

HIGH-SULFUR SHALE OIL AS A COMPONENT OF RUBBER STOCKS

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A plasticizer obtained from high-sulfur shale oil (S content 6.5 %) was investigated as an additive for rubber compounds in quantities of 15 and 30 % on medium-high acrylonitrile-butadiene rubber, in comparison with dioctyl phthalate (DOP). The chemical composition of the shale oil additive was studied by chemical and spectral methods. The shale oil additive consisted mainly of compounds C_{14} - C_{20} . About 40 % of the total product consisted of sulfur compounds, mainly heavy derivatives of thiophene. The shale oil additive contained 45 % polar aromatic and hetero-element components. As opposed to DOP, the shale oil plasticizer does not contain ester groups. However, high content of sulfur compounds and polar components result in chemical interaction and a satisfactory compatibility of the additive with rubber. Rubber compounds containing shale oil had a lower hardness, tensile strength and tear resistance, as compared to compounds containing DOP. Regarding flexibility, resistance to low temperature, swelling in oil, fuel and water, both rubber compounds had similar properties at 15 % plasticizers. The properties of rubber compound containing 15 % shale oil are promising.

Introduction

Oil shales are one of the largest prospective sources of organic raw matter in the world and are the most important national source of energy in Israel. Its reserves (20 billion tons) are enough to organize a large scale production of chemicals. Israeli oil shale belongs to the family of high-sulfur fossils. Deposits of high-sulfur oil shales are found in many

countries, such as USA, Austria, Russia, Morocco, Jordan, Syria, Uzbekistan, etc. Technology of processing high-sulfur oil shales was thoroughly studied lately [1]. Utilization of the chemical potential of high-sulfur oil shales is a very important problem.

The oil produced from Israeli shale contains up to 6-7 % sulfur, 1-2 % nitrogen and 2-4 % oxygen. It consists mainly of non-hydrocarbon products and is a typical high-polar mixture of heteroatomic compounds [2-4]. Since Israeli shale oil contains sulfur compounds (an agent for rubber vulcanization), and N- and O-compounds, it can be a valuable component of rubber mixtures, acting as a multipurpose additive.

The plasticizing agents (softeners) for rubber compositions are widely used in industry to give suitable viscosity for processing, assist in the incorporation of fillers so as to reach the required vulcanisate hardness, modulus and low temperature flexibility [5, 6]. Plasticizers are necessary for successful compounding in almost all formulations. Diester plasticizers (phthalates and sebacates) also improve low temperature properties. The plasticizing agents, used at present in rubber stocks, are expensive. Therefore, it is of interest to investigate other possible additives to rubber compositions, such as shale oil.

We have obtained a satisfactory rubber additive, extracted from Baltic shale oil [7]. Shale oil products could be preferentially used in industrial rubber stocks based on polar rubbers: natural, chloroprene, and nitrile. As a multipurpose additive, sulfur oil may be tested also in other mixtures.

Table 1. Technical Characteristics of the Shale Oil Plasticizer

Characteristics	Total oil	Oil additive
Product yield, on total oil, wt. %	100	28
Density at 15 °C	0.989	0.976
Viscosity at 50 °C, cSt	12.3	4.15
Bromine value	72	67
Elemental analysis, %:		
C	79.45	80.61
H	9.82	11.31
O	2.11	0.53
N	1.56	1.02
S	6.86	6.55
Group composition, %:		
Saturated hydrocarbons		23
Naphtheno-aromatics		38
Polar aromatics		39
Asphaltenes	1.5	0
Molecular mass	238	241
Insoluble in heptane, % wt.	1.78	0
Insoluble in toluene, % wt.	0.04	0
Flash point, °C	27	140
Moisture, %	1.0	0
Volatility at 160 °C, %	-	0.4

There are hundreds of formulations of rubber stocks. It is practically impossible to investigate the behaviour of shale oil in all these stocks within the frame work of a single research. For the first stage of the study, it is sufficient to investigate typical rubber mixtures and determine their characteristics in relation to the amount of shale oil additive and the conditions of vulcanization.

Experimental

Investigations of the Chemical Composition of Shale Oil Plasticizer

A middle fraction of Israeli shale oil was chosen as a prime material for obtaining the additive to rubber stocks. The choice of this fraction was based on the following considerations:

- The middle fraction contains a relatively large amount of organic sulfur (the sulfur content decreases with the increase of the fraction boiling point) which is a good incentive for using it as an additive to rubber
- The middle fraction can be easily purified from undesirable compounds
- The oil product, being a component of the rubber mixture, must have a low pour point, and good plasticizing properties

These reasons dictate a definite upper boiling point of the fraction. As to the lower limit of the fraction boiling point, it is determined by a limit on the volatility (it must be less than 0.6 %) and a high value of flash point (it should be not lower than 130 °C). In addition, fractions which are too light are not compatible with rubbers.

For the above mentioned reasons, both the light components and heavy residues were excluded from the initial oil by means of vacuum distillation. The selected fraction was used after special purification as an additive to rubber stocks.

The shale oil additive was investigated by means of standard chemical procedures, gas and column chromatography, and IR and NMR proton spectroscopy. The gas chromatography was carried out using a GC Varian 3600 with Petrochem-100 column. Two detectors were used in parallel: FID and FPD. The content of polar compounds was determined using column chromatography on calcined F-20 alumina adsorbent, essentially according to Corbett's procedure (ASTM D 4124-86). The samples for the IR spectra were prepared in the form of a film between the plates of KBr. NMR spectra were obtained on a Bruker AC 400 spectrometer. The samples were dissolved in deuterio-acetone.

Preparation of Rubber Compounds

The experimental compound was based on a medium-high acrylonitrile butadiene rubber (NBR) medium (bound acrylonitrile content 33 %), which provides a relatively high tensile strength, good fuel and oil resistance, but poor low temperature properties. In order to improve low temperature properties, it is usually plasticized with dioctyl phthalate (DOP). In our experiments, we used parallel DOP and shale oil as plasticizers. The compound was prepared according to ASTM D 3182 [8].

Results and Discussion

1. Shale Oil Plasticizer Characteristics

Characteristics of the initial shale oil and the shale oil additive are shown in Table 1. The oil additive contains about 6.5 % sulfur; it may be of advantage in rubber compounding. It has a low viscosity, high value of flash point, and its technical characteristics meet the requirements for typical plasticizers.

Detailed identification of the compounds in such a complicated mixture as the shale oil additive requires special investigation, and this was not our goal. We concentrated mainly on obtaining the general chemical characteristics of the product. The GC chromatograms (Figures 1 and 2) reveal that the shale oil additive consists mainly of compounds of C_{14} - C_{20} . About 40 % of the total product consist of sulfur compounds, which are seen in the FPD chromatogram. The sulfur compounds are represented by heavy derivatives of thiophenes.

The shale oil additive contains about 40 % of polar aromatic components (that are desorbed from calcined F-20 alumina adsorbent using toluene and trichloroethylene eluents).

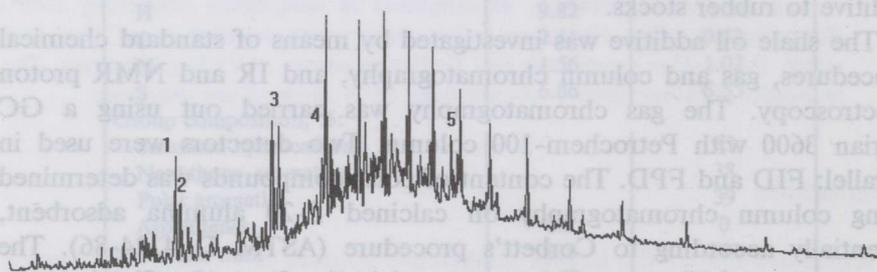


Fig. 1. FID chromatogram of the shale oil plasticizer: 1 - naphthalene, 2 - thionaphthene, 3 - methylnaphthalenes, 4 - dimethylnaphthalenes, 5 - phenanthrene

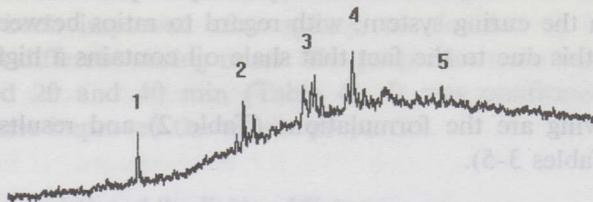


Fig. 2. FPD chromatogram of the shale oil plasticizer: 1 - thionaphthene, 2 - methylthionaphthenes, 3 - dimethylthionaphthenes, 4 - alkylthionaphthenes, 5 - dibenzothiophene

The IR spectrum of the product indicates the absence of OH-groups, interconnected with H-bonds. The ethers (COOR group) are absent as well (there is no absorption at the wave length of 5.7 microns). Compounds with the carbonyl groups (absorption at 5.8-6.1 microns) are present in small quantities.

The NMR shows that the hydrocarbon structures of the shale oil plasticizer consist mainly of naphthenic-paraffinic and one-ring aromatic compounds having 1-3 short side chains as substitutes. The shale plasticizer contains some quantity of unsaturated groups C=C. The NMR spectrum also indicates the absence of aldehydes, alcohols, Ar—O—R and R—O—R ethers, and Ar—COO—R and R—COO—R esters.

Contrary to DOP (an ester), the shale oil additive does not contain ester groups at all. However, a high content of sulfur compounds may result in a chemical interaction of the additives with the rubber, and a high content of polar components may promote good compatibility of both materials. Thus, the composition and properties (low viscosity, high flash point) of shale oil plasticizer allow us to expect that it can be a valuable component in rubber compounds by acting as a multipurpose vulcanizing and plasticizing agent.

2. Rubber Mixtures and Properties

We tested the influence of shale oil on the properties of rubber compounds at two different concentrations: 30 and 15 parts per 100 parts by weight of rubber (30 parts per 100 parts by weight of plasticizers is considered as the maximum quantity for incorporation in compounds based on NBR without causing exudation on the surface). In experiment series No. 1 the rubber compounds containing shale oil were compared to a compound containing no oil at all and another containing DOP.

In series No. 2 the influence of vulcanization time on the properties was tested.

Series No. 3 was based on a fixed quantity of plasticizers and changes performed on the curing system, with regard to ratios between sulfur and accelerators, this due to the fact that shale oil contains a high quantity of sulfur.

The following are the formulations (Table 2) and results of the tests performed (Tables 3-5).

Table 2. Composition of the Rubber Mixtures (parts per 100 parts of the rubber)

Components	Mixture number				
	1	2	3	4	5
NBR (33 % ACN)	100.0	100.0	100.0	100.0	100.0
Sulfur	1.5	1.5	1.5	1.5	1.5
Stearine	1.0	1.0	1.0	1.0	1.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0
SRF	60.0	60.0	60.0	60.0	60.0
DOP	-	30.0	-	15.0	-
Shale oil	-	-	30.0	-	15.0
MBTS	1.5	1.5	1.5	1.5	1.5

The following conclusions can be drawn from these data:

1. The two oils tested (DOP and shale oil) act similarly as plasticizers: minimum viscosities at equal concentrations are very close (see Table 3).
2. DOP has no influence on scorch ($t + 2$) whereas shale oil considerably shortens the scorch time. This is probably caused by the high quantity of sulfur present in the oil. Shale oil in rubber compounds causes a decrease in the following properties: hardness, tensile strength, tear resistance, etc., as compared to compounds containing DOP. Of course the differences are bigger when the quantity of plasticizers is 30 % and smaller with 15 % of plasticizers.
3. After heat ageing, there is a rise in tensile properties of all the compounds, but those containing shale oil are much higher, this fact pointing to continuation of curing.
4. Regarding flexibility and resistance to low temperature, it is apparent that in 15 % concentrations the plasticizers have similar properties in the two cases. DOP in 30 % concentrations is somehow preferred.
5. After swelling in oil, fuel and water, the effect of the two additives is close as regards to changes in properties. Shale oil is preferred. Even here, as with heat ageing there is a tendency to continuation of cure in heat.

6. Due to the fact that tensile properties in compounds containing shale oil have been improved after ageing, we decided to investigate the process at different curing times. The properties were studied on plates vulcanized 20 and 40 min (Table 4). It was confirmed that longer curing times improved the tensile properties.

Table 3. Characteristics of the Rubber Mixtures

Characteristics	Mixture number				
	1	2	3	4	5
Rheological properties					
Minimal viscosity, dN/m	1.79	0.41	0.42	0.71	0.93
Scorch $t + 2$, min : sec	6:00	6:43	3:18	6:23	3:59
Time of vulcanization t_{90} , min : sec	13:12	14:17	9:20	14:22	17:22
Maximum torque, dN/m	15.02	6.23	3.24	9.88	7.66
Time of vulcanization, min	15	20	20	20	20
Mechanical properties					
Hardness, Shore <i>A</i> scale	67	47	37	54	51
Tensile strength, kg/cm^2	216	155	70	197	147
Elongation, %	723	956	1116	838	928
100 % modulus, kg/cm^2	26	14	7	19	13
200 % modulus, kg/cm^2	55	23	10	32	21
300 % modulus, kg/cm^2	95	39	15	55	35
Tear resistance, kg/cm^2	70.7	43.1	35.1	57.1	53.7
Permanent set at the 25 % compression for 70 s at 100 °C	49	59	74	57	54
Herzley elasticity, %	64.5	57.6	51.6	61	60
Change in the properties after 70 hr curing at 100 °C					
Change in hardness, Shore <i>A</i> scale	+2	+3	+12	-4	-3
Change in tensile strength, %	+15.8	+19.0	+115	+6	+33
Change in elongation, %	-23.9	-28.9	-20.5	-28.4	-21.7
Brittleness temperature, °C	-35	-45	-40	-37	-37
Change in the properties after 48 hr immersion into liquid fuel at ambient temperature					
Change in hardness, Shore <i>A</i> scale	-20	-1	-9	-13	-14
Change in tensile strength, %	-28.2	-36.1	-8.6	-39	-33
Change in elongation, %	-28.5	-25.4	-24.5	-24	-17
Change in volume (swelling), %	+29.5	+20.6	+23.5	+26	+25
Change in the properties after 70 hr immersion into oil (ASTM No. 3) at 100 °C					
Change in hardness, Shore <i>A</i> scale	-5	+10	+17	0	+7
Change in tensile strength, %	+12.0	+27.1	+150	+14.2	+45.6
Change in elongation, %	-20.3	-25.5	-20.6	-18.7	-15.6
Change in volume (swelling), %	+9.5	-7.0	-6.1	+1.0	-1.0
Change in the properties after 70 hr immersion into water at 100 °C					
Change in volume (swelling), %	+3.7	+3.8	+3.5	+4.4	+3.12

7. In order to follow the effect of sulfur concentration on the vulcanization process, a series of experiments was carried out. In these experiments the time of vulcanization was constant (40 min), and the quantities of sulfur and accelerator were changed (Table 5). When the quantity of sulfur, accelerator, or both agents was decreased, scorch time $t + 2$ and vulcanization time $t + 90$ prolonged. It indicates that in spite of the high sulfur content in shale oil, it is impossible to reduce the quantities of elemental sulfur or accelerator in the compound.

Table 4. Effect of the Time of Vulcanization on the Characteristics of the Rubber Compounds

Characteristics	Mixture number							
	5-1		5-2		5-3		5-4	
Sulfur content, pph	1.5	1.5	1.5	1.5	1.0	1.0	1.0	1.0
MBTS content, pph	1.5	1.5	0.75	0.75	1.5	1.5	0.75	0.75
Time of vulcanization, min	20	40	25	45	20	40	25	45
Hardness, Shore A scale	51	54	50	52	50	49	50	49
Tensile strength, kg/cm ²	164	192	143	151	89	106	56	76
Elongation, %	950	972	915	903	1450	1143	1050	1200
100 % modulus, kg/cm ²	15	16	16	15	12.5	12	12.5	13
300 % modulus, kg/cm ²	41	42	43	37	26	23	22	21

Conclusions

A plasticizer obtained from high-sulfur shale oil (S content 6.5 %) was investigated as an additive for rubber compounds in quantities of 15 and 30 % on medium-high acrylonitrile butadiene rubber, in comparison with dioctyl phtalate (DOP). The chemical composition of the shale oil additive was studied by chemical and spectral methods. The shale oil additive consisted mainly of compounds C₁₄-C₂₀. About 40 % of the total product consisted of sulfur compounds, mainly heavy derivatives of thiophene. The shale oil additive contained 45 % polar aromatic and hetero-element components. Contrary to DOP, the shale oil plasticizer does not contain ester groups. However, high content of sulfur compounds and polar components result in chemical interaction and a satisfactory compatibility of the additive with rubber. Rubber compounds containing shale oil had a lower hardness, tensile strength and tear resistance, as compared to compounds containing DOP. Regarding flexibility, resistance to low temperature, swelling in oil, fuel, and water, both rubber compounds had similar properties at 15 % plasticizers. The properties of rubber compound containing 15 % shale oil are promising.

Table 5. Effect of the Sulfur and Accelerator Contents on the Characteristics of the Rubber Compounds (time of vulcanization 40 min)

Characteristics	Mixture number			
	5-1	5-2	5-3	5-4
Sulfur content, pph	1.5	1.5	1.0	1.0
MBTS content, pph	1.5	0.75	1.5	0.75
Rheological properties				
Minimal viscosity, dN/m	0.70	0.73	0.84	0.83
Scorch $t + 2$, min : sec	2:57	4:16	3:48	6:42
Time of vulcanization t_{50} , min : sec	4:00	5:45	4:04	5:38
Time of vulcanization t_{90} , min : sec	16:45	19:59	15:13	19:40
Maximum torque, dN/m	7.67	6.53	5.28	4.27
Time of vulcanization, min	40	45	40	45
Mechanical properties				
Hardness, Shore <i>A</i> scale	54	52	49	49
Tensile strength, kg/cm^2	192	151	106	76
Elongation, %	972	903	1143	1200
100 % modulus, kg/cm^2	16	15	12	13
200 % modulus, kg/cm^2	27	22	16	17
300 % modulus, kg/cm^2	42	37	23	21
Tear resistance, kg/cm^2	59	52.5	43.5	34
Permanent set at the 25 % compression for 70 s at 100 °C	79.5	71.1	75.2	88.6
Herzley elasticity, %	57.3	58.1	58.3	58.1
Change in the properties after 70 hr curing at 100 °C				
Change in hardness, Shore <i>A</i> scale	+11	+13	+17	+16
Change in tensile strength, %	+10.9	+23.2	+48	+97
Change in elongation, %	-36.0	-38.0	-39.6	-31.8
Change in the properties after 48 hr immersion into liquid fuel at ambient temperature				
Change in hardness, Shore <i>A</i> scale	-16	-17	-20	-26
Change in tear strength, %	-41.5	-35.1	-47.5	-52.6
Change in elongation, %	-24.4	-21.74	-39.2	-38.5
Change in volume (swelling), %	+24.2	+23.8	+25	+25
Change in the properties after 70 hr immersion into oil (ASTM No. 3) at 100 °C				
Change in hardness, Shore <i>A</i> scale	+4	+4	+5	+4
Change in tensile strength, %	+5.2	+28.5	+43.4	+63.2
Change in elongation, %	-24.6	-12.3	-18.8	-21.4
Change in volume (swelling), %	+3.2	+2.8	+3.6	+4.2
Change in the properties after 70 hr immersion into water at 100 °C				
Change in volume (swelling), %	+5.5	+5.7	+6.6	+7.0

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