IJIAET International Journal of Innovative Analyses and Emerging Technology

| e-ISSN: 2792-4025 | http://openaccessjournals.eu | Volume: 1 Issue: 5

Synthesis and Properties of White Oils Based on Petroleum Sulphonic Acids as Raw Materials

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ABSTRACT: White oils are made by sulphuric acid treatment of petroleum distillates. Petroleum sulphonic acids are the main byproducts from the manufacture of white oils. In the manufacture of white oil and sulphonates there are six stages. The simplest method for producing white oil is by the batch process.In this process the lube oil fraction, contained in a cone bottomed tank, is treated with oleum in a series of dumps using air for agitation. The medicinal grades of white oils are widely used for the treatment of chronic constipation. Due to the inert character of the white oil and its resistance to oxidation, the major volume of white oil is consumed in technical applications and in the process industries. The yield of white oil is very poor in the case of heavier oils. Indian specifications for industrial white oilsand Indian, British and USA pharmacopia specifications are given following tables.

Keywords: white oil, textile oils, leather oils, heavy duty motor oils, raw materials.

Today petroleum sulphonates seem to be major product as they find extensive application in the formulation of various products consumed in huge quantity in the world. Among them are (i) heavy duty motor oils, (ii) cutting oils, (Hi) rust preventives, (iv) textile oils, (u) leather oils, (ui) spray oils and (uii) crude oil emulsion breakers (demulsifiers). Large quantities of sulphonates in the form of calcium and barium salts are being utilized in the manufacture of motor oils as detergents usually with, oxidation and corrosion inhibitors.

White oil may be produced from any of the three types of crude, i.e. paraffinic intermediate and naphthenic. For example, the naphthenic crude is usually selected to produce white oil of high specific gravity and viscosity. The paraffinic crude yields awhite oil of lower viscosity and specific gravity. White oil from paraffinic crude has excellentheat resistance and lubricating qualities as well as affinity for certain waxes. This latter property is important in the manufacture of cosmetics. Most distillates are given a variety of pretreatments before acid treatment in order to either produce an oil having special characteristics or to increase the yield and reduce the amount of acid required. Types and degree of pretreatment depend on the crude source, viscosity, presence of objectionable constituents such as sulphur and the proportion of naphthenes, paraffins, aromatics, unsaturates and asphaltic materials. It is usually essential to deasphaltize by means of propane and then remove part of the aromatic contents by solvent extraction with solvent such as furfural and phenol. It is desirable to dewax the distillates containing high percentage of wax, especially to produce medicinal grades of white oils.

Various steps involved in the manufacture of white oil and sulphonates are:

A. Acid treatment:

B. Neutralization and sulphonate extraction;

C. Solvent removel and steaming to remove light ends;

D. Treatment with clay to remove colour constituents;

E. Solvent recovery and sulphonate purification; and

F. Sludge disposal and acid recovery.

The simplest method for producing white oil is by the batch process. In this process the lube oil fraction, contained in a cone bottomed tank, is treated with oleum in a series of dumps using air for agitation. Between acid dumps, settling period of 24 to 48 hours is used to permit separation of the sludge which is drawn off and disposed to the sewer or recovered in special facilities for further treatment to avoid pollution of rivers, etc. The sludge can be roasted to produce byproduct coke and sulphur dioxide which is reconverted to oleum. Such a plant exists with M/s Madras Petro-Chemicals, Madras. The process of sludge treatment is economical only when sufficient quantity of sludge is produced and the plants for white oil and transformer oil run at their full capacity.

The addition of too much oleum in the oil at a time chars the oil. Therefore, most efficient action of oleum can be realized by successive contacts with oil which results in better reaction time and temperature. Total acid treatment can

ISSN 2792-4025 (online), Published under Volume: 1 Issue: 5 in October-2021

IJIAET International Journal of Innovative Analyses and Emerging Technology
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spread into four or five such contacts which are called "Shots" in white oil industry. After each contact or shot, the sludge is allowed to settle and separated. This sludge contains unreacted acid, most of the water soluble sulphonic acids, called "green acids", other reaction products and impurities. The remaining oil contains oil soluble sulphonic acids called mahogany acids.

When sufficient acid has been used to remove most of the unsaturated and aromatic components, the oil is transferred to a neutralizer and the sulphonic acids present in the oil are neutralized with aqueous caustic or sodium carbonate solution. An emulsion is formed and broken with equimolar mixture of isopropyl alcohol and water. On settling, the lower layer of aqueous solvent containing nearly all the mahogany soap and inorganic salts is drawn off and processed for solvent recovery and sulphonate purification. After the final water or alcohol wash, the oil is heated and blown with air or superheated steam to remove residual moisture and alcohol.

Finished oil is produced from the neutral oil by contacting with or percolating through an active clay or bauxite. Sulphonates are purified by concentrating the crude solution of the soap to a minimum water content and extracting the soap from the salts with concentrated isopropyl alcohol. The alcohol is distilled from the soap after blending in a suitable oil to produce a product having the proper concentration which may vary from 30 to 60 percent.

Table 1. Yields of white oil and sulphonates from various base stocks

		MRL, Madras					HPCL Bombay
Sl.No.	*Characteristics*	*HVI Spindle*	*LVI Spindle*	*Intermediate neutral HVI*	*Intermediate neutral LVI*	*Heavy Neutral HVI*	*500 Neutral HVI*
1.	Kinematic viscosity, cSt						
	(a) At 37.8°C	14.67	15.92	61.06	85.67	144.88	103.87
	(b) At 97.8°C	3.24	3.15	7.67	8.47	13.23	10.72
2	Viscosity index	96.0	46.0	93.0	69.0	93.0	95.0
3	Specific gravity at 15.5/15.5°C	0.8647	0.9149	0.8823	0.9282	0.8937	0.8890
4	Pour point, °C	-6.0	-9.0	-6.0	-3.0	-3.0	-6.0
5	Conradson carbon residue, wt.%	0.01	0.01	0.02	0.06	0.05	-
6	Oleum consumption, wt.% on base stock	41.0	62.0	33.0	51.0	34.0	44.0
7	Yield of white oil, wt.%	63.0	38.0	37.0	26.0	12.5	32.0
8	Yield of sulphonates, wt.% (pure)	10.0	7.0	12.0	16.0	9.0	18.6
9	Equivalent weight of sul-phonates	450.0	421.0	578.0	530.0	612.0	522.0

The total amount of both water and oil soluble sulphonic acids formed for any particular degree of acid treatment is reported to be independent of the temperature at which acid treatment takes place. The percentage of oil soluble sulphonic acids which are recoverable from the oil phase, however, is a direct function of the temperature at which the acid treatment is conducted. At lower temperatures such as 10°C or 30°C, the partition of the mahogany acid is in the direction of sludge layer but as the temperature is raised, the solubility of the mahogany acid in the oil phase is favored to the extent that it is possible to treat under conditions where only traces of mahogany acid remain in the sludge. With the rise in treating temperature to 70°C or 80°C, the sludge releases some oil which is normally held in solution by the mahogany acid contained in the sludge, so that in general somewhat higher yields of oil are obtained at higher temperature. The extent to which advantage can be taken of the oil and mahogany sulphonate yields obtained by high treating temperatures may be limited by the characteristics of the base stock being treated. The quality of white oils made at higher temperatures is somewhat poorer than corresponding products made at lower temperatures.

Oleum is reported to be the most effective in terms of the total acid required to produce a white oil from a given distillate and yield of sulphonates per unit volume of acid used.

Table 1.gives the properties of various naphthenic oils and their white oil yields, sulphonate yields with their average molecular weight, consumption of oleum. The yield of white oil is very poor in the case of heavier oils. Indian

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specifications for industrial white oils are given Table 2. Indian, British and USA pharmacopia specifications are given in Table 3.

The medicinal grades of white oils are widely used for the treatment of chronic constipation. Due to the inert character of the white oil and its resistance to oxidation, the major volume of white oil is consumed in technical applications and in the process industries. A considerable volume of medicinal grade oil is sold in emulsion form, usually of the oil in water type, the emulsifying agent being agar-agar, gelatine, acacia.

The lighter white oils are used as a vehicle in ointments such as a base for nasal sprays. When mixed with effective concentrations of germicides, white oil finds extensive use as a baby oil applied after the bath to prevent chafing and rash.

In the cosmetic industry white oils have become indispensable ingredient in the preparation of cold creams, cleansing cream, vanishing cream. When added in small amounts to tooth paste and shaving cream, the lighter white oils are useful in preventing caking and drying of these preparations.

White oil is also consumed in the manufacture of petroleum jelly. A good petroleum jelly consists of roughly 20 percent microcrystalline waxes and paraffin waxes and 80 percent white oil.

Table 2. Requirements for industrial white oils (IS : 1083-1978)

Sl. No	*Characteristics*	*Requirement for*		
		Light	Medium	Heavy
1	Kinematic viscosity at 37.8°C, cSt	30.0	31.0-63.0	64.0
		(Max.)		(Min.)
2	Relative density at 20/20°C	<——————0.815-0.910——————>		
3	Cloud point, °C	5.0	5.0	5.0
4	Pour point, °C	-3.0	-3.0	-3.0
5	Flash point, Pensky-Martens (closed), °C, Min.	150	150	150
6	Saponificationvalue	0.5	0.5	0.5
7	ColourSaybolt, Min.	+25.0	+25.0	+25.0
8	Sulphur and sulphides	<—————— To pass the test ——————>		
9	Carbonizable substances	<—————— To pass the test ——————>		
10	Ash, %, Max	0.01	0.01	0.01
11	Copper-corrosion at 100°C for 3 hours	<—— Not worse than No. 1———>		
12	Ultra violet absorbance			
	At 275 millimicrons	<——————0.3 (Max.) ——————>		
	295-299 millimicrons	<——————1.0 (Max.) ——————>		
	300-400 millimicrons	<——————0.8 (Max.) ——————>		

Table 3. Specifications of Britain, India and U.S.A. pharmacopia for liquid paraffin

	Specific gravity at 20/4°C		*Kinematic viscosity at* 37.8°C, *cSt*		*Colour Saybolt*	*Readily carbonizabletest*	*Solidparaffintest*	*PbOtest*	*UV absorbance*
	Heavy	*Light*	*Heavy (Min.)*	*Light (Max.)*					
Britain	0.87-0.89	0.83-0.87	64.0	30.0	+30	Pass	Pass	Pass	250-290 (Min.)
India	0.865-0.89	0.85-0.875	64.0	30.0	+30	Pass	Pass	Pass	Nil
U.S.A	0.86-0.905 @ 15.5/15.5°C	0.828-0.88 @ 15.5/15.5°C	38.1	37.0	+30	Pass	Pass	Pass	260-350 (0.1)

ISSN 2792-4025 (online), Published under Volume: 1 Issue: 5 in October-2021

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ISSN 2792-4025 (online), Published under Volume: 1 Issue: 5 in October-2021