USE OF SICCATIVE OILS FOR BIO-BASED COATINGS

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Introduction

Ordinary coatings are manufactured from a wide range of ingredients synthesised primarily from petro-chemicals. The solvents generally used for these applications in the field of paints and varnishes are classified as Volatil Organic Compounds (VOCs) which have to be reduced.

Different vegetable oils and derivatives, due to their particular characteristics, namely their fatty acid profile, can be used as reactive diluent in such applications and allow to formulate Bio-based coatings.

The use of siccative oils such as Calendula oil (*Calendula officinalis*), Camelina oil (*Camelina sativa*) and Pomegranate oil (*Punica granatum*) has been tested and compared to classical oils such as linseed and tung oils.

Materials and Methods

☞ ***Oil seeds***

- *Calendula officinalis* seeds have been selected, sown and harvested in four European sites in the framework of the CARMINA research program (FAIR CT 98-3713).
- *Camelina sativa* commonly known as “gold of pleasure” or “false flax” is developed as an oilseed crop in north-western Europe. This plant like rapeseed, belongs to the Cruciferae family. The seeds have been obtained from a French farmer.
- *Punica granatum* seeds have been obtained from a fruit-juice producer located in Turkey.

☞ ***Oil recovery***

- Komet screw press has been used for small quantities of seeds (30kg).
- Larger quantities have been processed on **CREOL** facilities (www.creol.fr) providing grinding, flaking, cooking equipments, screw presses (500 kg/h) and a complete solvent extraction unit.

☞ ***Oil refining***

Oil refining has been studied on **ITERG**’s refining pilot plant and industrial unit, including degumming and neutralization reactors (up to 900 kg/batch), bleaching and winterization reactors, a centrifugal separator and a high performance deodorizer for both classical deodorization and physical refining.

ITERG’s refining unit

☞ ***Oil modification***

Methylation and other transformations (standolisation, resin alkyd synthesis) have been performed following internal methods developed by ITERG’s Lipochemistry laboratory and based on industrial processes.

☞ ***Analytical controls***

- Classical analytical controls have been done following standardized methods : oleic acidity, peroxide and para-anisidine values, iodine value, fatty acid composition by GC, polymers content.
- A Beck Koller system has been used for the measurement of the drying properties of the oils and their derivatives.

Results and Discussion

Oil recovery and refining

- *Calendula* oil has been produced by solvent extraction after dehulling, flaking and direct extraction under mild conditions.
- *Camelina sativa* oil has been obtained according to the classical process of rapeseed oil production, *i.e.* pressing after flaking and cooking steps. Solvent extraction of the press cake allows to produce crude oil with a good yield.
- *Pomegranate* oil has been produced by solvent extraction after flaking (yield 9%).

Special care has to be taken during the refining of these oils to minimize the formation of oxidation products and polymers during the whole process ; the use of Activated Bleaching Earth increases the diene and triene formation.

Refining step	Calendula oil	Camelina Oil	Pomegranate Oil
Acid conditioning	0.1% H_3PO_4 60°C	0.1% H_3PO_4 60°C	0.1% H_3PO_4 65°C
Chemical neutralization	70°C caustic soda, 6 washings emulsion formation	70°C caustic soda in small excess, 3 washings	70°C caustic soda in small excess, 3 washings
Bleaching	Activated bleaching earth (ABE) 2%, 70°C, 40 min.	ABE: 1 % 90°C, 40 min	Charcoal 0.3% + ABE 1.7 %, 70°C, 40 min.
Deodorization	Not advisable polymerisation	160°C, vapour in large quantity, 5 h, 3 mbar	Not advisable Polymerisation at 130°C

Tab 1 : Optimized refining conditions applied to the different oils

Fatty acid	Usual name	Calendula	Camelina	Pomegranate
14 : 0	Myristic		0.1	< 0,1
16 : 0	Palmitic	3.1	6.2	3,3
16 : 1	Palmitoleic	0.1	0.2	0,1
17 : 0	Margaric	*0.1*		*ND**
17 : 1	-	<0.1		< 0,1
18 : 0	Stéaric	1.9	2.6	2,4
18 : 1	Oléic	4.9	19.2	7,4
18 : 2	Linoleic	29.8	18.7	7,7
18 : 3	Linolenic	0.8	29.1	0,2
20 : 0	Arachidic	0.3	1.6	0,5
20 : 1	Gondoïc	0.3	15.0	0,6
20 : 2	-		1.5	
20 : 3	-	0.9		
18 : 3 *9c,11t,13c*	Punicic	58.4		67,8
Conjugated Linolenic Acids 18 : 3 (*different isomers*)				6.8
22 : 0	Béhénic	0.3		0,2
22 : 1	Erucic	3.2		2,1
24 : 0	Lignoceric	0.2		0,1
24 : 1	Nervonic	0.6		< 0,1
ND	-			0,8

Tab 2 : Fatty acid composition of the oils determined by GC

Refined oils show good classical characteristics :
peroxide value (< 1meq O_2/kg), oleic acidity (< 0.1%).

Poly-unsaturated and conjugated fatty acid content do not decrease during refining (*see fatty acid compositions*).

Calendula and *Pomegranate* oils having the highest content of conjugated acids, are highly reactive. During storage these oils should be kept at cold temperature, under nitrogen, to protect them before use.
Their drying properties are good, allowing to use them for coatings. These drying properties can be classified as followed :

Tung = Calendula > Pomegranate >> Linseed >> Camelina >> Soy

Standoils have been made with *Camelina* and *Calendula* oils. They show interesting properties compared to classical linseed standoils :
- at same viscosity, iodine and acid values are lower.
- high viscosity standoils are less coloured.

These oils can be transformed into methyl esters, following mild conditions of interesterification. Their methyl esters can be used as solvent in a lot of applications.

Conclusion

Calendula oil (*Calendula officinalis*), Camelina oil (*Camelina sativa*) and Pomegranate oil (*Punica granatum)* can be used as binders or additives in coatings. Refining is a key point which has been optimized in order to get good quality oils and to avoid by-product formation. Their drying properties allow them to be used in the field of coatings. Their methyl esters have been synthesized, satisfactory under soft conditions, and are new reactive diluents which can enter coating formulations as alternatives to classical petro-chemical solvents. Other derivatives such as standoils, resins, ... show also some promising properties.

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