic oil and yielded remarkable improvement of stability in many cases. Through comparatively simple raffination poweful additives were obtained.

(4) In similar ways, Seria crude was tested, but was found to be less effective than the former. The raffinate was, however, assumed to be useful as a filler or diluent for high performance oil.

(5) Some commercial mobile oils, which can not be used for aeroengines owing to a somewhat low VI, were tested to dilute the high performance oil. Results were satisfactory.

(6) The influences of tetraphenyl tin, which was highly effective among synthetic additives, were tested in detail with favorable results.

(7) The influences of tributyl phosbhite, which was another effective additive, were also tested in detail with satisfaction.

(8) Cooperative effect of natural additive (raffinate of Niitsu oil) and synthetic additive (tetraphenyl tin) was studied precisely. More satisfactory results than by any one component of additives were obtained.

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