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THE COLD WATER PROCESS FOR THE RECOVERY OF THE BITUMEN FROM THE BITUMINOUS SANDS OF ALBERTA

3. The Evaluation of Surface Active Agents for Use in the Cold Water Separation Process.

by

D.S. Montgomery and M.P. Pleet

Fuels Division

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D.S. Montgomery^{1/} and M.P. Pleet^{2/}

SUMMARY

A procedure was developed to evaluate surface active agents for use in the cold water separation process for the recovery of the bitumen from the bituminous sands of Alberta. Some sixty wetting agents and combinations of these substances were tested. Wetting agents of each of the three major types, anionic, cationic and non-ionic were examined. The nonionic class appeared to be preferable as smaller amounts of water and mineral matter were obtained in the oil phase with less loss of bitumen on the sand tailings. The most satisfactory reagents of all those tested were Span 40, Span 80, and Rosin Amine D Acetate at a concentration of 0.006g per 100 ml water added to the ball mill. This evaluation technique shows promise as a means of selecting wetting agents for use in the water injected in oil fields to improve the oil recovery.

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INTRODUCTION

The historical development of the cold water process has been briefly described in a previous report by Rosewarne and Swinnerton (1). However there are certain facts relating to the development of this process which may bear repeating to provide a historical background for this and subsequent reports of this series.

At the termination of the experimental operations of Abasand Oils Ltd., in 1942 which used the McClave process, the conclusion was that although this process was capable of producing fairly clean separations under carefully controlled conditions it was too sensitive to minor changes in the amount of gravel and clay in the feed, as well as to fluctuations in the feed water temperature, and in the water temperatures maintained throughout the separation process. In addition the cost of heating the quantities of water demanded by this process appeared to be excessive. The open tanks involved in this operation gave rise to extremely uncomfortable and unhealthy conditions of humidity and temperature inside the buildings, both in winter and summer. It also became apparent that the refinery was incapable of handling the quantity of bitumen produced by the separation plant. As it was beyond the means of Abasand Oils Ltd., to bring about the necessary changes, the Dominion Government undertook to provide the funds required for remodelling the plant. Accordingly the separation plant was dismantled in 1943 and reassembled

by December 1944 still using what was essentially the McClave process.

In the meantime further experimental work had been performed in the laboratory of Abasand Oils Ltd., which indicated that bitumen could be separated from the sand by using much cooler water than was used in the McClave process. Briefly, this modified process consisted of feeding the bituminous sand to a mixer together with a certain proportion of light petroleum distillate and water at room temperature; then transferring the resultant mixture to General Engineering Company (Geco) flotation cells and removing the diluted bitumen froth from the cells to a settling chamber. In February 1945 an experimental circuit of this type was set in operation in the Abasand plant. It was referred to as the "Cold Water Process" or the "Geco Process". Early experiments with this cold water process were found to be so encouraging that the management of the project decided to increase the installation of this type of equipment in order to thoroughly test the process within the shortest possible time. Unfortunately the Abasand separation plant was destroyed by fire in June 1945. As all the records relating to the Geco process were also destroyed, it was decided to investigate this process at the Mines Branch in Ottawa in order to evaluate its merits.

A Denver Sub-aeration cell and a Fagergren cell were studied, but were abandoned as unsuitable. It was felt that the

deficiencies of these machines with regard to their capacity to remove the bitumen from the sand could not be rectified by any slight modification, and therefore the selection of this type of equipment was incorrect in principle. The introduction of air to form a froth caused a very substantial amount of mineral matter to float in the oil phase. A new flow sheet was therefore devised by H. L. Beer* which formed the basis from which the initial Mines Branch cold water process was developed. The modification of this pilot plant and the performance of various flow sheets have been described by Djingheuzian (2). This process should not be confused with the Geco cold water process as every effort was made to prevent aeration of the oil phase in the Mines Branch cold Water process no matter what flow sheet was employed.

As was mentioned in the first report of this series (3), the Mines Branch of the Department of Mines and Technical Surveys began operating the cold water separation pilot plant in Ottawa in April 1949. This project was undertaken jointly by the Mineral Dressing and Process Metallurgy Division and the Fuels Division. The responsibilities of the Fuels Division were the development of analytical methods, the execution of all the analytical work necessary for the control and evaluation of the process, the evaluation of surface active agents for use in the cold water process, and the
* Metallurgical Engineer, Mineral Dressing and Process Metallurgy Division.

study of the mechanism of separation process. The present report describes the work done to devise a suitable scheme for evaluating some sixty wetting agents and six of their combinations. The experiments to be described were conducted between May 12, 1949, and July 30, 1950 under the direction of Dr. T. E. Warren and D. S. Montgomery.

In the previous laboratory work on the cold water process by Rosewarne and Swinnerton (1), the bituminous sand employed was a composite sample obtained from the drill cores of bitumen taken from the Mildred and Ruth Lakes area of Northern Alberta. However, in all the experiments described in the present report the bituminous sand came from the Horse River property of Abasand Oils Ltd., (4). Bitumen from the same source was employed in the pilot plant up until October 30, 1949.

The previous laboratory work on the cold water separation process had shown that the separation occurred as a result of the different densities of the three components oil, water and sand (1). However it was also found that certain substances, such as sodium silicate, and sodium carbonate, facilitated the removal of the oil from the sand, which indicated that detergents also played a significant role in this process. This suggested that a study should be made of the influence of a wide variety of synthetic organic wetting agents upon the cold water separation process. It was hoped that by undertaking such experiments, it might be possible to find a

wetting agent or combination of wetting agents which would reduce the mineral matter and water content of the bitumen kerosene phase, and at the same time reduce the loss of bitumen-kerosene in the sand tailings.

In studying the data contained in this report it must be firmly kept in mind that these values were obtained when kerosene was used as the diluent unless otherwise stated. It was demonstrated in the course of the laboratory work on the cold water process that the degree of separation of bitumen from the sand was, to a limited extent, dependent upon the type of diluent employed. Up to the present time the diluents obtained from the distillation of the bitumen have possessed higher specific gravities and viscosities than kerosene, which may account for the greater loss of bitumen on the sand tailings when these diluents were used.

EXPERIMENTAL

Determination of the Desirable Wetting Agent Concentration

The work of Killner (5) showed that at low concentrations surface active substances tend to break emulsions, whereas at high concentrations they promote emulsion formation. A qualitative experiment was undertaken using water, kerosene, and a number of wetting agents to determine the concentrations at which emulsion formation and breaking would take place. A stoppered 100 ml graduated cylinder was filled with 30 ml of kerosene together with 48.4 ml of water and wetting agent. This mixture was shaken

violently by hand for 30 seconds and placed on the bench. The time required for the two phases to separate, as compared with the time when pure water was used, was taken as the measure of the capacity of a given wetting agent to make or break an emulsion. It was found that for several wetting agents, emulsion formation began above a concentration of .012g per 100 ml of water, and emulsion breaking occurred at concentrations in the order of .006g per 100 ml of water.

On the addition of wetting agents to heterogeneous systems such as bitumen-kerosene, sand and water, the wetting agent distributes itself between the oil and water phases and is adsorbed at the phase boundaries between water and sand, and water and oil. In view of this complicated distribution of the wetting agent it was more convenient to express the wetting agent concentration as though it were entirely contained in the water phase.

Killner demonstrated that bunker oils contained substances of considerable surface activity so that it seems reasonable to assume that bitumen likewise possesses compounds of this type. It was therefore expected that the preliminary experiments with kerosene and water to determine the concentrations at which emulsions would be formed and broken would have to be modified considerably when the oil phase was changed to a mixture of bitumen and kerosene in equal parts by weight. This expectation was not confirmed by experiment. It may be seen from the results of the

experiments shown in Table 1 where bituminous sand, kerosene, and water were ball milled and separated in a standard manner, that usually, whenever the wetting agent was increased from .0093 to .0186g per 155 ml of water added to the ball mill, the water content of the bitumen kerosene layer increased. This showed that the interesting range of wetting agent combination appeared to lie between zero and .006g per 100 ml of water. The water content of the bitumen kerosene phase after 24 hours settling was frequently somewhat lower when no wetting agent was used, than when .0093g of wetting agent was incorporated in the charge. This showed that the concentration probably was a little high as far as industrial practice may be concerned, but it appeared to be very convenient concentration for testing and comparing wetting agents. It should be emphasized that while the wetting agent concentrations are herein expressed in terms of the water added to the ball mill, this was done merely as a matter of convenience. It is possible that an equally significant factor, is concentration of the wetting agent in the total quantity of water, that is, the water added to the ball mill plus the water added during the settling operation, per unit mass of bituminous sand. As the water added to the ball mill and the total quantity of water was maintained constant in the following experiments, the wetting agent concentration could be expressed in terms of either of these quantities. To conserve heat in large scale industrial operations it may be desirable to reduce the water

added during the settling operation. This may require an adjustment in the quantity of wetting agent added to the water in the ball mill.

Procedure for Evaluating the Influence of Wetting Agents Upon the Cold Water Separation Process

The procedure to be described was designed to study the influence of wetting agents upon the process as a whole and not upon the various basic operations such as milling, agitation, classification and thickening. This approach was made so as to enable the results to be applied directly to the pilot plant as a whole, since the flow sheet was to a large extent already arbitrarily fixed. The wetting agents need not be added during the milling operation, but may be added at any point in the system. There may be instances where it is desirable to make the addition after milling to bring about a specific effect such as the dehydration of the oil. The reason for adding the wetting agents to the ball mill was to ensure an equilibrium distribution of the wetting agent between the various phases and surfaces. The existence of the condition of equilibrium was assumed to improve the reproducibility of results. It will be recalled that the ratio of water to bituminous sand in the ball mill was approximately one ninth of that at the thickening stage in the separation process. As it is known that high wetting agent concentrations induce emulsion formation whereas low concentrations lead to emulsion breaking, it is desirable to look for a wetting agent concentration which will enhance the detergent action of the water during milling and assist emulsion

breaking at subsequent stages in the separation process where large quantities of water are added.

To preserve the continuity of the experimental work, the procedure described by Rosewarne and Swinnerton (1) was followed closely. A sample of approximately 100 lbs. of bituminous sand was mixed by shovelling on a concrete floor and then placed in a calcium carbide drum. The drum was closed to prevent the loss of moisture and excessive contact with air. For each test the following charge was added to a porcelain jar mill containing 3200g of flint pebbles:

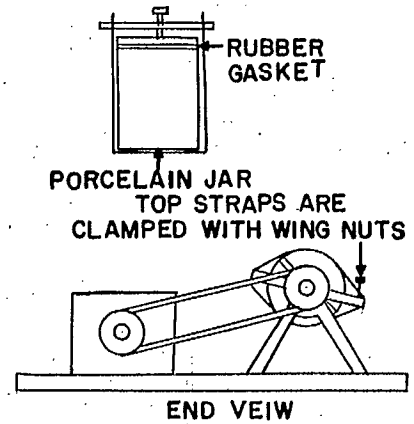
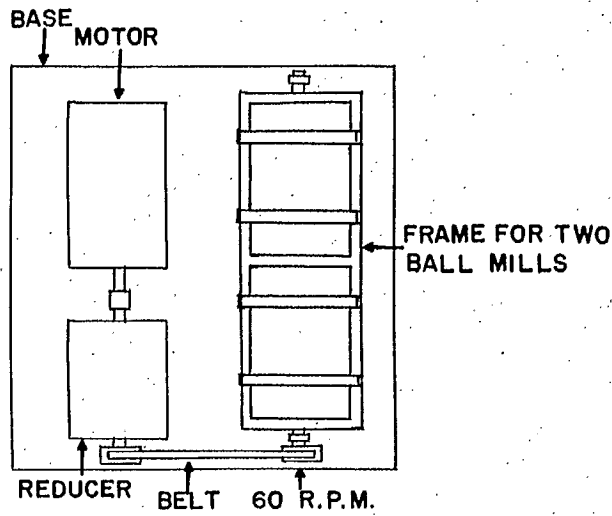
500 g	bituminous sand
155 cc	tap water
77.5 cc	kerosene
.0186 or .0093g	wetting agent

A schematic diagram of the apparatus involved in this procedure is shown in Figure 1.

The bituminous sand was ground by closing the jar mill and rotating it for 20 minutes at 60 r.p.m. The contents of the mill were then discharged into a funnel provided with a screen to retain the pebbles. The sand and bitumen were washed from the pebbles with 1190 ml of water at 75° F into a glass separatory funnel which consisted of an inverted Winchester with the bottom removed. This mixture was stirred at 1700 r.p.m. for 15 minutes and allowed to stand for one hour. The sand and water were then withdrawn from

LABORATORY SCALE COLD WATER SEPARATION PROCESS

BALL MILL



SEPARATING AND SETTLING APPARATUS

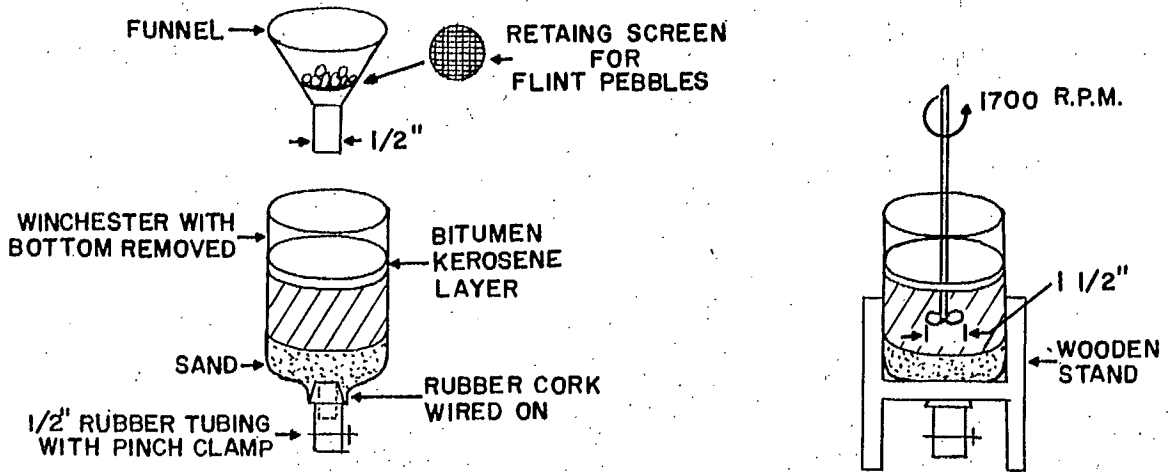


FIGURE 1

the bottom of the funnel into a second separatory funnel for further treatment which will be described under the section entitled, "Treatment of the Water-Sand Pump". The supernatant bitumen-kerosene was drained into a 250 ml graduate and the volume was measured. The water contents of 25 ml samples withdrawn with a pipette from the upper surface of this bitumen-kerosene after standing in the graduate for one hour, and twenty-four hours, was determined by the following procedure.

Analysis of the Oil Phase

The water content of the bitumen-kerosene layer was determined following the A.S.T.M. procedure D 95-46. The method of analysis was briefly as follows: a 25 ml sample of bitumen-kerosene was placed in a glass flask and weighed. To this was added 100 ml of naphtha. Following assembly of the apparatus, distillation was continued until no more water was collected in the trap. The volume of water was ascertained and assuming a value of unity for the density of the water, the percentage of water in the bitumen was determined.

The determination of the mineral matter in the bitumen-kerosene layer was made by weighing 4 to 5 g of bitumen-kerosene into a crucible of known weight. The water was removed by evaporation under a heat lamp to prevent bumping during the subsequent ignition of the bitumen-kerosene. When the bitumen was burned down to a

solid black residue the crucible was transferred to a muffle furnace to complete the ignition. The ash was weighed as mineral matter. No attempt was made to correct this weight for the loss in weight of the clay that takes place on ignition.

Treatment of the Water-Sand Pump

It was found that when the sand was drawn off and analysed after the initial 15 minute stirring, and one hour standing, the bitumen content of the sand was considerably higher than that which was rejected by the classifier in the pilot plant. To obtain comparable results in the laboratory it was necessary to drain the sand and water into a second separatory funnel as mentioned previously and stir at 1700 r.p.m. for an additional 10 minutes. This was followed by a 30 minute settling period to permit the sand to settle firmly on the bottom of the separatory funnel so that it would remain in place during the decanting operation.

The supernatant bitumen was floated off the top by the addition of water to the separatory funnel and the bitumen adhering to the funnel walls was removed beneath the water surface with a cloth. The supernatant water was decanted leaving the moist sand.

Analysis of the Sand

The moist sand was then removed from the separatory funnel and dried in an oven at 110°C overnight. Some kerosene was undoubtedly lost during this operation but no correction was made for this

fact. A sample of the dry sand was taken and extracted with carbon tetrachloride in a Soxhlet apparatus for 2 hours. The percentage loss in weight of the dry sand without correction for the fine clay passing through the double thimble was reported as the percentage of bitumen-kerosene in the water free sand tailings.

RESULTS AND DISCUSSION

Table 1 is a tabulation of the results obtained on milling 500 g of bituminous sand, 155 ml Ottawa tap water and 77.5 ml kerosene with a variety of wetting agents at two concentrations .006 and .012g per 100 ml of ball mill water. The most satisfactory wetting agent is the one which yields the lowest value of the water and mineral matter in the oil, as well as the smallest loss of bitumen on the sand tailings, at the lowest cost. The wetting agent which most nearly fulfils this requirement is Span 40. It will be observed that while some wetting agents yield extremely dry oil, this desirable quality may be counteracted by a high mineral matter content of the oil phase or an excessive loss of oil in the sand tailings. A compromise between these three factors and the cost of the wetting agent must be made. Table 2 summarizes those wetting agents which were considered to be the most suitable. In each experiment to test a given wetting agent the sum of the percentage loss of bitumen in the sand tailings and the mineral matter in the oil phase was calculated. In Table 2 these sums were arranged in

TABLE I
SUMMARY OF THE RESULTS OBTAINED ON ADDING WETTING
AGENTS TO THE LABORATORY SCALE COLD WATER PROCESS

Wetting Agent	Manufacturer	Cost in Cents Per Pound	Type	Weight of Agent per Standard Charge g*	Bitumen Kerosene Layer				% of Bitumen Kerosene in Dry Sand Tailings	Temperature Degrees F	
					% of Water After 1 Hour	% of Water After 24 Hours	Volume in ml	% of Mineral Matter		Room	Wash Water
Standard Charge*					21.1	0.92	156	1.70	0.58	62	75
Aerosol 18	American Cyanamid Co.		anionic	0.0093	19.8	8.19	167	2.91	1.10	76	75
Alkaterge C	Commercial Solvents Corp.		cationic	0.0093	17.1	4.97	106	1.39	0.92	72	75
Amine 220	Carbide and Carbon Chem. Corp.	75	cationic	0.0093	19.8	0.91	152	0.93	0.58	82	76
Amine 220	Carbide and Carbon Chem. Corp.	75	cationic	0.0186	23.0	1.35	155	1.17	0.51	82	76
Antarox A 400	Gen. Aniline and Film Corp.	30	nonionic	0.0093	3.48	0.63	109	0.81	1.18	70	70
Antarox A 400	Gen. Aniline and Film Corp.	30	nonionic	0.0186	3.77	1.54	136	0.85	1.34	70	70
Armoc CD	Armour and Co.		cationic	0.0093	12.7	2.03	90	1.21	1.17	82	75
Armoc TD	Armour and Co.		cationic	0.0093	21.6	2.02	54	2.16	2.25	82	75
Arquad C	Armour and Co.		cationic	0.0093	22.6	0.89	40	2.71	4.68	78	75
Duponol G	Canadian Industries Ltd.	25	anionic	0.0093	31.3	1.36	167	2.17	0.82	61	75
Duponol G	Canadian Industries Ltd.	25	anionic	0.0186	26.8	3.09	176	4.53	0.62	61	75
Duponol LS	Canadian Industries Ltd.	9	anionic	0.0093	16.3	3.47	96	1.34	1.21	65	75
Duponol L-144-WD	Canadian Industries Ltd.	20	anionic	0.0093	27.9	1.42	156	1.90	1.05	64	75
Duponol ME	Canadian Industries Ltd.	117	anionic	0.0093	16.2	0.70	136	0.85	0.44	73	75
Duponol MP-189-S	Canadian Industries Ltd.	4	anionic	0.0093	29.4	1.79	162	1.76	0.50	73	75
Duponol OS	Canadian Industries Ltd.	23	anionic	0.0093	26.7	3.77	134	1.57	0.88	64	75
Duponol WAT	Canadian Industries Ltd.	9	anionic	0.0093	27.3	1.46	155	1.79	0.68	67	75
Duponol WS	Canadian Industries Ltd.	26	anionic	0.0093	20.9	16.5	106	1.33	1.39	64	75
Duponol 80	Canadian Industries Ltd.	7	anionic	0.0093	23.9	1.39	142	1.46	0.86	64	75
Experiment 2608-1	Gen. Aniline and Film Corp.		nonionic	0.0093	6.50	0.81	130	1.07	1.35	76	75
Experiment 2608-1	Gen. Aniline and Film Corp.		nonionic	0.0186	8.18	1.36	112	1.06	1.22	76	75
Experiment 2608-3	Gen. Aniline and Film Corp.		nonionic	0.0093	2.94	0.34	105	2.12	4.02	78	75
Experiment 2608-3	Gen. Aniline and Film Corp.		nonionic	0.0186	1.67	0.81	55	2.83	2.95	78	75
Experiment 2608-8	Gen. Aniline and Film Corp.		nonionic	0.0093	1.85	0.50	38	1.31	3.63	74	75
Experiment 2608-8	Gen. Aniline and Film Corp.		nonionic	0.0186	1.54	1.67	46	1.51	2.76	74	75
Experiment 2608-206											
Agent 362-BL	Gen. Aniline and Film Corp.		nonionic	0.0093	8.47	0.65	109	1.37	1.30	70	75
Experiment 2608-206											
Agent 362-BL	Gen. Aniline and Film Corp.		nonionic	0.0186	3.05	0.76	123	1.29	2.15	70	75
Experiment 2608-226											
Agent 362-LE	Gen. Aniline and Film Corp.		nonionic	0.0093	3.45	0.91	36	0.95	1.50	73	75
Experiment 2608-226											
Agent 362-LE	Gen. Aniline and Film Corp.		nonionic	0.0186	3.39	1.45	102	1.11	2.31	73	75
G-1226 (Renex)	Atlas Powder Co.	26	nonionic	0.0093	8.87	0.81	72	1.27	1.65	78	76
G-1256	Atlas Powder Co.	32	nonionic	0.0093	11.5	1.89	127	0.81	1.06	78	76
G-1266	Atlas Powder Co.	32	nonionic	0.0093	14.8	1.40	138	1.16	1.09	76	76
G-8916-T	Atlas Powder Co.	32	nonionic	0.0093	18.6	1.35	129	1.06	0.60	76	76
Igepal CA	General Dyestuff Corp.		nonionic	0.0093	29.3	0.97	153	1.72	1.13	67	75
Igepon T	General Dyestuff Corp.		anionic	0.0093	10.7	-	190	1.36	3.56	78	72
Igepon T	General Dyestuff Corp.		anionic	0.0186	19.4	-	171	1.57	0.62	78	75
Lissopol N-300	Canadian Industries Ltd.	8	nonionic	0.0093	12.8	1.42	128	1.00	0.92	65	75
Nekal BX	General Dyestuff Corp.		anionic	0.0093	27.7	0.0	178	2.56	0.29	63	75
Nekal BX	General Dyestuff Corp.		anionic	0.0186	12.3	1.35	162	3.29	0.45	63	75
Nekal NS	General Dyestuff Corp.		anionic	0.0093	14.3	2.21	90	1.40	1.41	71	75
Polyethylene-Glycol 200 Mono Palmitate	Carbide and Carbon Chem. Corp.		nonionic	0.0093	4.31	0.0	135	1.04	1.53	70	70
Polyethylene-Glycol 200 Mono Palmitate	Carbide and Carbon Chem. Corp.		nonionic	0.0186	2.78	0.71	108	0.83	1.86	70	70
Polyethylene-Glycol 400 Mono Oleate	Carbide and Carbon Chem. Corp.		nonionic	0.0093	1.22	0.39	104	0.93	2.72	70	70
Polyethylene-Glycol 400 Mono Oleate	Carbide and Carbon Chem. Corp.		nonionic	0.0186	5.07	0.79	100	1.14	1.80	70	70

* Standard charge equals 500 g bituminous sand plus 77.5 ml kerosene and 155 ml tap water, no wetting agent and no Na_2CO_3 present.

TABLE I CONTINUED

Wetting Agent	Manufacturer	Cost in Cents Per Pound	Type	Weight of Agent Per Standard Charge g*	Bitumen Kerosene Layer				% of Bitumen Kerosene in Dry Sand Tailings	Temperature Degrees F	
					% of Water After 1 Hour	% of Water After 24 Hours	Volume in ml	% of Mineral Matter		Room	Wash Water
Rosin Amine D Acetate	Hercules Powder Co.	22	cationic	0.0093	22.2	1.40	149	0.71	0.45	70	78
Rosin Amine D Acetate	Hercules Powder Co.	22	cationic	0.0186	21.1	2.05	170	0.54	0.89	70	78
Sorapon SF	General Dyestuff Corp.		anionic	0.0093	22.5	0.94	158	1.52	0.87	71	75
Span 20	Atlas Powder Co.	33	nonionic	0.0093	16.3	0.0	148	0.70	0.43	82	75
Span 20	Atlas Powder Co.	33	nonionic	0.0186	43.1	0.32	176	0.50	0.39	82	75
Span 40	Atlas Powder Co.	33	nonionic	0.0093	8.45	0.91	170	0.65	0.23	82	75
Span 40	Atlas Powder Co.	33	nonionic	0.0186	10.7	1.38	195	0.52	0.57	82	75
Span 60	Atlas Powder Co.	33	nonionic	0.0093	26.4	5.99	153	1.56	0.31	76	75
Span 60	Atlas Powder Co.	33	nonionic	0.0183	28.6	11.8	167	1.77	0.26	76	75
Span 62	Atlas Powder Co.	33	nonionic	0.0093	30.7	2.31	160	1.83	0.18	76	75
Span 62	Atlas Powder Co.	33	nonionic	0.0186	30.0	3.54	158	1.13	0.80	76	75
Span 65	Atlas Powder Co.	32	nonionic	0.0093	8.13	1.20	124	0.87	1.04	70	75
Span 65	Atlas Powder Co.	32	nonionic	0.0186	6.30	1.55	97	1.09	2.10	70	75
Span 80	Atlas Powder Co.	33	nonionic	0.0093	21.0	1.39	164	0.52	0.47	82	75
Span 80	Atlas Powder Co.	33	nonionic	0.0186	20.5	1.36	177	0.57	0.76	82	75
Span 85	Atlas Powder Co.	32	nonionic	0.0093	26.1	1.40	158	0.64	0.35	70	75
Span 85	Atlas Powder Co.	32	nonionic	0.0186	29.0	3.60	170	1.63	0.45	70	75
Tamol N	Rohm and Haas Co.	15	anionic	0.0093	5.68	0.67	98	1.97	1.58	81	75
Tamol N	Rohm and Haas Co.	15	anionic	0.0186	-	-	16	2.06	4.60	80	75
Tamol N	Rohm and Haas Co.	15	anionic	0.0387	15.2	1.93	151	1.61	0.93	80	75
Teepol	Shell Chemical Ltd.		anionic	0.0093	18.1	5.84	130	2.23	1.96	76	75
Tergitol 7	Carbide and Carbon Chem. Corp.		anionic	0.0093	30.7	0.57	164	2.84	0.97	62	75
Tergitol 7	Carbide and Carbon Chem. Corp.		anionic	0.0186	23.4	16.7	154	1.88	1.03	62	75
Tergitol-NPG-101-S-18400	Carbide and Carbon Chem. Corp.		nonionic	0.0093	5.04	1.37	50	1.06	0.94	77	75
Tergitol-NPG-101-S-18400	Carbide and Carbon Chem. Corp.		nonionic	0.0186	2.36	1.39	124	0.96	1.69	77	75
Tergitol-TMN-650	Carbide and Carbon Chem. Corp.		nonionic	0.0093	5.41	2.90	62	0.86	0.75	75	75
Tergitol-TMN-650	Carbide and Carbon Chem. Corp.		nonionic	0.0186	2.92	1.64	112	0.91	1.43	75	75
Triton W-30	Rohm and Haas Co.	22	anionic	0.0093	23.7	1.41	174	1.12	2.95	66	75
Triton W-30	Rohm and Haas Co.	22	anionic	0.0186	34.0	1.63	177	.52	0.26	66	75
Triton X-100	Rohm and Haas Co.	37	nonionic	0.0093	30.1	7.01	152	2.62	0.49	77	76
Triton X-100	Rohm and Haas Co.	37	nonionic	0.0186	30.3	4.05	166	2.11	0.50	77	76
Tween 20	Atlas Powder Co.	43	nonionic	0.0093	25.1	2.27	146	1.09	0.65	72	75
Tween 21	Atlas Powder Co.	43	nonionic	0.0093	21.3	1.87	167	0.73	0.59	76	75
Tween 21	Atlas Powder Co.	43	nonionic	0.0186	14.9	2.24	95	0.94	0.59	76	75
Tween 40	Atlas Powder Co.	43	nonionic	0.0093	7.11	1.39	100	0.68	0.82	72	75
Tween 40	Atlas Powder Co.	43	nonionic	0.0186	16.1	1.77	138	0.73	0.35	72	75
Tween 80	Atlas Powder Co.	43	nonionic	0.0093	4.69	1.43	148	0.85	0.31	74	75
Tween 80	Atlas Powder Co.	43	nonionic	0.0186	8.33	1.33	160	0.58	0.62	74	75
Tween 81	Atlas Powder Co.	43	nonionic	0.0093	24.2	15.7	152	0.60	0.32	74	75
Tween 81	Atlas Powder Co.	43	nonionic	0.0186	22.4	1.77	164	0.75	0.40	74	75
Tween 85	Atlas Powder Co.	43	nonionic	0.0093	6.85	2.38	148	0.61	0.77	75	75
Tween 85	Atlas Powder Co.	43	nonionic	0.0186	31.1	2.73	164	1.09	0.32	75	75
Wetfot ID	General Dyestuff Corp.			0.0093	18.0	2.58	44	1.73	0.67	76	75

* Standard charge equals 500 g bituminous sand plus 77.5 ml kerosene and 155 ml tap water, to which the above wetting agents were added.

TABLE 2

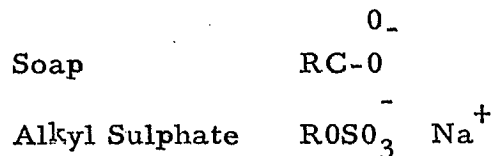
SUMMARY OF THE SIX MOST SUITABLE WETTING AGENTS FOR IMPROVING
THE PERFORMANCE OF THE LABORATORY SCALE COLD WATER PROCESS

Wetting Agent	Manufacturer	Cost in Cents per Pound	Type	Weight of Agent Per Standard Charge g*	Bitumen Kerosene Layer				% of Bitumen Kerosene in Dry Sand Tailings	Temperature Degrees F	
					% of Water After 1 Hour	% of Water After 24 Hours	Volume in ml	% of Min- eral Matter		Room	Wash Water
Span 40	Atlas Powder Co.	33	nonionic	0.0093	8.45	.91	170	0.65	0.23	82	75
Span 85	Atlas Powder Co.	32	nonionic	0.0093	26.1	1.40	158	0.64	0.35	70	75
Span 80	Atlas Powder Co.	33	nonionic	0.0093	21.0	1.39	164	0.52	0.47	82	75
Span 20	Atlas Powder Co.	33	nonionic	0.0093	16.3	0.00	148	0.70	0.43	82	75
Rosin Amine D Acetate	Hercules Powder Co.	22	cationic	0.0093	22.2	1.40	149	0.71	0.45	70	78
Tween 80	Atlas Powder Co.	43	nonionic	0.0093	4.69	1.43	148	0.85	0.31	74	75

* Standard charge equals 500 g bituminous sand plus 77.5 ml kerosene and 155 ml tap water, to which the above wetting agents were added.

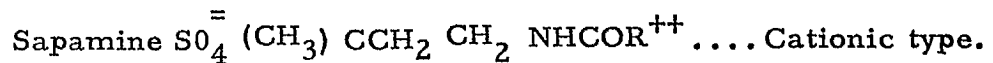
descending order; the most suitable wetting agent therefore appears at the top of the table. When the sum of these two quantities was the same for two detergents another factor such as the water content of the oil or the cost was used to decide the order of precedence.

The wetting agents in Table 1 fall into three chemical types, anionic, nonionic and cationic. Those detergents and wetting agents which ionize in water like soap belong to the anionic type.



Those wetting agents which do not ionize in water, such as the ethylene oxide condensate of an alkyl phenol (Igepal CA), or esters of a fatty acid such as glycerol monostearate, belong to the nonionic type.

The third class is the cationic type of compound in which the organic radical bears a positive charge, and for this reason this group of compounds is called the invert soap class. For example, sapamine belongs to this type of wetting agent.



To this group belong the sanitizing and bactericidal agents and a few detergent and wetting agents (6).

In certain instances it has been found that a combination of wetting agents yields the most desirable result. In view of the large number of wetting agents which had to be tested, it was not

possible to examine in detail many combinations of these surface active agents. It was of interest however to determine whether there was any merit in combining the most suitable wetting agent of the nonionic type with the best anionic and cationic agents. Table 3 gives the tabulated results obtained on combining equal proportions by weight of the nonionic and anionic type, as well as the nonionic and cationic types. These limited results gave no indication that there was any particular virtue in combining wetting agents of these types. In Table 3 are also listed several other combinations of wetting agents belonging to the same chemical type. The Hercules Powder Company suggested that desirable results might be secured by combining Polyethanol Rosin Amine D 12 with Rosin Amine D Acetate in various proportions. The experimental result obtained with the mixed wetting agents was found to be inferior to those obtained when Rosin Amine D Acetate was used alone. No thoroughly successful scheme has yet been devised for selecting the most suitable wetting agent for a given purpose. The Atlas Company have, however, proposed a numerical scheme for selecting the most suitable combination of their wetting agents (5). Each of the Atlas wetting agents is assigned an HLB (Hydrophile-Lipophile-Balance) number. The procedure is to try all of the Atlas wetting agents singly in the particular process under investigation and to determine the HLB number corresponding to the most suitable reagent. The Atlas wetting agents are then combined two at a time in such proportions that the HLB number

TABLE 3

THE RESULTS OF ADDING MIXTURES OF WETTING AGENTS OF DIFFERENT TYPES TO THE LABORATORY SCALE COLD WATER PROCESS

Wetting Agent Mixtures				Types		Total Wt. of Agents per Standard Charge g*	Bitumen Kerosene Layer				% of Bitumen Kerosene in Dry Sand Tailings	Temperature Degrees F	
							% of Water After 1 Hour	% of Water After 24 Hours	Volume in ml	% of Mineral Matter		Room	Wash Water
Alkaterge C	50%	Span 40	50%	cationic	nonionic	0.0093	2.18	0.69	82	1.11	1.27	76	75
Alkaterge C	50%	Span 40	50%	cationic	nonionic	0.0186	6.78	1.39	126	1.02	0.87	76	75
Nekal BX	50%	Span 40	50%	anionic	nonionic	0.0093	5.38	3.57	112	0.80	0.91	75	75
Nekal BX	50%	Span 40	50%	anionic	nonionic	0.0186	4.24	1.45	146	0.94	1.17	75	75
Polyethanol Rosin Amine D-12		Rosin Amine D											
X5736-83	50%	Acetate	50%	cationic	cationic	0.0093	10.8	1.38	116	1.05	1.43	78	75
Polyethanol Rosin Amine D-12		Rosin Amine D											
X5736-83	25%	Acetate	75%	cationic	cationic	0.0093	22.4	0.88	162	1.79	0.82	74	76
Span 20	50%	Span 85	50%	nonionic	nonionic	0.0093	28.4	0.91	150	1.76	0.40	78	75
Span 20	50%	Span 85	50%	nonionic	nonionic	0.0093	28.4	0.87	166	1.67	0.29	78	75
Span 80	50%	Tween 80	50%	nonionic	nonionic	0.0093	25.9	2.31	159	0.70	0.35	80	75
Span 80	50%	Tween 80	50%	nonionic	nonionic	0.0186	20.5	1.34	164	0.85	0.44	80	75

* Standard charge equals 500 g bituminous sand plus 77.5 ml kerosene and 155 ml tap water, to which the above wetting agents were added.

will always remain at the optimum value. On testing the various Atlas wetting agents in the cold water process there did not appear to be any correlation between the HLB number and any of the quantities such as the mineral matter in the oil phase, the water in the oil or the loss of bitumen-kerosene on the sand tailings. The HLB numbers of Span 40 and Span 80 were 6.7 and 4.3 respectively. A mixture of Span 20 and Span 85 which possessed an HLB number of 5.2 was not superior to either of the two agents used singly. Among the wetting agents tested there was a considerable range in the HLB number from 8.6 to 10 in which no wetting agent was available. However, Span 80 and Tween 80 were combined to yield an HLB number of 9.6. The results obtained using this combination were again not superior to those found on using the same reagents singly.

CONCLUSIONS

The laboratory experiments showed that the quality of the oil recovered from the sand, could be improved and the loss of oil in the sand tailings could be reduced by the addition of small quantities of Span 40, Span 80, and Rosin Amine D Acetate in the cold water separation process. This conclusion was confirmed by the observations in the pilot plant, though operations here were under somewhat different conditions, because sodium carbonate was employed to raise the pH of the water to a value of approximately 10. From the present information available on the cost of these wetting agents it would appear to be economically desirable to use these substances with the

present pilot plant flow sheet. The laboratory cold water separation procedure gave a comparatively small loss of bitumen-kerosene on the sand tailings even when no alkali or wetting agent was used. This was not confirmed in the pilot plant. The laboratory results indicate the possibility that if equipment in the pilot plant were modified the need for wetting agents could be reduced.

Unfortunately the chemical compositions of many of the surface active agents were not supplied so that generalizations based upon the chemical structure were not possible. A comparison of the three types of wetting agents, anionic, cationic, and nonionic indicated that the nonionic wetting agents were preferable, in that lower values of the water and mineral matter contents of the oil phase were achieved with smaller losses of bitumen on the sand tailings. A good separation was achieved with Triton-W. 30 which is an anionic type wetting agent but the concentration required was twice that necessary with the best nonionic types.

In general, it was observed that when the water content of the oil phase was high the loss of oil on the sand tailings was low whatever the type of wetting agents used, though there were some exceptions to this rule. It was also noticed in many cases that as the wetting agent concentration was increased, the water content of the oil phase after standing for one hour decreased; however the water content of the oil phase after twenty-four hours standing invariably increased with increasing wetting agent concentration to

values substantially above those obtained when no wetting agent was used. It was therefore concluded that there was no necessity to investigate wetting agent concentration higher than .0186g per 155 ml of water added to the ball mill charge.

The procedure for evaluating wetting agents for use in the cold water separation process, appeared to be adequate from the point of view of screening a large number of surface active agents. A detailed study would require the examination of the effect of the pH of the water upon the separation achieved with a given wetting agent. The results of this experimental work definitely established the fact that surface active agents have a marked influence on the performance of the cold water separation process. As it is well known that the pH of the aqueous phase has an influence upon the surface activity of many substances as well as the interfacial tensions between oil, water, and silica, it is evident that further work should be conducted to clarify the role of the pH of the aqueous phase on the cold water separation process.

This procedure for evaluating wetting agents has potential applications far beyond its use in the cold water separation process. It is a convenient means of testing the efficiency of any wetting agent in removing an oil from any solid which does not react with water. The procedure would involve the drying and pulverizing of the solid concerned before its mixture with dry oil. This mixture would then be subjected to the standard cold water separation

procedure and associated analyses. This technique may be useful in evaluating wetting agents that are contemplated for use in water flooding operations which are designed to secure improved oil recovery from certain types of oil fields.

REFERENCES

1. P. V. Rosewarne and A. A. Swinnerton, Report of Laboratory Investigations on the Cold Water Separation of Bitumen from Alberta Bituminous Sand. Mines Branch, Department of Mines and Technical Surveys, Canada. F.R.L. No. 90.
2. L. E. Djingheuzian. Pilot Plant Investigations on the Cold Water Separation of Bitumen from Alberta Tar Sand. Department of Mines and Technical Surveys. Research Report MD. 70.
3. F. E. Goodspeed, J. G. Holland, R. G. Draper, and H. McD. Chantler, The Cold Water Process for the Recovery of Bitumen from the Bituminous Sands of Alberta, Part 1. Mines Branch, Department of Mines and Technical Surveys, Canada, F. R. L. No. 260.
4. The bituminous sand was taken from an excavation two feet in depth and 30' x 75' in area in the floor of the quarry due east of the buildings of Abasand Oils Ltd. The centre of the area from which the 10 ton sample was withdrawn is 50' west of Hole No. 2 Section 4 shown in Vol. III of "Drilling and Sampling of Bituminous Sand Northern Alberta - Results of Investigation 1942-47". The map of this area is entitled "Exploratory Drilling Horse River Reserve Northern Alberta Township 89 Range 9 West of 4th Meridian.
5. W. Killner and A. S. C. Lawrence. J. Inst. Petroleum 34 821, 1948.
6. J. W. McCutcheon. Synthetic Detergents up to Date. McNair and Darland Co., New York, 1949.