

IRENA GAWEL^{1),*}, JERZY PILAT²⁾, PIOTR RADZISZEWSKI³⁾, LUKASZ NICZKE¹⁾,
JAN KROL²⁾, MICHAŁ SARNOWSKI²⁾

Bitumen fluxes of vegetable origin

Summary — Methods of preparation of bitumen fluxes from rapeseed and linseed oil methyl esters were developed. The methods consist in the catalytic oxidation of vegetable oil methyl esters in the absence or presence of peroxides as the accelerators. The products obtained can be used as environmentally friendly bitumen fluxes. The rapeseed oil methyl ester has to be oxidized at elevated temperature in the presence of a catalyst. Linseed oil methyl ester does not need pre-oxidation before mixing with bitumen, but mixing with the catalyst is necessary. Contrary to conventional bitumen solvents, the fluxes are not volatile and have an ignition point of approximately 200 °C, so they do not raise safety problems. The hardening of the fluxed bituminous binder is going not by evaporation of the flux but by oxidative polymerization in the presence of a catalyst. The use of the fluxes let considerably reduce the mixing or spreading temperature of the binder, as well as the compacting temperature of the binder-aggregate mix.

Key words: bitumen fluxes, vegetable raw materials, fatty acids methyl esters, rapeseed oil, linseed oil, catalytic oxidation, oxidative polymerization.

UPLYNNIACZE ASFALTÓW OTRZYMANE Z SUROWCÓW ROŚLINNYCH

Streszczenie — Opracowano metodę otrzymywania upłynniaczy asfaltów z estrów metylowych olejów rzepakowego i lnianego (tabela 1). Polega ona na utlenianiu estrów w obecności katalizatora kobaltowego oraz nadtlenuków jako przyspieszaczy reakcji lub bez nadtlenuków (tabela 2). Estry metylowe oleju rzepakowego wymagają utleniania w podwyższonej temperaturze w obecności katalizatora, podczas gdy estry metylowe kwasów tłuszczowych oleju lnianego przed zmieszaniem ich z asfaltem nie muszą być utleniane, ale dodatek katalizatora utleniania jest niezbędny. Otrzymuje się w ten sposób produkty, które mogą być stosowane jako upłynniacze asfaltów przyjazne dla środowiska naturalnego. W przeciwieństwie do konwencjonalnych upłynniaczy asfaltów, nie są one lotne i charakteryzują się wyższą temperaturą zapłonu wynoszącą ok. 200 °C, są zatem bezpieczne dla środowiska. Utwardzanie asfaltów upłynnionych nimi następuje nie wskutek odparowania rozpuszczalnika, lecz w wyniku utleniającej polimeryzacji w obecności katalizatora. Zastosowanie opisywanych upłynniaczy pozwala na znaczne obniżenie temperatury otaczania kruszywa lepiszczem lub spryskiwania lepiszcza w technologii powierzchniowego utrwalańa, a także na obniżenie temperatury zagęszczania mieszanki mineralno-asfaltowej (tabela 3).

Słowa kluczowe: upłynniacze asfaltów, surowce roślinne, estry metylowe kwasów tłuszczowych, olej rzepakowy, olej lniany, katalityczne utlenianie, utleniająca polimeryzacja.

“BIOFLUXES” — GENERAL DESCRIPTION

In conventional techniques of road construction, the bituminous binder is hot mixed with the aggregate or hot spread. In cold-mix operations the bituminous emulsions or liquid bitumen binders (cutback) are used. In areas of a more severe climate, the application of bitumi-

nous emulsions is limited. The cutback is a bitumen system to which a volatile solvent is added in order to maintain a low initial viscosity of the binder. Traditional liquid binders contain the solvents of petro- or carbochemical origin, rich in aromatic compounds. Evaporation of the solvent allows the binder to recover its high consistency. However, the evaporated solvent pollutes the atmosphere and contributes to the greenhouse effect. Furthermore, cutbacks raise safety problems because they have relatively low flash point values. The new European environmental regulations referring to the emission of volatile organic compounds (VOCs) necessitate limiting or even abandoning the use of conventional bitumen cutbacks and searching for environmentally friendly substitutes of the solvents currently used.

As has been shown, vegetable oils and methyl esters of fatty acids, obtained by transesterification of these

¹⁾ Wrocław University of Technology, Faculty of Chemistry, Department of Fuels Chemistry and Technology, Gdanska 7/9, 50-344 Wrocław, Poland.

²⁾ Warsaw University of Technology, Faculty of Civil Engineering, Department of Building Materials Engineering, Armii Ludowej 16, 00-637 Warsaw, Poland.

³⁾ Białystok Technical University, Faculty of Civil Engineering and Environmental Engineering, Chair of Highway Engineering and Building Physics, Wiejska 45, 15-351 Białystok, Poland.

^{*} Corresponding author: irena.gawel@pwr.wroc.pl

oils, can be used as bitumen fluxing oils [1]. In that case, the hardening of the binder after spreading is going on not by evaporation of the solvent but by crosslinking of the unsaturated fatty acids as a result of reaction with oxygen. Antoine *et al.* applied a sunflower oil and its fatty acid methyl esters as environmentally friendly bitumen fluxes [2–5]. The initial viscosity of the binder should be low to facilitate effective wetting of the aggregate at relatively low temperature. This is the reason why the investigators have substituted sunflower oil with the fatty acid methyl esters of the oil. The bituminous binder compositions were shown to be suitable for surface dressing [1–5].

Usefulness of vegetable oils and the corresponding methyl esters for the production of environmentally friendly bitumen fluxes depends on their susceptibility to oxidative polymerization, which leads to crosslinking of the unsaturated fatty acids, thus contributing to the hardening and drying of the oil (or corresponding methyl ester) [6–11].

The ability of fatty acids to react with oxygen and polymerize until a solid film is formed is well known in the paint and varnish industry. The efficiency of crosslinking depends on the number of double bonds and their position in the aliphatic chain of the fatty acid. Oils rich in fatty acids with three and two double bonds are easier to dry than those where fatty acids with one double bond prevail. This is why the reactivity of the rapeseed oil to oxidative polymerization is relatively low, but in the areas of temperate climate rapeseed oil is not only easily available but also notably cheaper than the sunflower oil applied by Antoine *et al.* as the bitumen “bioflux” [2–5].

Current experience with the use of “bioflux” has shown the following advantages of applying binders with these fluxes to paving construction [3]:

- fume formation during pavement construction can be eliminated,
- the flash point increased to about 200 °C,
- adhesion between binder and aggregate is good,
- renewable resources are used,
- a new market for agricultural products can be established.

Relatively few papers have been published on the use of vegetable oils and the corresponding alkyl esters in bitumen but a certain number of recent patents relates to bituminous compositions that contain vegetable oils or fatty acids obtained from the oils, as well as alkyl esters of fatty acids as bitumen diluents [1, 12–15]. The application of these compositions, however, is limited to surface dressing. Liquid bituminous binders suitable for road construction contain polymers to improve their properties [13–15]. But in this case a major role of the fluxing oil is to reduce the initial viscosity of the polymer-modified bitumen binder in order to keep the proper processability of an asphalt mixture.

An earlier study by Gawel *et al.* has shown that the most characteristic change in the rapeseed oil methyl ester structure upon catalytic oxidation at 200 °C was the formation of oligomers *via* intermolecular crosslinking, which accounted for an increase in the molecular weight of the liquid product [9].

The aim of this study was to optimize the oxidation conditions for rapeseed and linseed oils, as well as for the corresponding methyl esters, in order to obtain the products suitable for use as environmentally friendly bitumen fluxes. So, an effort was made to find the optimum composition of the flux-bitumen blend for production of warm mix asphalt (WMA) having lower mixing and compacting temperatures as compared to hot mix asphalt (HMA).

EXPERIMENTAL

Materials

Rapeseed and linseed oils, as well as the methyl esters obtained by transesterification of these oils (see [9]), were used as raw materials for the preparation of bitumen fluxes. The properties and molecular compositions of the oils are characterized in Table 1. Cobalt naphthenate acted as a catalyst of oxidation while dicumyl or benzoyl peroxides and cumene hydroperoxide were used as promoters of the reaction.

The 70/100 penetration grade bitumen was used as a component of the binder. The properties of the bitumen were as follows:

- flash point — 338 °C
- softening point — 47 °C
- penetration at 25 °C — 80 · 0.1 mm
- dynamic viscosity at 60 °C — 171,4 Pa · s

Procedure

Rapeseed oil or its methyl esters were mixed with the catalyst and subjected to oxidation at ambient temperature or at 200 °C with an air flow rate of 500 L/(kg · h). Oxidation time ranged from 2 to 25 h. The processes were also performed in the presence of peroxides as promoters of the oxidation reactions or in the absence of the catalysts. In this latter case, the experiments were performed in the presence of benzoyl peroxide/*N,N*-dimethylaniline mixture; the last one let peroxides be decomposed at low temperature.

Linseed oil methyl ester was not subjected to long-term oxidation at elevated temperature but was oxidized only for 2 h at ambient temperature, in the presence either of a catalyst itself or of a catalyst/promoter system. In some experiments, linseed oil as well as its methyl ester were only mixed with the catalyst or the catalyst and peroxide for 15 min at ambient temperature. Table 2 gives the compositions, conditions of oxidation process, and flash point values of the products.

The bitumen was mixed with the fluxing oil at 100 °C for 10 min. The flux content in the mixture was in the range 7–15 %.

The fluxed bitumen was spread onto a metallic plate to form a 1 mm layer, and conditioned at 20 °C for 31 days.

Methods of analyses

The physicochemical properties of vegetable oils and their methyl esters were analyzed by standard methods. Molecular composition was determined by GC-FID method using Hewlett-Packard HP 6850 GC apparatus.

The fluxed bituminous binders were analyzed just after their preparation, as well as after 7, 14 and 31 days of conditioning. The measurements included the softening point, viscosity and flash point. The softening point was determined by R&B method, viscosity was measured over the temperature range from 40 to 135 °C using a Brookfield DV-II+ Pro apparatus produced by Brookfield Engineering Laboratories, and flash point of the binder was determined after the preparation procedure using Marcusson flash-point apparatus produced by Labor Muszeripari Muvek "Esztergom".

Table 1. Physicochemical properties of vegetable oils and their methyl esters and molecular composition of esters

Physicochemical properties	Rapeseed oil methyl ester	Rapeseed oil	Linseed oil methyl ester	Linseed oil
Density at 25 °C, g/cm ³	0.8787	0.9131	0.8795	0.9195
Flash point, °C	197	322	194	317
Dynamic viscosity at 25 °C, Pa · s	0.006	0.055	0.004	0.045
Iodine value, g I ₂ /100 g	109	110	153	152
Average molecular weight	296	882	326	919
Molecular composition				
Fatty acid methyl ester	Molecular formula (number of double bonds)	Composition, wt. %		
Palmitic acid methyl ester	C ₁₇ H ₃₄ O ₂ (0)	6.9	5.6	
Stearic acid methyl ester	C ₁₉ H ₃₈ O ₂ (0)	2.0	3.5	
Oleic acid methyl ester	C ₁₉ H ₃₆ O ₂ (1)	53.1	17.5	
Linoleic acid methyl ester	C ₁₉ H ₃₄ O ₂ (2)	31.9	60.6	
Linolenic acid methyl ester	C ₁₉ H ₃₂ O ₂ (3)	6.1	12.8	

Table 2. Symbols, compositions, conditions of oxidation process and flash point values of environmentally friendly fluxes

Flux symbol	Composition	Oxidation conditions	Flash point, °C
Fluxes from rapeseed oil			
A	rapeseed oil + cobalt catalyst (0.1 %) ^{a)}	Oxidation at 200 °C for 20 h	295
B	rapeseed oil methyl ester + cobalt catalyst (0.1 %) ^{a)}	Oxidation at 200 °C for 25 h	207
C	rapeseed oil methyl ester + cobalt catalyst (0.1 %) ^{a)} + dicumyl peroxide (1.0 %)	Oxidation at 200 °C for 25 h	210
D	rapeseed oil methyl ester + cobalt catalyst (0.1 %) ^{a)}	Oxidation at ambient temperature for 2 h	191
E	rapeseed oil methyl ester + <i>N,N</i> -dimethylaniline (0.1 %) + benzoyl peroxide (1.0 %)	Oxidation at ambient temperature for 2 h	194
F	rapeseed oil methyl ester + cobalt catalyst (0.1 %) ^{a)} + cumene hydroperoxide (1.0 %)	Oxidation at ambient temperature for 2 h	136
Fluxes from linseed oil			
G	linseed oil + cobalt catalyst (0.1 %) ^{a)}	Mixing at ambient temperature for 15 min	275
H	linseed oil methyl ester + cobalt catalyst (0.1 %) ^{a)}	Mixing at ambient temperature for 15 min	189
I	linseed oil methyl ester + cobalt catalyst (0.1 %) ^{a)} + benzoyl peroxide (1.0 %)	Mixing at ambient temperature for 15 min	185
J	linseed oil methyl ester + cobalt catalyst (0.1 %) ^{a)}	Oxidation at ambient temperature for 2 h	186
K	linseed oil methyl ester + <i>N,N</i> -dimethylaniline (0.1 %) + benzoyl peroxide (1.0 %)	Oxidation at ambient temperature for 2 h	192
L	linseed oil methyl ester + cobalt catalyst (0.1 %) ^{a)} + cumene hydroperoxide (1.0 %)	Oxidation at ambient temperature for 2 h	119

^{a)} In terms of cobalt content.

RESULTS AND DISCUSSION

As can be seen from the data in Table 1, the content of fatty acids with two and three double bonds (linoleic and linolenic acid) in the linseed oil methyl ester is twice as high as in the rapeseed oil methyl ester. This explains the higher reactivity of the linseed oil methyl ester in oxidative polymerization.

The fluxes obtained have flash points above 180 °C (see Table 2). Exceptions are the products obtained by oxidation of the fatty acid methyl esters in the presence of cumene hydroperoxide (fluxes F and L). When the flux containing this hydroperoxide is heated during flash point determination, cumene hydroperoxide decomposes (its half-life temperature is decreased by the cobalt catalyst), and the hydroxyl radicals formed initiate scission of the double bonds. This results in the formation of low molecular compounds with a flash point lower than those of the esters. The higher flash points of the fluxes A—C obtained from rapeseed oil methyl ester by many - hour - long catalytic oxidation at 200 °C are attributable to the fact that the molecular weights of the liquid oxidation products increase with the rise in temperature [9]. It is essential to note, however, that all fluxed binders have flash points above 260 °C (Table 3).

The data in Table 3 show the effects of flux type and flux content in the binder on the softening point and viscosity (η measured at 60 °C) of the product. The increase in these two properties of the binders after 31 days of conditioning at 20 °C was calculated and is presented in Fig. 1.

The addition of a promoter (peroxide) results both in a higher initial softening point and higher viscosity of the fluxed bituminous binder (see, for instance, binders B and C with 10 % of a binder). A recent study of the authors has shown that the addition of dicumyl peroxide into the rapeseed oil methyl ester oxidized at 200 °C in the presence of a cobalt catalyst enhanced cross-linking up to the point when the most reactive double bonds were exhausted [16]. Further oxidation at elevated temperature gradually reduces the content of peroxides, and this can explain the fact that the binder C exhibits lower increase in the softening point and viscosity during conditioning than binder B (Fig. 1). When the peroxide is added to vegetable oil methyl ester at temperature lower than the half-life temperature of the peroxide, it acts as a promoter of oxidative polymerization of unsaturated fatty acid methyl esters. Therefore, the binder with a flux obtained under such conditions hardens to a higher extent than the binder with a flux obtained in the absence of peroxide (compare the increase in softening point and viscosity of binder H with those of binder I, Fig. 1).

The *N,N*-dimethylaniline/benzoyl peroxide mix was found to be the least effective in the oxidative polymerization of the fatty acid methyl esters under experimental conditions. Tertiary amine does not decrease the temperature of peroxide decomposition to such an extent as the cobalt catalyst does, and thus the concentration of the free radicals participating in the polymerization reaction is relatively low at ambient temperature. This is the reason why the increase in softening point and viscosity of binder E and binder K with time of conditioning is

Table 3. Effects of flux type and content on changes in the consistence of the binder with time

Binder ^{b)}	Flux content, %	Softening point, °C	Viscosity at 60 °C, Pa · s	Temperature corresponding to viscosity 0.2 Pa · s, °C	Temperature corresponding to viscosity 10 Pa · s, °C	Temperature corresponding to viscosity 20 Pa · s, °C	Flash point, °C
Binders containing fluxes from rapeseed oil							
Binder A	10	38.0	54.0	137	77	69	335
Binder B	10	34.0	30.9	132	72	65	293
	7	37.5	53.1	136	76	69	—
Binder C	10	35.0	34.3	133	73	67	296
	15	26.0	8.8	120	58	52	—
Binder D	10	23.0	7.7	118	57	50	279
Binder E	10	23.0	7.7	118	56	49	278
Binder F	10	24.0	7.9	119	57	51	269
Binders containing fluxes from linseed oil							
Binder G	10	29.5	17.4	124	66	59	326
	7	28.5	14.6	123	64	57	—
Binder H	10	22.0	6.8	115	56	49	277
	15	11.0	2.6	110	44	38	—
Binder I	10	22.5	7.1	115	56	49	275
Binder J	10	22.5	7.1	115	56	49	274
Binder K	10	22.0	6.5	115	56	49	277
Binder L	10	23.0	7.8	116	56	49	265

^{b)} Binder stands for the mixture of bitumen 70/100 and flux; the composition of fluxes A—L is given in Table 2.

Fig. 1. Rise in softening point and in viscosity of fluxed bitumens after 31 days of conditioning at 20 °C

lower as compared to the other binders obtained under the same conditions (Fig. 1).

The binders containing the fluxes obtained by oxidation of vegetable oil methyl esters in the presence of the cobalt catalyst and cumene hydroperoxide harden to the highest extent (Fig. 1, samples F and L). This can be explained by the higher mobility and reactivity of the hydroxyl radicals which formed as a result of the decomposition of hydroperoxide, as compared to the alkoxy radicals released during peroxide decomposition.

Bituminous binders containing oxidized linseed oil methyl ester harden with time to a higher extent than those fluxed with rapeseed oil methyl ester oxidized under the same conditions (compare the increase in softening point after 31 days for binder D and binder J, for binder E and binder K, and for binder F and binder L; Fig. 1). The hardening of the fluxed binders over time is confirmed by the increase in viscosity at 60 °C (Fig. 1), which is higher in the binders containing linseed oil and its methyl ester. This is due to the mentioned higher number of double bonds in linseed oil as compared with rapeseed one.

The correlation between binder viscosity (η) and temperature (T) was plotted and the relation $\log(\eta) = f(\log T)$ was derived from the plots. The equations describing the relations of the binders tested were used to calculate the temperatures at which viscosity amounted to 0.2 Pa · s, 10 Pa · s, and 20 Pa · s. These temperatures correspond to mixing and spreading temperatures of the binder, as well as with the final compacting temperature of the mix. Relevant values are summarized in Table 3. As shown by these data, the mixing and spreading temperatures of the binder, as well as the compacting temperature of the binder-aggregate mix, can be considerably reduced by mixing of bitumen with the new fluxes obtained from vegetable oil methyl esters. The use of fluxes obtained from vegetable oils (binders A and G) instead of their methyl esters lead to lower reduction in these temperatures. The higher the flux content, the lower the technological temperatures (see binders C and H). How-

ever, the binders with a high flux content (15 %) have low softening point and viscosity so their hardening time is longer. Moreover, a high flux content in the binder is disadvantageous economically. The optimum flux content in the binder seems to be 10 %.

After 31 days of conditioning, the softening point of the binders increased approximately 10 °C and their viscosity rose more than of 300 % (Fig. 1). Exceptions are the binders that contain fluxes obtained from rapeseed oil methyl ester by many - hours - long catalytic oxidation at 200 °C (A—C), as well as those containing fluxes obtained by oxidation of vegetable oil methyl esters at ambient temperature in the presence of *N,N*-dimethylaniline and benzoyl peroxide (E, K), which show smaller increase in softening point and viscosity.

It is possible to mix the fluxed binders with the aggregate and spread them at temperatures that do not exceed 120 °C and 57 °C, respectively. The final compacting temperature of the mixtures which contain 10 % of these binders approaches 50 °C (Table 3).

CONCLUSIONS

— Catalytic oxidation of vegetable oil methyl esters yields the products which can be used as environmentally friendly bitumen fluxes.

— The hardening of the fluxed binders with time is confirmed by an increase in softening point and viscosity.

— It has been shown that cumene hydroperoxide used in the presence of a cobalt catalyst is more effective promoter of the oxidative polymerization of vegetable oil methyl esters at ambient temperature than peroxides are.

— The new bitumen fluxes have noticeably higher flash points as compared with the conventional ones, and thus raise no safety problems.

— The use of the fluxes let reduce considerably mixing and spreading temperature of the binder, as well as compacting temperature of the binder-aggregate mix.

REFERENCES

1. *Pat. USA* 6 156 113 (2000).
2. Antoine J. P., Marcilloux J.: *Rev. Gén. Routes* 1999, No. 779, 30.
3. Antoine J. P., Marcilloux J.: *Travaux* 2000, No. 761, 42.
4. Antoine J. P., Marcilloux J.: *Rev. Gén. Routes* 2002, No. 806, 27.
5. Antoine J. P., Pelon M.: *Rev. Gén. Routes* 2000, No. 787, 93.
6. Güler Ö. K., Güner F. S., Erciyas A. T.: *Prog. Org. Coat.* 2004, **51**, 365.
7. Hess P. S., O'Hare G. A.: *Ind. Eng. Chem.* 1950, **42**, 1424.
8. Mallécol J., Lemaire J., Gardette J. L.: *Prog. Org. Coat.* 2000, **39**, 107.

9. Gawel I., Niczke L., Czechowski F.: *Polimery* 2007, **52**, 658.
10. Stiepanowicz-Orchimienko I., Wasiljewicz-Wiercholancew W.: "Chemia i technologia substancji błonotwórczych", WNT, Warszawa 1982, str. 298—334.
11. Wexler H.: *Chem. Rev.* 1964, **64**, 591.
12. *Pat. EU* 1 645 595 A1 (2005).
13. *Pat. EU* 1 482 012 A1 (2004).
14. *Pat. Intern.* 087 869 A1 (2005).
15. *Pat. EU* 0 568 757 A1 (2006).
16. Niczke L., Czechowski F., Gawel I.: *Prog. Org. Coat.* 2007, **59**, 304.

Received 10 XI 2008.

W kolejnym zeszycie ukaza się m.in. następujące artykuły:

- J. Łukaszczyk, M. Śmiga-Matuszowicz — Polimerowe i kompozytowe cementy kostne oraz materiały pokrewne. Cz. II. Kompozycje resorbowalne i wykazujące aktywność biologiczną
- J. Jęczalik, M. Baumann — Synteza i fotoutwardzanie metakrylouretanów z polibutadienoli o różnych ciężarach cząsteczkowych
- J. Paciorek-Sadowska, B. Czupryński, J. Liszkowska, W. Jaskółowski — Nowy polioli boroorganiczny do produkcji sztywnych pianek poliuretanowo-poliizocyjanurowych. Cz. II. Otrzymywanie sztywnych pianek poliuretanowo-poliizocyjanurowych z zastosowaniem nowego polioli boroorganicznego
- K. Piszczek, J. Tomaszewska, T. Sterzyński — Wpływ temperatury poli(chlorku winylu) na stan równowagi procesu żelowania (*j. ang.*)
- E. Makarewicz, I. Dobiąła, E. Kałużna — Badania reologiczne plastizoli poli(chlorku winylu) zawierających środek powierzchniowo-czynny i organiczny pigment
- M. Żenkiewicz, J. Richert, P. Rytlewski, K. Moraczewski, M. Stepczyńska — Wybrane właściwości kompozytów polipropylenu z szungitem
- J. Sentek, Z. Rżanek-Boroch, M. Brykała, K. Schmidt-Szałowski — Zastosowanie impulsywnego wyładowania barierowego do osadzania na folii polietylenowej powłok ze związków krzemu (*j. ang.*)
- I. Korus — Usuwanie jonów Pb(II) w procesie ultrafiltracji wspomagananej działaniem polielektrolitu (*j. ang.*)
- E. Gurdzińska, J. Zieliński, B. Liszyńska, T. Brzozowska, B. Osowiecka, W. Ciesińska — Utylizacja odpadów polistyrenu spienionego w kompozycjach z wtórnymi bitumami naftowymi