

CLEANING UP THE SLOP

Dr. Goldman, Avron Corporation, USA, describes a new solution that has been developed to utilise slop oil and paraffin waxes and to minimise maintenance costs, corrosion and environmental problems.

The petroleum industry of the 1990s saw a growth in production of oil followed by a severe decline in consumption worldwide caused by an economic slowdown. This led to a decrease in crude oil prices and production. However, during this time, the petroleum industry kept exploring for oil in new geographical areas.

It has been estimated that the world reserves of crude oil (not including natural gas, natural gas liquids, and coal) could last at most 50 to 60 years considering the world's present and projected rates of consumption. The estimated growth in the rate of consumption has been put at 2% per year with the USA still being the largest consumer, currently consuming over 30% of the world's daily oil. The major factor in consumption is going to be the growth of the global population.

Every few years, an innovation arises in the petroleum industry that has a significant effect on the present and the future of industry operations. Every oil company would list among their major problems: how can we utilise slop oil and paraffin waxes that separate from crude produced, pipelined and stored in tanks as refinery feedstocks? Also, how can we minimise maintenance costs (pigging and tank cleaning), corrosion and environmental problems?

A solution to these problems has now been developed. The slops and paraffin waxes can be recovered at extremely low cost and can supply an additional 0.5 billion bpy of crude oil to refineries worldwide. At a crude oil market price of US\$ 10 per bbl, this amounts to US\$ 5 billion. Using the product described in this article, the chemical treatment costs could be as low as 1 cent (US\$ 0.01) per bbl, much cheaper than pigging crude oil pipelines.

Avron Corporation has developed a chemical product that will liquefy and disperse into the crude the waxes and other heavy paraffinic compounds that separate. This product, Avron Slop Oil Dispersant 505-SD (patent pending), has been shown to work at ambient temperatures without the need for an external heat source. Using this product in pipeline operations will add less than US\$ 0.01 per bbl of crude oil transported and will reduce or eliminate costly downtime and pigging operations. The reduction of the pipeline operator's maintenance costs by 85% or more through the use of this product is realistically achievable and will dramatically improve the operator's profitability and bottom line (Figure 1).

Avron Slop Oil Dispersant 505-SD is biodegradable (environmentally safe), non-toxic and contains no high or low flashpoint hydrocarbons or chlorinated hydrocarbons. It contains no heavy metals that can poison catalysts during refining operations. 505-SD is a 97% concentrate formulated with proprietary polymers and patented. Tests with a major pipeline company have shown that 505-SD can liquefy wax residues from a pipeline pigging operation when used at concentrations as low as 0.005% (50 ppm).

Avron 505-SD performs five separate functions. It converts the wax in the slop oil from a crystalline to an amorphous material. It disperses the amorphous material into the crude oil diluent (or other diluents such as diesel, gasoil, fuel oil, and lube oil). It acts as a demulsifier which

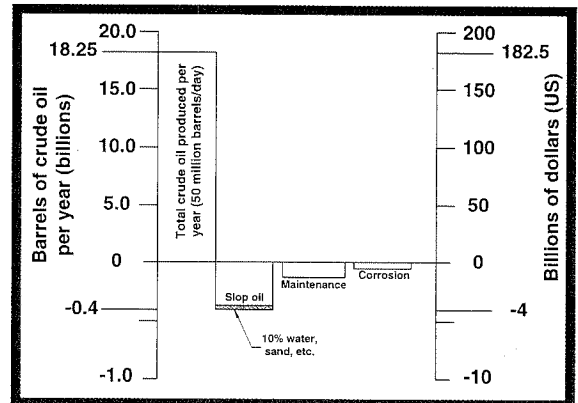


Figure 1. Economics of recovering slop oil for use as hydrocarbon feedstock (per year based on US\$ 10/bbl crude price).

separates any water present in the slop oil, as well as a degreaser and works at very low activity - 0.005% (50 ppm), and it also acts as a pour point depressant for wax.

Case studies

Case study one

Tests show that the addition of 2% Avron 505-SD to one bbl of slop oil/tank bottoms under rapid mixing at 80 °C (176 °F), followed by the addition of three bbls of crude oil (at ambient temperature) resulted in a crude oil blend that was stable (no wax precipitates) for well over 12 months.

Case study two

In additional tests, 3% Avron 505-SD was added to one bbl of slop oil/tank bottoms at 40 °C (104 °F) under constant rapid mixing followed by the addition of two bbls of crude oil (at ambient temperature). The resulting product was a homogeneous and viscous blend of crude oil and slop oil/tank bottoms that showed no separation of the slop oil/tank bottoms component from the blend. The blend remained homogeneous and viscous at ambient temperature for well over 12 months.

The tests described in these two case studies were performed by a major national oil company (an OPEC member) located in the Middle East.

Case study three

This study was performed by a major tank cleaning company in Houston, USA. A small sample (50 g) of heavy waxy slop oil was taken from a storage tank. This slop oil had been in the tank for many years. The slop oil was melted into a liquid mass at approximately 80 °C and stirred to obtain a homogeneous mixture. 2 ml of Avron 505-SD was added to the liquefied wax and the resulting blend was stirred for two minutes at approximately 75 °C.

After it was determined that the 505-SD was thoroughly dispersed throughout the liquefied wax, 150 ml of crude oil tank bottoms (an extremely viscous liquid oil fraction) was added to the mixture and the resultant blend was stirred for

an additional ten minutes at 75 °C to obtain a homogeneous mixture. The mixture was removed from the heat and allowed to cool down to ambient temperature (25 to 30 °C). After reaching ambient temperature, the mixture was separated into two halves and poured into glass bottles for observation.

Each sample indicated two layers: a water layer on the bottom that contained suspended solids (sand etc.) and an upper layer of oil. The samples were allowed to sit for a period of 120 days at ambient temperature during which time it was observed that the oil layer remained completely homogeneous. There was no separation of any solid wax material. One of the samples was centrifuged at ambient temperature and three layers were formed: a layer of sand and grit (3%), a layer of water (27%) and an oil layer (70%). The oil layer remained homogeneous for a period of over ten months with no separation of any solid paraffin. The oil layer remains homogeneous with no separation.

Case study four

A 150 000 bpd refinery in South America, owned by a major European oil company, has performed trial tests on 505-SD to recover the hydrocarbon sludge from the refinery's API separator. 50 ppm of 505-SD was added to a sample of API separator pond sludge at ambient temperature. To the mixture of sludge and 505 was added, at ambient temperature, crude oil at a ratio of four bbls of crude oil to 1 bbl of API pond sludge. All mixing was performed in the absence of heat. Upon the addition of the crude oil, the sludge dissolved into the crude oil forming a homogeneous mixture. After standing for a period of three days, no separation of sludge (paraffin) from the crude oil was observed. The only separation observed was a clear water layer below the crude oil mixture. The hydrocarbon component of the sludge was completely dissolved into the crude oil.

This same refinery repeated the test using crude bottoms taken from its crude oil storage tank. The slop was analysed and found to be 90% paraffin. The trials were performed using 500 ppm of 505-SD. In this trial, a sample equivalent to one bbl of tank bottoms was treated with 500 ppm of 505-SD followed by the addition of three bbls of crude oil. The tank bottoms dissolved completely upon mixing with the crude oil. A completely homogeneous mixture of crude oil and tank bottoms was observed with a lower layer separation of water and suspended solids. On standing, the solids separated from the water. The crude oil tank bottom hydrocarbon mixture (processable oil) was sent for distillation to see if the end point of the distillation increased, which would reflect the presence of the higher boiling point paraffin components.

As a follow up to this last test, the refinery plans to inject 505-SD directly into the crude line that supplies the refinery's storage tanks. The proposed injection ratio would be 25 to 50 ppm. All mixing was performed at room temperature (ambient temperature). No heat was added in either trial test. The results of both tests have convinced this refinery that 505-SD should be used on their first crude oil tank to be cleaned. In this tank, the idea is to recover the tank bottoms, estimated to be as large as 10 000 bbls.

Case study five

A major international oil company with lube oil blending technology faced a serious problem of finding a product that would lower the cloud point of hydroprocessed lube stocks. The only other method suitable for lowering the cloud point was to hydroprocess the lube. Unfortunately, this leads to a lower viscosity product, thus a low shear oil.

Tests with 505-SD at concentrations as low as 750 ppm lowered the cloud point of the lube oil from 15 °C to 3 °C without affecting the viscosity. These studies are positive

proof that 505-SD can change the behaviour of wax in lube oil. This company considers 505-SD to be a good dehardening compound. The addition of 505-SD to lube oil base stocks for lowering cloud points could add no more than US\$ 0.25/bbl to the overall cost of the lube oil.

Case study 6

A refinery in South Louisiana, having experienced a major upset at their delayed coker, used 505-SD as an aid in cleaning two towers. Both the blowdown tower (capacity of 800 bbls) and the stub tower (capacity of 1500 bbls) were treated with an aqueous solution of 505-SD (0.5%) and water (99.5%). Initially the water + 505-SD mixture was added to the towers. The coke and the aqueous chemical mixture were heated to 220 °F and 150 psig with steam for a period of 24 hours without recycling. During this period, the coke was intermingled with the chemical + water + steam mixture. Samples taken after 24 hours indicated that the coke was completely washed (degreased) of any hydrocarbons. After standing in a static condition for 24 hours, the mixture of water + chemical was recycled for two days. At the end of the recycling period, the L.E.L. (lower explosive limit) was safe enough for cleanup to occur in the towers.

The results showed that all hydrocarbon materials (gasoil etc.) were washed of coke and the walls of the towers. It was also observed that residue formed from gasoil was washed away by the water + 505-SD mixture. The refinery was pleased with this result since it saved five days of extra work during cleanup. About 25% of the coke was dispersed. Workers entering the towers for the final cleanup found the coke to be very brittle and easy to break up and clean.

There are many other applications for Avron 505-SD, dispersing slop oil in oceangoing oil tankers, studies are underway to determine what effect 505-SD has in keeping paraffins from separating out of crude oil during transport: in crude oil production wells, it has been tested with success in unplugging heavy paraffin residues from the annulus of the wells: as a dispersing agent for paraffin wax formed in various petrochemical processes, the chemical disperses waste paraffins into heavy fuel oils used as boiler feedstocks: to disperse sediments in asphalt: to clean paraffin waxes and other waste byproduct hydrocarbons separating in gas plants and condensation plants: to disperse heavy sediment in oil recycling plants: to disperse paraffin in finished fuel stocks such as kerosene and gas oil: to disperse heavy paraffinic acids (naphthenic acids) extracted from chemical processes into heavy fuel stocks: to disperse B.S.W. sludge from A.P.I. separators into crude oil for use as a feedstock for visbreakers and delayed cokers: to disperse coke fines during cleanups in the stub and blowdown towers of delayed cokers: to aid in the dispersing and liquefaction of wax compounds in large environmental oil spills by dispersing the paraffins into the crude oil during cleanup: to clean paraffin sludge in heat exchangers in catcrackers: to lower the cloud point of finished lube oil base stocks.

Conclusion

In many countries such as Russia, Eastern Europe and China, the problem with slops is so great that it has been estimated that under proper conditions up to 500 million bpy of crude can be recovered. Avron Slop Oil Dispersant 505-SD has been used in the USA by several companies including Mobil Pipeline Company, Exxon Pipeline Company, Chevron Pipeline Company, Ultramar Diamond Shamrock, Citgo Pipeline and Unocal Pipeline. Overseas it has been under trial testing by Repsol in Argentina, ARAMCO in Saudi Arabia and Sonatrach in Algeria.

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