SCANNING OF TOM REEL 252

Reel 252 contains papers from the private files of Dr. M. Pier

Frames 1-11

Ignition Accelerators for Diesel Oils, Extracts from Report of Ammonia Laboratory of Oppau, 11/20/1940

1. Ammonium nitrate cannot be used because its homogeneous distribution in oil is impossible.

2. Oxides of nitrogen (1-2%) improved the ignitability by 6-18 cetane numbers.

Oils saturated with NO_2 at 50° C. (2% NO_2 saturation limit), and the pitch is filtered off.

The effect of NO_2 upon the fuel is not explained.

NO_2 treatment is still more effective with cracked (unsaturated) oils.

Nitric acid, chlorine, ammonia, potassium permanganate, potassium bichromate, sulfuric acid did not improve the fuel.

3. The following ignition accelerators may be considered:

	Objections
Ethylnitrate) Amylnitrite) Amylnitrate)	Formation of oxides of nitrogen on combustion, corrosion

Acetone peroxide - The peroxide is unstable and explosive. Flash point lowered

Other substances investigated and found less effective were:

Nitromethane, nitroethane, etc.
Tetranitromethane (relatively good)
Nitrobenzene
Di- and tri-nitrobenzene
o, m, p-nitrotoluene
Nitrophenol
Peroxides: Benzoyl peroxide
  Tetraline peroxide
  Acetyl peroxide

Metal compounds: Oleates, compounds of lead, tin, zinc, antimony, mercury

Table of ignition accelerators:

% ignition accelerator	Fuel	Rise in cetane number	Remarks
Alkyl nitrates and nitrites:			
0.5 ethyl nitrate	Gas oil	8	
1 ethyl nitrate	do.	14	
1.5 do.	do.	16	
2 do.	do.	16	
3 do.	do.	18	
4 do.	do.	24	
5 do.	do.	27	
2 ethyl nitrate	do.	14	
2 i-butylnitrate	do.	9	
5 do.	do.	20	
1 sec. butylnitrate	do.	9	
3 do.	do.	17	
5 do.	do.	23	
1 i-amylnitrate	do.	6	
3 do.	do.	17	
5 do.	do.	25	
1 sec. amylnitrate	do.	9	
3 do.	do.	18	
5 do.	do.	25	
1 i-amylnitrite	do.	6	
3 do.	do.	18	
5 do.	do.	25	
1 sec. hexylnitrate	do.	10	
3 do.	do.	23	
10 nitromethane	do.	3	
20 do.	do.	4	
6 nitroethane + nitropropane 50-50	do.	4	
nitrobutane nitrohexane nitroheptane			Not miscible
5 nitrooctane	do.	7	
0.5 tetranitromethane	do.	10	
1 do.	do.	15	
Aromatic nitro compounds:			
1.5 nitrobenzene	do.	1	
2 do.	do.	1	
o-dinitrobenzene			Not miscible
m-dinitrobenzene			do.
1 2,3 trinitrobenzene	do.	1	
1.5 o-nitrotoluene	do.	1	
1.5 m-nitrotoluene	do.	0	
1.5 p-nitroxylene	do.	0	
nitrotoluene dissolved in benzene	do.	-	Solution breaks
1.5 p-nitrophenol	do.	-1	

% ignition accelerator	Fuel	Rise in cetane number	Remarks
Peroxides:			
Dimethylperoxide	Gas Oil	Strong action	
Diethylperoxide	do.	do.	
Diacetone peroxide	do.	do.	
Monooxydiethyl peroxide	do.	do.	
Ethylidene peroxide	do.	do.	
Acetyl benzoyl peroxide	do.	do.	
Tetraline peroxide	do.	Weak action	
Acetone peroxide	do.	do.	
0.25 benzoyl peroxide*	do.	6)	
0.50 do.	do.	9)	Values from S.O. Co. laboratories, report 11/10/36 *(We have found no effects).
1 tetraline peroxide	do.	3)	
3 do.	do.	9)	
5 do.	do.		
1.2 acetyl peroxide	do.	10	
4.8 acetyl peroxide	do.	33	
Peroxide formation by aeration	do.	2-5	
Diazo compounds:			
0.5 ethyl diazo acetate	do.	5	
1 do.	do.	8	
(diazo acetic acid ethyl ester)			
Metal compounds:			
<1 magnesium oleate	do.	-1	
1 calcium oleate	do.	0	
1 barium oleate	do.	4	
0.5 barium diphenylamine sulfonate	do.	4	
5 tetraethyl lead	do.	-15	
1.0 tetraethyl tin	do.	-13	
0.5 diethyl zinc	do.	1	
0.5 dibutyl mercury	do.	5	
0.5 tributyl antimony	do.	5	
1 do.	do.	9	
<1 butyl Hg nitrate	do.	8	
1 tributyl methyl antimony hydroxide	do.	6	
1 tributyl chloroacetate	do.	4	Soluble only up to 1% in gas oil
0.1 do.	do.	3	
0.1 tributyl iodide	do.	2	
0.75 tributyl nitrate	do.	2	

TABLE 2. - Lowering of flash point by the addition of nitrates to American gas oil

%	Addition to gas oil	Lowering of flash point	I.b.p., °C.
1	ethyl nitrate	20	88
3	do.	32	
5	do.	37	
1	butyl nitrate	11	
3	do.	18	
5	do.	22	
1	amyl nitrate	3	148
3	do.	9	
5	do.	16	
1	hexylnitrate	1	
3	do.	4	
5	do.	8	

TABLE 3. - Increase in cetane number through absorption of NO_2 at 18-20° C.

%, Absorbed NO_2	Increase in cetane number
0.12	0
0.31	0
0.67	3
1.20	7
1.58	10.5
2.08	18 (saturation)

Subsequent tests showed that gasoil saturation with NO_2 varies irregularly with the temperature.

TABLE 4.

Saturation with NO_2 at	Increase in cetane number
25° C.	11
50° C.	21
70° C.	0
100° C.	7

Frames 12-28

Preliminary calculations of costs of production of aviation gasoline from bituminous coal hard pitch and pitch-tar mixtures in Poelitz, dated 11/6/1941.

Frames 29-37

Preliminary calculations of costs of production of aviation gasoline from Romanian crudes in Poelitz, dated 10/30/1941.

Frames 38-42

Status of synthesis oil production experiments by the Synol Process. Ludwigshafen, June 24, 1941.

Fine grain synol catalyst (3 - 5 mm. grain size) was used in 4 liter gas recycle reactors for 5 weeks at 195° C. The space time yield was 0.4 at first, then rose to 0.5, and stayed afterwards between 0.4 and 0.5 with a throughput of about 50 percent and a $CO:H_2$ proportion of 60:40 or 55:45.

The products were investigated (see tables below). The alcohol content in the samples sent from Leuna was considerably better, and the time of residence was reduced by 1/3 by trebling the throughput. This caused at first the space time yield to rise to 0.6, but it dropped rapidly, and was equal to only 0.1 after 1 day. The reactor was disconnected, and showed an incipient decomposition of the catalyst (without the formation, however, of soot). The catalyst was extracted and put back.

Another, coarser sample of synol catalyst (15 mm. size) was also used in recycle reactor at 195° C. In this case the space time yield was only 0.2.

Powdered synol catalyst was next used in a mixer-foam reactor. The space time yield was entirely unsatisfactory at 195°, and the temperature was raised to 210° C. with a space time yield of 0.12-0.15. The products are still being investigated. At present, the question cannot as yet be answered, whether products obtained in the liquid phase are identical with those from the vapor phase.

The space time yield was much too small for the mixer-reactor, the catalyst concentration in the liquid phase was greatly increased, and the catalyst ground much finer. This failed to improve the space time yield.

Explanation of Tables

The sample from Leuna (table 3) had a higher alcohol content in the middle oil range, than our samples (tables 1 and 2). Olefins in the products obtained with gas recycling (table 2) are considerably above those in tables 1 and 3.

Large Scale Tests with our Own Catalyst in a 30 Liter Foam Reactor

The head was equipped with a recycle pump for the liquid. Difficulties were continuously encountered in the stuffing boxes. The space time yield with the carbon monoxide-hydrogen mixture used remained poor in spite of passing it through Lux mass filter, but good results were obtained with the butyl off gas from Oppau with its high inert contents. An iron catalyst from red iron oxide operated with about 0.15 space time yield at 250°.

An activated coal filter was inserted to regenerate the carbon monoxide-hydrogen mixture.

300-Liter Mixer-Reactor

The bottom stuffing box caused continuous difficulties, and was rebuilt, but caused new difficulties. It was intended to test whether reactor operations would be improved by increasing the catalyst concentrations, or whether the gas intake or catalyst removal design was wrong in principle. In this case somewhat lower but wider reactor case should be selected (as used in laboratory tests).

Large Recycle Reactor

It operates for about four weeks at 320° C. (instead of 325° used previously), operating with butyl off gas with CO added. It operated normally for the first 12 days, but was slightly overheated because of troubles with the cooling water temperature, and the space time yield dropped since then steadily, so that today it operates at only half the former value. No overheated spots are visible. The catalyst may have been plugged up with high molecular weight compounds, which usually occurred after 10 to 14 days at 310°, but could no longer be observed at 325°-330° C.

TABLE 1. - Vertical vapor phase reactors, synol catalysts, 3 mm. size.
Space time yield 0.2, conversion 20-30%, temperature 195° C., 20 atm.

	a	b	c	d	e	f	g	h
	47-100°	100-150°	150-200°	-100°/3 mm.	100-150°/2mm.	150-200°/2mm.	200-250°/2mm.	Residue
	27.4%	15.3%	12.7%	7.8%	19.8%	16.3%	4.7%	
	Gasoline - 200° = 55.4%				Middle oil 200-350° 39.6%			5%
Alcohols	22.2	24.0	24.0	24.0	21.3	14.7	21.5	11.5
Aldehydes and ketones	24.8	16.5	8.9	7.4	4.6	5.1	7.1	68.0
Free acids	0.15	4.1	2.7	0.1	0.1	0.1	0.2	0.5
Olefins by hydrogenation	33.0	22.2	17.5	20.6	14.7	9	12.2	-
Olefins, Hanus	45	19.4	20.7	25.0	18	18	26	-

TABLE 2. - Synol catalyst, 3.5 mm. grain, gas recycling.
Temperature 195° C., 20 atm., space time yield 0.4-0.5 conversion 50-60%

	46-100	100-150	150-200	60-100/5 mm.	100-150/2 mm.	150-200/2 mm.	200-250/2mm.	Residue
	11.7%	8.9%	9.8%	3.9%	14.6%	14.5%	6.4%	
	Gasoline 30.4%				Middle oil 200-350° 38.8%			30.9%
Alcohols	15.4	27.5	24.1	19.0	13.2	9.4	16.7	15.0
Ketones and aldehydes	6.6	9.5	4.4	5.4	3.2	3.1	6.8	26.0
Free acids	0.6	6.1	4.9	0.8	0.5	0.3	0.4	0.6
Olefins by hydrogenation	46	39	47	48	34	21	28	6.5
Olefins, Hanus	53	39	47	49	34	28	39	41
Olefins, Klein	44	33	37	43	26	19	21	-

TABLE 3. - Synol products from Leuna

	-100	100-150	150-200	-100/2 mm.	100-150/2 mm.	150-200/2 mm.	200-250/2 mm.	Residue
	19.4%	18.2%	19.2%	7.8%	14.6%	10.9%	4.5%	
	Gasoline	50-200°	56.8%		Middle oil 200-350°	36.8%		6.4%
Alcohols	7.5	21.8	24.0	14.6	30.0	26.1	19.0	-
Aldehydes and ketones	8.7	11.8	4.1	3.7	3.5	2.3	1.6	-
Free acids	0.05	0.6	0.6	0.1	0.1	0.1	0.3	-
Olefins, hydrogenation	44.8	29.0	21.8	27.2	23.4	19.0	13.7	9
Olefins, Klein	47.0	27.0	20.6	25.0	21.4	18.5	18.3	-
Olefins, Hanus	51.0	30.5	22.6	28.6	26.0	22.6	19.8	41