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THE APPLICATION OF WASTE SYNTHETIC FIBRES TO REMOVE OIL SPILLS FROM WATER SURFACES

C o n t e n t s: 1. Experimental work, 2. Results and discussion, 3. Conclusion; Streszczenie; References.

The method of removing oil spills from sea-water surfaces by means of buoyancy sorbents is becoming increasingly significant as improved equipment is used in the counteracting of pollution. Of the many substances used for this purpose unstructured synthetic fibres should be singled out. From among other substances they have several advantages such as: their chemical composition and natural surface properties which give them high hydrophobic and low hydrophylic properties. Hence the fibres do not require additional treatment to increase their oleophilic properties. Synthetic fibres have a highly developed surface, and disintegration, to give their structure very good absorbant properties, is easy. As the fibres often constitute waste material, their use for the sorption of petroleum products is advantageous from the economical point of view. By squeezing out the absorbed oil, the fibres can be utilized several times whereas their sorption capacity remains as high as before. The oil is absorbed by the fibres which are in the form of disintegrated particles, booms, belts and mats. In each of these forms the oil sorption capacity depends on fibre packing density, oleophilic properties, density and viscosity of the oil, the quantity of oil on the water surface, the temperature at which the process takes place. The sorption capacity will be influenced by all these factors.

The sorbent material is capable of holding the absorbed oil as the result of two processes: adsorption and absorption. The adsorption capacity depends primarily on the chemical structure of the substances which form the fibres, that is on the surface properties of the fibres. The absorp-

tion capacity is a function of the structure of the fibres in their sorbent wads, the distances between them, the diameter and cross section of each filament. Hitherto, many investigators have attributed the main role of oil sorption to the process of adsorption while the process of absorption has been underestimated. On fibre sorbents, however, the oil is mostly held due to their capillary forces, as well as to the existance of oil bridges between the fibres. Obviously the absorption depends on adsorption processes. Depending on the contact angle of the oil drop with respect to the fibre surface the capillary forces are stronger or weaker [1]. The extent to which crude oil is removed from artificial sea-water by means of disintegrated synthetic fibres has been investigated by Johnson et al. [4]. The sorption tests were conducted with good contact between the oil and sea-water being maintained. The influence of fibre surface properties on the sorption capacity is considerable. Therefore, apart from the sorption yield value, the contact angle for the oil on the sorbent is one of the basic quantities needed in the characterization of the sorbent material [7]. Zahid et al. [9] emphasis that the distance between the fibres and their geometry are an important factor in the sorbing capacity observed while oil is removed from water surface by means of specially constructed matrices. They also observed that the change of the fibres surface properties have little influence on the yields obtained. Both papers mentioned quote literature concerning the process of deoiling of water. The authors suggest various conceptions of oil sorption mechanisms. The purpose of this paper is to relate petroleum products sorption to fibre surface properties and the structural arrangement of fibres in the wads. A new type of sorbent has been proposed.

1. EXPERIMENTAL WORK

Sorbing agent

In most experimental work a sorbent material obtained from the tyre cord of spent automobile tyres was used. The manner of obtaining the sorbent and its fundamental physicochemical properties were described in our previous paper [3]. The sorbent consists of 60% viscose rayon fibres, 38% polyamide fibres, the remaining 2% being small rubber particles closely adhering to the tyre cord fibres. Tyre cord was disintegrated to obtain fibres of suitable size.

The sorption of viscose and polyamide fibres, being a raw material used in tyre body production, viz. pure and not waste fibres was also determined.

Oils

The sorption process was carried out for crude-oil and "Lux 10" engine-oil. As the gradual evaporation of lighter fractions is always taking

place in crude-oil spills, this process was simulated by weathering the crude-oil for 48 hours. In experimental work, crude oil so devoid of low-boiling fractions was used.

An infrared spectrum of crude oil is shown in Fig. 1. The normal hydrocarbon absorption bands at 2925, 2849, 1455, 1375 cm^{-1} are observed. In addition to these, aromatic bands absorption is represented by peaks at: 869, 810, 745 and 1600 cm^{-1} [6]. The density and viscosity of crude-oil and „Lux 10" oil are given in Table 1.
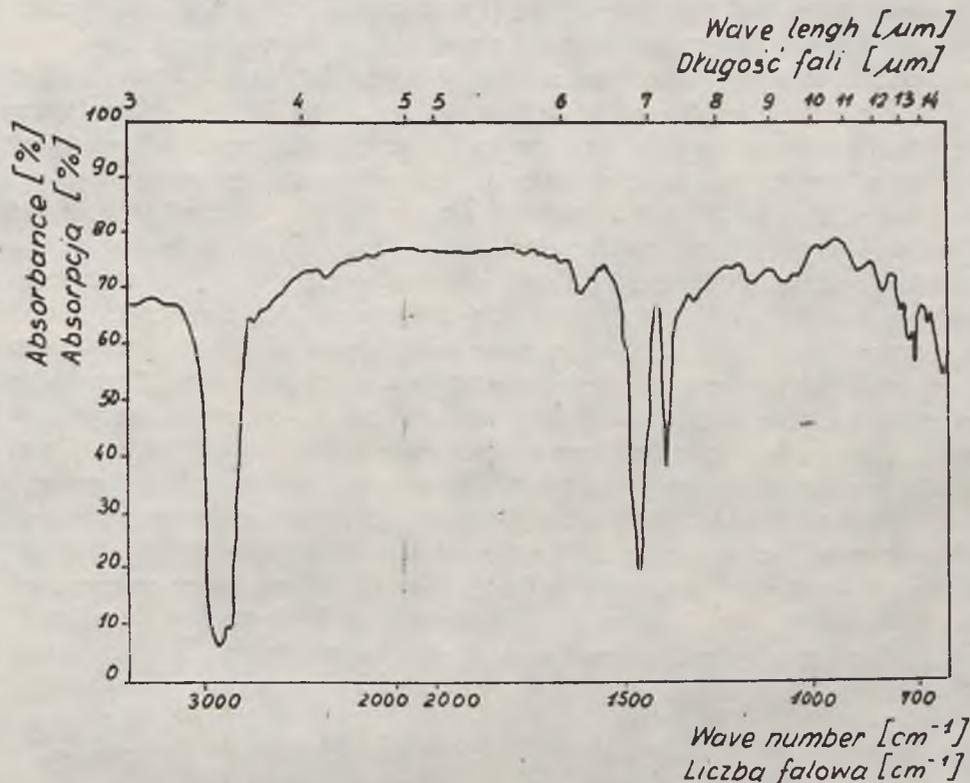

Fig. 1. Infrared spectrum of crude oil

Ryc. 1. Widmo w podczerwieni dla ropy naftowej

Table 1

Tabela 1

Characteristics of oil products used in sorption processes

Charakterystyka produktów naftowych stosowanych w procesie sorpcji

Oil	Density g/cm³ 20°C	Kinematic viscosity c St 20°C
Crude oil a) as received b) after 48 h weathering	0.840 0.868	4.8 8.1
Engine oil „Lux 10"	0.895	458

Procedure

In order to examine the oil absorption capacity cylinder-shaped sorbent wads 25 mm in diameter and 50 mm long were formed. By changing the quantity of fibres in the same volume, the required packing density was obtained. The cylinders were placed on the oil surface and the sorbing time was measured. By sorbing time is meant the time which elapsed between the moment the fibres came into contact with the oil and the instant these fibres disappeared beneath the oil surface. Mention must be made of the fact that the sorbing time does not conform to the oil saturation of the cylinders as oil products of higher viscosity (e.g. „Lux 10" oil) penetrate into the sorbent slower than the lighter fractions do. The cylinders sink when the oil density and that of the fibre-oil-air mixture are equal, but some of the free spaces between the fibres is not occupied by the oil for a certain time. After sinking, each cylinder was pulled out by means of a metal clamp and the excess oil was allowed to drip for 1 hour. The cylinders were weighed and the sorption capacity was calculated. The conglomerate of oil and sorbent was squeezed in a press in such a manner as not to damage the cylinders and the absorption was once more calculated. Cylinders from pure viscose and polyamide fibres were also formed and identical experiments were conducted. Two kinds of sorbents were applied: sorbent I and sorbent II. Sorbent I, as well as the viscose and polyamide fibres had an average filament of about 15 μm, while sorbent II had about 50 μm. The contact angles on the sorbent fibres and polyamide and viscose fibres for the oils used were measured. Measurements were performed by means of a microscope [5]. The contact angles of 5—7 oil drops for each fibre-oil-artificial sea-water composition were measured and the results summarized in Table 2. A 3.5% solution of NaCl in fresh water was used as artificial sea-water.

Table 2

Tabela 2

Contact angles for oil on synthetic fibres in artificial sea-water

Kąt zwilżania włókien syntetycznych przez produkty naftowe w środowisku sztucznej wody morskiej

Oil	Fibres			
	Sorbent I	Sorbent II	Polyamide fibres	Viscose fibres
	1.21 g/cm³	1.21 g/cm³	1.13 g/cm³	1.26 g/cm³
Crude oil	14.6°	12.3°	68.4°	79.1°
„Lux 10" engine oil	23.5°	22.8°	71.5°	82.5°

The sorption of sorbent I, polyamide and viscose fibres after saturation with sea-water was also investigated. For this purpose, cylinders with densities of 0.1; 0.2 and 0.3 g/cm³ were shaken with artificial sea-water in a wide-necked, conical flask for 5 minutes, after which the absorption capacity was measured in the same manner as for the fibres not saturated with water. All measurements were carried out at $20 \pm 1°C$.
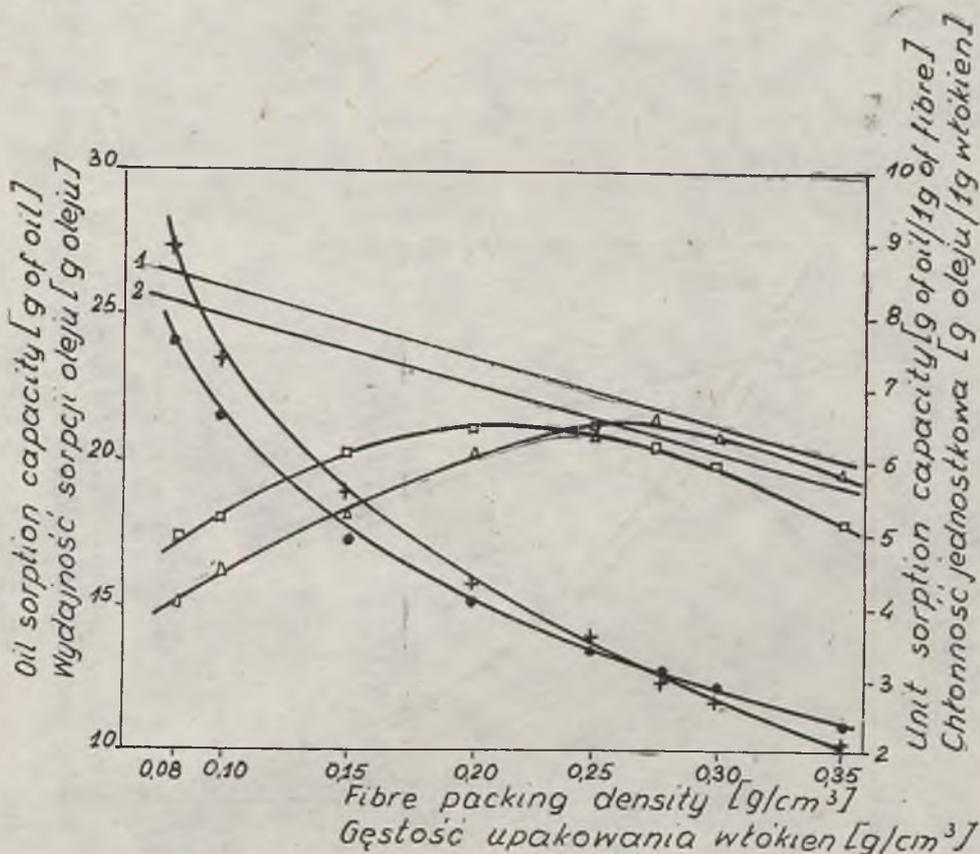

Fig. 2. Oil sorption on sorbing agent I

1 — crude oil		
2 — „Lux 10" oil	theoretical sorption capacity	
△ crude oil		
▢ „Lux 10" oil	experimental sorption capacity	
● crude oil		
+ „Lux 10" oil	unit sorption capacity	

Ryc. 2. Chłonność sorbenta I

1 — ropa naftowa		
2 — olej „Lux 10"	chłonność teoretyczna	
△ ropa naftowa		
▢ olej „Lux 10"	chłonność wyznaczona doświadczalnie	
● ropa naftowa		
+ olej „Lux 10"	chłonność jednostkowa	

2. RESULTS AND DISCUSSION

The volume of the cylinders formed from fibres is known, hence for each given packing density the theoretical absorption i.e. the quantity of the oil filling all the free spaces between the fibres can be calculated. Figs. 2—4 give the values of the theoretical absorption, as well as the experimental absorption as a function of the fibre packing density. The
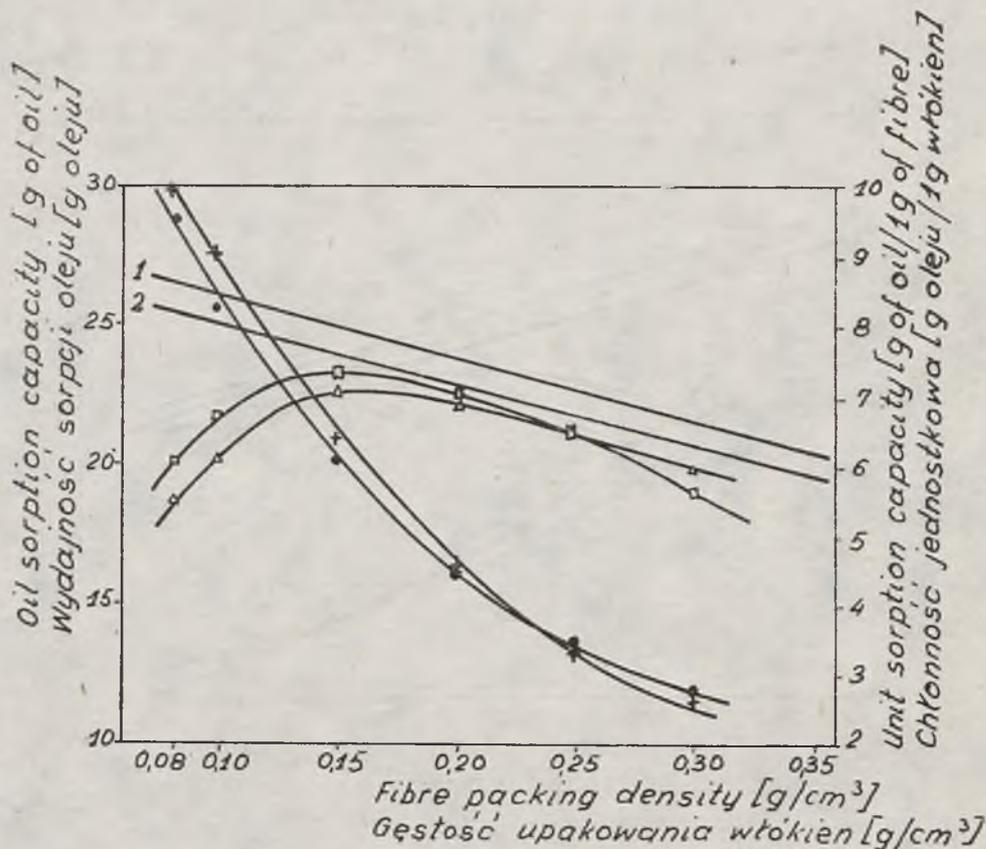
Fig. 3. Oil sorption on viscose fibres

1 — crude oil
2 — „Lux 10" oil   } theoretical sorption capacity

△   crude oil
□   „Lux 10" oil   } experimental sorption capacity

●   crude oil
+   „Lux 10" oil   } unit sorption capacity

Ryc. 3. Chłonność włókien wiskozowych

1 — ropa naftowa
2 — olej „Lux 10"   } chłonność teoretyczna

△   ropa naftowa
□   olej „Lux 10"   } chłonność wyznaczona doświadczalnie

●   ropa naftowa
+   olej „Lux 10"   } chłonność jednostkowa

analysis of the diagrams shows that the theoretical and experimental absorption curves do not agree. The experimental absorption for the small and the high packing density is less than that calculated. The effect at small packing density is more evident for crude-oil, while at greater packing density — for „Lux 10" oil. In the case of small packing density the distances between fibres are far too great to retain the absorbed oil. At
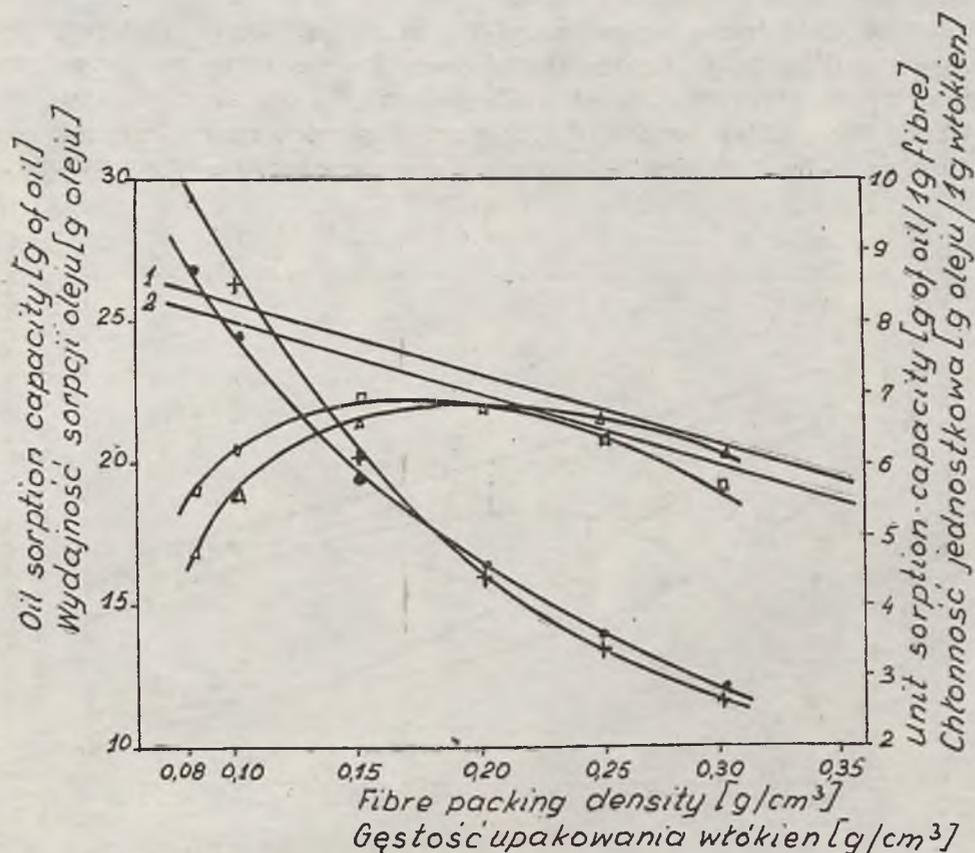

Fig. 4. Oil sorption on polyamide fibres

1 — crude oil	}	
2 — „Lux 10" oil		theoretical sorption capacity
△ crude oil	}	
☐ „Lux 10" oil		experimental sorption capacity
● crude oil	}	
+ „Lux 10" oil		unit sorption capacity

Ryc. 4. Chłonność włókien poliamidowych

1 — ropa naftowa	}	
2 — olej „Lux 10"		chłonność teoretyczna
△ ropa naftowa	}	
☐ olej „Lux 10"		chłonność wyznaczona doświadczalnie
● ropa naftowa	}	
+ olej „Lux 10"		chłonność jednostkowa

packing densities greater than a certain size, the petroleum products may not fill the entire free space, particularly when their viscosity is too high. The results obtained confirm the measurement results published by Zahid et al. [9]. These investigations show that the geometrical arrangement of the fibres and the oil bridges stretched between them suggest the existence of a spacing between the fibres at which the amount of absorbed oil has a maximum value.

The yield curves in respect of 1 g of sorbent fibres (unit sorption capacity) (Figs. 2—4), suggest that the sorption yield does not depend, in practice, on the sorbent used while maintaining the same thickness of fibres. For packing density of 0.08 g/cm³ this value ranges between 1—10 g/g and for 0.30 g/cm³ — 2.5 g/g. Very often because of construction
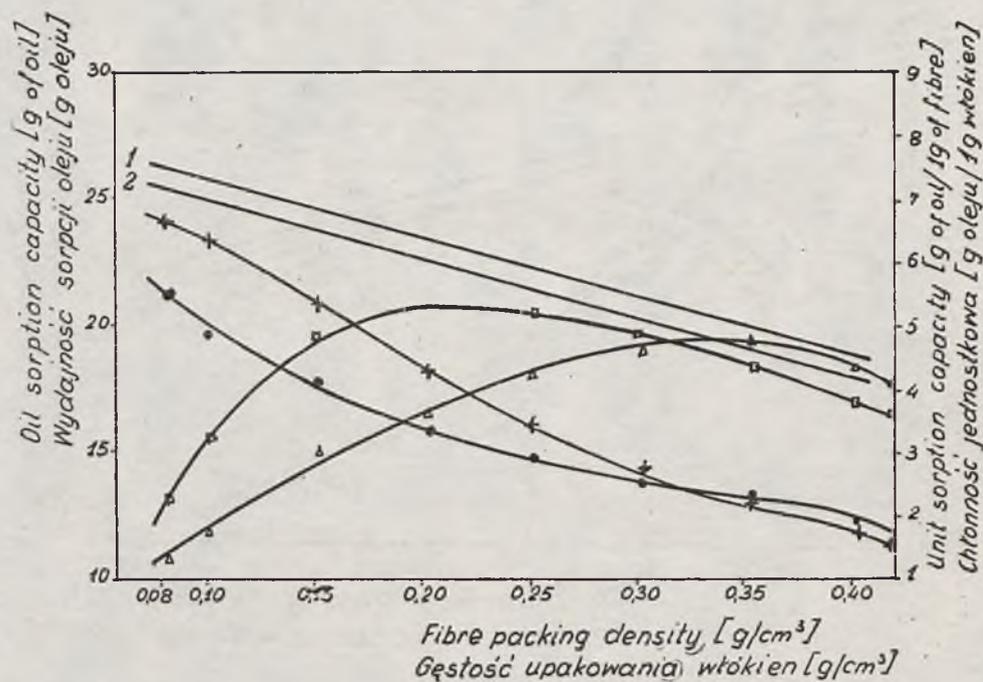

Fig. 5. Oil sorption on sorbing agent II

1 — crude oil	
2 — „Lux 10" oil	theoretical sorption capacity
△ crude oil	
□ „Lux 10" oil	experimental sorption capacity
● crude oil	
+ „Lux 10" oil	uni sorption capacity

Ryc. 5. Chłonność sorbenta II

1 — ropa naftowa	
2 — olej „Lux 10"	chłonność teoretyczna
△ ropa naftowa	
□ olej „Lux 10"	chłonność wyznaczona doświadczalnie
● ropa naftowa	
+ olej „Lux 10"	chłonność jednostkowa

and strength conditions the packing density of fibres in mats, booms or belts is 0.3 g/cm³. At these packing density values there is much less oil in 1 g of fibres than that marked in commercial characteristics of sorbents, which should be taken into account in calculations of oil-spill removal. Curves of the sorption capacity in the case of crude-oil and „Lux 10" oil are identical for all fibres. For packing density not greater than 0.20 g/cm³ there is more oil than crude-oil per 1 g of fibres, wheres at densities greater than 0.25 g/cm³ crude oil sorption is higher.

Fig. 5 shows sorption curves of oil for sorbent II which has thicker filaments. Unit sorption capacity for crude-oil and „Lux 10" oil is less than in the case of sorbent I. The maximum total sorption is attained at a higher packing density. This corroborates the experimental data published by Zahid et al. [9]. They state that the sorption yield was inversely proportional to the filament diameter. The figures presented in this work show that the lowest packing density was 0.08 g/cm³. At values of less than 0.08 g/cm³ it was imposible to form cylinders that would be resistant to deformations after being saturated by oil. A higher sorption than 11 g/g was not attained for a density of 0.08 g/cm³. Sorption values sometimes as high as 40 g/g [4] are found in several papers. In our case, a sorption value higher than 40 g/g could be achieved for fibres with a packing density of the order of 0.02 g/cm³. In our experimental system this is impossible as the use of polypropylene fibres at the most advantageous disintegration gives an average yield of about 15 g/g. How then can such appreciable yields be achieved. First of all it is necessary to state precisely whether we are concerned with an agglomeration of oil on the water surface, or with permanent oil sorption in the fibre mass. In the case of an attempt to remove a poorly bounded oil-sorbent conglomerate from water, at least half the quantity of oil would be lost. The bounding of the oil on the water surface prevents the spread of the oil spill, but is not sufficient to remove it. High sorption values can be obtained while using disintegrated sorbent to eliminate heavy mineral oil of high viscosity. Oil-sorbent agglomeration occupies a considerably greater volume than freely arranged filaments of the sorbent alone. Therefore 30—40 g of oil, or even more, may be found per 1 g of fibres.

The sorption time as a function of packing density is shown in Fig. 6. Oil sorption time for wads is considerably greater than that for „Lux 10" oil. The viscosity of the latter is much higher than that of crude-oil, hence its much lower penetration speed. There are no great differences between particular kinds of fibres. The change of sorption time with packing density increases 6—7 times for crude-oil and 1.5—2 times for „Lux 10" oil.

In field conditions the sorbent very often comes into contact with water before coming into contact with oil. Often both media are absorbed simultaneously, but the contact spot differs for each one. The sorption

time, the contact surface and the surface proporties of the fibres, decide
whether the sorption of water or that of the oil is greater. The oleophilic
properties of the fibres are specified by the contact angle for the oil on
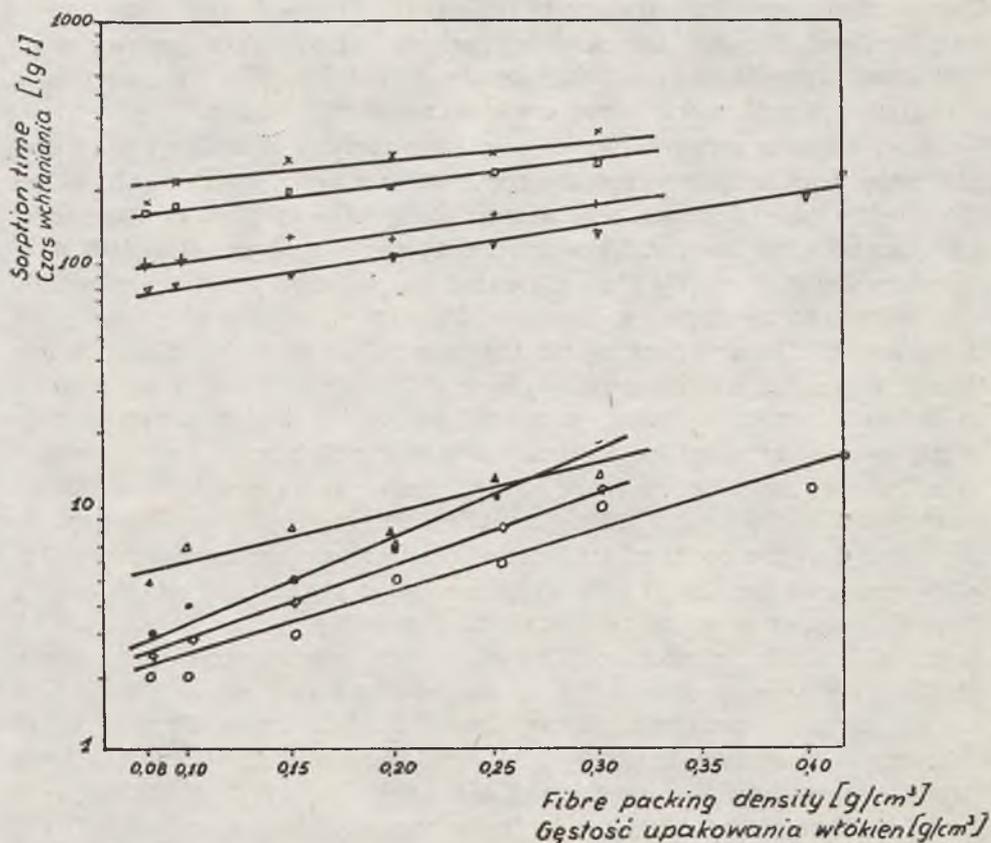the sorbent. The contact angle was measured on fibres 0.5 mm in diameter

Fig. 6. Sorption time as a function of fibre packing density

□	sorbing agent I
▽	sorbing agent II
×	viscose fibres
+	polyamide fibres

„Lux 10" oil

△	sorbing agent I
○	sorbing agent II
●	viscose fibres
◇	polyamide fibres

crude oil

Ryc. 6. Czas wchłaniania w funkcji gęstości upakowania włókien

□	sorbent I
▽	sorbent II
×	włókna wiskozowe
+	włókna poliamidowe

olej „Lux 10"

△	sorbent I
○	sorbent II
●	włókna wiskozowe
◇	włókna poliamidowe

ropa naftowa

obtained from plaiting small filaments. Tab. 2 shows that the sorbent obtained from disintegrated waste tyre-body has higher oleophilic properties than the raw polyamide and viscouse fibres which the sorbent contains. The process of tyre production strongly influences the surface properties of the fibres forming the tyre-body, and makes them highly oleophilic. Hence the conclusion is that primarily, the sorbent should not change its sorption properties in respect of oil, in the presence of an oil-water mixture. Experimental data on the sorption properties of water-saturated fibres are shown in Tab. 3.

Table 3

Tabela 3

Sorption capacity of oils and water on synthetic fibres (g/1g fibre)

Wydajność sorpcji produktów naftowych i wody na włóknach syntetycznych (g/1g włókien)

Fibres packing density g/cm³	Fibres											
	Sorbing agent I			Sorbing agent II			Polyamide fibres			Viscose fibres		
	crude oil	water	„Lux 10" oil	crude oil	water	„Lux 10" oil	crude oil	water	„Lux 10" oil	crude oil	water	„Lux 10" oil
0.1	6.0	0.5	7.0	4.2	0.7	5.2	4.0	3.9	4.1	2.6	5.1	2.5
0.2	4.0	0.4	3.8	2.8	0.65	3.8	2.2	2.0	1.8	2.0	2.2	1.5
0.3	2.8	0.25	2.5	2.1	0.4	1.8	1.1	1.6	0.5	0.7	1.8	0.2

Experiments were carried out for three fibre packing densities. The quantity of water was measured gravimetrically after shaking and being left to drip. An analysis of the table 3 shows the minimal loss of sorption properties for sorbents I and II (comp. Figs. 2, 5). The quantity of water per 1 g of sorbent does not exceed 70% of the weight of fibres for a packing density of 0.10 g/cm³ and is less by halt for 0.30 g/cm³. This phenomenon can be explained by the greater distances between particular filaments at a packing density of about 0.10 g/cm³ hence the more effective penetration of water inside the wads. Capillary depression occurs at greater packing densities as for all practical purposes, the water is unable to wet the sorbent fibres. Contact angles for oil on polyamide and viscose fibres show their lower hydrophobic properties, which is compatible with the results obtained for sorption yields. In the case of low packing densities 1 g fibres absorbs 2 g of water. At 0.30 g/cm³ the quantity of water related to 1 g of sorbent drops to 1.6—1.8 g, but there is a rapid simultaneous decrease in the sorption properties of the „Lux 10" oil to 0.2—0.5 g/g. This is the result of competitive water penetration inside the sorbent bulk and the simultaneous hydraulic closure of the empty

spaces existing inside of the cylinders. Hence the oil sticks only to the surface layers of the fibres and is unable to force the water out. It should be mentioned that very severe model conditions were assumed for the contact of fibres with water. In practice, the sorbent is always in contact with both oil and water — which results in the oil-covered fibres becoming strongly hydrophobic, the sorption then being much higher.

Preliminary investigations on the possibility of re-use of the sorption substance were carried out. An average of 75% of the crude-oil and 50% of the „Lux 10" oil was recovered by the pressing method. The sorption capacity of sorbent I and sorbent II cylinders remained unchanged for both water and oil, whereas in the case of polyamide and viscose fibres the oil sorption capacity increased while that of water decreased during succesive sorption-desorption processes. Temperature has a substantial effect on the viscosity of petroleum products and consequently on its penetration into the sorbent bulk.

In summer the sorption of heavy oil products will be relatively easier when using sorbing booms and endless belts.

Disintegrated fibres spread by an air blow-pipe and collected by means of nets are an economical form of sorbent in winter [2]. This method is also recommended in the case of larger oil spills.

3. CONCLUSIONS

1. The capacity of fibre sorbent does not depend only on the structural and geometrical arrangement of fibres in the wads, but also on the capacity to wet the fibres by oil removed from the water surface. The data indicate that the surface properties of filaments have a marked effect on the capacity observed when sea-water and oil can penetrate into the sorbent bulk. When all the filaments are in contact with the petroleum products only, the capacity is determined by the sorbent structure. The effect on the capacity in relation to the surface properties of the fibres is negligible in this case.

2. The best packing density of fibres in sorbing booms, mats and endless belts depends on the mechanical properties of the fibres and the oil bonding force of the sorbent required. It is difficult to evaluate the packing density of the sorbent in the form of particular filaments. Where this density is too low, there is danger of an appreciable loss of oil when removing the oil-sorbent mixture from the water surface.

3. A lower fibre packing density facilitates more rapid penetration of water inside the sorbent bulk, simultaneously decreasing the oil sorption capacity.

4. The most effective sorption capacity is achieved for the particle form of the sorbent and oil products of moderate viscosity.

5. The sorption capacity of commercial products is mostly given for the particle form. It will be much lower for sorbing booms, mats, pillows or endless belts. This fact should be taken into account in calculations related to oil spill removal.

6. Sorbent obtained from waste car tyres can be economically competitive as a sorption material comparable even with such cheap ones as straw or sawdust, because of their high sorption properties and regeneration possibilities.

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ZASTOSOWANIE ODPADOWYCH WŁÓKIEN Z TWORZYW SZTUCZNYCH DO USUWANIA ROZLEWÓW OLEJOWYCH Z POWIERZCHNI WÓD

Streszczenie

W artykule przedyskutowano wyniki badań mających na celu określenie przydatności odpadowych włókien z tworzyw sztucznych do usuwania produktów naftowych z powierzchni wód morskich. Wydajność wchłaniania oleju odniesiono do własności powierzchni włókien oraz struktury ułożenia włókien w kłębuszkach sorbenta. Przytoczono prace innych autorów omawiające zagadnienie zastosowania sorbentów włóknistych do likwidacji rozlewów olejowych. Wykonano szereg doświadczeń i rozważono zależności między wynikami eksperymentalnymi a obliczeniami teoretycznymi. W części doświadczalnej stosowano sorbent otrzymany z osnowy zużytych opon samochodowych oraz włókna wiskozowe i poliamidowe. Sposób przygotowania sorbenta oraz jego podstawowe własności fizyko-chemiczne podano we wcześniejszej pracy [3]. Sorpcję prowadzono dla ropy naftowej oraz oleju silnikowego „Lux 10".

Wnioski:

1. Otrzymane rezultaty wskazują na fakt, że własności powierzchni włókien mają znaczny wpływ na zaobserwowaną wydajność wówczas, gdy woda morska i olej penetrują razem w głąb masy sorbenta. Kiedy zaś wszystkie włókna stykają się z olejem, wydajność wchłaniania zależy od struktury sorbenta. Wpływ związany z własnościami powierzchni włókien można w tym wypadku zaniedbać. Ilość pochłoniętego oleju wzrasta z rosnącą gęstością upakowania włókien, osiągając maksimum w granicach 0.15—0.30 g/cm³ w zależności od rodzaju sorbenta. Jest ona mniejsza od wydajności teoretycznej.

2 .Najbardziej korzystna gęstość upakowania włókien w zaporach sorbujących, matach, wstęgach zależy od własności mechanicznych włókien i wymaganej siły wiązania oleju przez sorbent. Trudno jest ocenić gęstość upakowania sorbenta w postaci włókien rozdrobnionych, przy czym gdy będzie ona zbyt mała, należy się liczyć ze znacznym uwolnieniem oleju przy podejmowaniu mieszaniny sorbent-olej z powierzchni wody.

3. Mniejsza gęstość upakowania włókien umożliwia szybszą penetrację wody w głąb masy sorbenta, obniżając jednocześnie chłonność produktów naftowych.

4. Najwyższe chłonności uzyskuje się dla sorbenta rozdrobnionego i dość lepkich produktów naftowych.

5. Wydajność sorpcji substancji handlowych podaje się z reguły dla postaci rozdrobnionej. Wydajność będzie znacznie mniejsza w przypadkach występowania tej substancji w postaci zapór sorbujących, mat, poduszek czy wstęg. Fakt ten należy wziąć pod uwagę w czasie obliczeń dotyczących likwidacji rozlewów olejowych.

6. Sorbent uzyskany z osnowy zużytych opon samochodowych może stanowić konkurencyjny materiał wiążący nawet dla tak tanich sorbentów, jak słoma czy trociny, m.in. ze względu na wysokie własności chłonne oraz możliwość regeneracji. Charakteryzuje się on znacznie wyższymi własnościami chłonnymi, względem produktów naftowych, od surowych włókien poliamidowych i wiskozowych.

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