



Project no: 508753

Project acronym: **STANLUB**

Project title: Development of new bio-lubricants and coatings using standoils from
linseed, castor and tung oils

CO-OPERATIVE RESEARCH PROJECT

SECOND PERIODIC ACTIVITY REPORT

Period covered: from 01/07/2005 to 30/09/2006 Date of preparation: Sept 2006

Start date of project: 01/07/2005

Duration: 27 Months

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Project coordinator organisation: ITERG

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PUBLISHABLE EXECUTIVE SUMMARY

Description of the project Objectives

a) Technical objectives

The STANLUB project comprises 2 main objectives:

Development of “green” fabrication processes for the synthesis of the bio-lubricants and coatings by substitution of petroleum products by vegetable oil derivatives, using as raw materials standoils from linseed, castor and tung oil;

Development of bio-lubricants and solvent for coating formulation using the physical and chemical characteristics of vegetable oil esters and test of technical performances at industrial scale.

These 2 global objectives will be reached through :

The valorisation of renewable raw material sources (standoils from linseed oil, castor oil and tung oil) for high added value applications

The valorisation of standoils by products The development of standoil derivatives using few chemical steps at an affordable price for SMEs (4 steps instead of 6 for traditional processes).

The development of derivatives for bio-lubricants and coatings with improved mechanical and physico-chemical properties

b) Societal objectives

Preservation and/or enhancement of the environment and natural resources

Vegetable oils have a number of inherent qualities that give them advantages over petroleum oils as the feedstock for lubricants. Because vegetable oils are derived from a renewable resource, their use avoids the upstream pollution associated with petroleum extraction and refining. It is also true that the use of biodegradable lubricants (biodegradability enhanced by a factor 100 compared to traditional lubricants), in itself, is an improvement towards environmental friendly industry.

STANLUB aim is to fulfil the important and growing demand for bio-lubricant by proposing cost-effective lubricants.

It should be recalled that lubricants are often polluting through leakage without possible treatment.

The STANLUB project will help to generalise the use of biodegradable lubricants and therefore, lower the level of hydrocarbon pollution.

Improvement of employment prospects and the level of skills in Europe

In addition to their physical advantages, plant-based lubricants and paints hold great potential for rural economic development. Farmers could benefit not only from increased demand for vegetable oils but also, and more significantly, from collective ownership of a company manufacturing value-added products.

The STANLUB project will help to create new jobs in the agricultural field by creating a demand for plant based products.

c) Policy objectives

Decrease mineral oil impact on environment

The impact on environment of used mineral oils wastes has lead the EU to take legislative measures as Council Directive 75/439/EEC of 16 June 1975 on the disposal of waste oil (amended by Council Directive 87/101/EEC of 22 December 1986 and Council Directive 91/692/EEC of 23 December 1991). However, in the Communication COM (1999) 752 final Commission Report of 10 January 2000 to the Council and the European Parliament on the implementation of Community waste legislation for the period 1995-1997 (Directives 75/442/EEC, 91/689/EEC, 75/439/EEC and 86/278/EEC) “The Commission notes that the hierarchy of principles for waste oil management (regeneration, combustion and safe destruction/tipping) has not been respected”.

Development of bio-lubricants and bio-coatings will contribute to decrease uses oil quantities that are released in the environment.

Decrease the impact of industrial activities on the environment

STANLUB Bio-lubricants and coating solvents will be highly biodegradable (factor 100) compared to traditional mineral lubricants and coatings. In the field of environment, the IPPC Directive 96/61/EEC (Integrated Pollution Prevention and Control) aims at a sustainable production through industrial pollution prevention and control, which in practice will mean defining permitting conditions in a co-ordinated and integrated way.

Development of safe raw materials for lubricant and coating industry

From a worker safety perspective, plant-based lubricants are more attractive than their petroleum counterparts because of their relative low toxicity, high flash point and low volatile organic compound (VOC) emissions.

The development of non-toxic raw materials for lubricants and coatings participates directly to the implementation of two EU regulation and decision:

Regulation (EC) No 1980/2000 of the European Parliament and of the Council of 17 July 2000 on a revised Community eco-label award scheme [Official Journal L 237, 21.09.2000].

Decision 2001/608/EC - Official Journal L 214, 08.08.2001: Commission Decision of 19 July 2001 prolonging the period of validity of Decision 1999/10/EC establishing the ecological criteria for the award of the Community eco-label to paints and varnishes.

Contractors Details

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Summary of Work performed

A mixture of 3 different oils (including a linseed oil) was identified as the best raw material. This choice was very important because it impacts on the standolisation process and on the oxidation stability of the final products. The process was then adapted according to the raw material and also to the specification of the partners. The results showed that the improvement of the process reduces the number of steps and the cost of process. The new lubricant bases were formulated into bio-lubricants. These biolubricants were tested in many application fields by the partners. Their performances were satisfying in metal working applications, lubrication of rail way switches and chainsaws. The “green” solvents formulated thanks to the STANLUB by-products were also tested.

Expected end results, intentions for use and impact

Identification and selection of the best raw material sources from a range of three vegetable oils. The evaluation was carried out using technical and economical criteria.

Development of a “green” fabrication process for the synthesis of the bio-lubricants and paints by replacing petroleum products by vegetable oil methyl esters from linseed, castor and tung standoils.

Formulation of bio-lubricants and solvents using the physical and chemical characteristics of selected standoils derivatives and testing technical their performances at industrial scale.

Publishable results of the PUDK

A poster was made and can be seen at Itegr. The poster was presented at the 4th Euro Fed Lipid Congress. Unfortunately there can't be any broad dissemination for the moment. The results obtained are still confidential and need to be kept secret in order to provide an advantage to the partners of the project. Once the production will be launched, public will be informed.

1 Stanlub Objectives and Major Achievements

1.1 General Objectives

a) Technical objectives

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1.2 Actual progress

1.2.1 Objectives of the Period

The objectives are to

- Optimise the process and transfer it to pilot scale (VDP-OLEO and ITERG),
- Produce samples of monomers and dimers at pilot scale (ITERG)
- Determine their properties (ITERG, BFB, coating partners and lubricant partners)
- Test them in the different application fields by the different partners (BFB, coating partners and lubricant partners)

1.2.2 Work performed and main achievements.

For this period, ITERG and VDP-OLEO carried out the optimisation of the process, the scale-up to pilot scale and a first economical evaluation of the process (WP3, 4 & 6). In September, operating parameters were optimised at lab-scale by Iterg and VDP-OLEO in order to prepare a semi-industrial scale production. A scale transfer was carried out to adapt the process and the analytical follow-up to VDP-OLEO.

The next workpackages (WP5 and WP6 and 7) dealt with the evaluation of the performances of the final products (monomers as solvent for coatings and dimers of 2ethylhexyle as lubricant bases). Monomers were tested by Toyal Europe as solvent for aluminium coatings and by Unikalo as solvent for alkyde paints. Motul, Baraldi, Zero-waste and Pewas tested the dimers as lubricant bases. Several fields of applications were tested : die casting, metal working, railway switches, ...

Motul obtained very interesting results in metal working lubrication. That is why Vandeputte Oleochemical decided to produce a batch of product at semi-industrial scale. Concerning the coating applications, encouraging results were obtained and comparable to other “green” solvents. Nevertheless, a few problems remain (yellowing and hardness of the coatings).

1.2.3 Contractors involved

SME name	Contact Name
Vandeputte Oleochemicals S.A.	Pierre-Marie BAUDOIN Stéphanie CONCEICAO da
Baraldi Lubrificanti	Luca BARALDI
Zero Waste	Audrey BOUTEVILLAIN
PeWas Ltd.	Bohuslav Zuzi,
Unikalo	Jacques Ducos

Other User	Contact Name
Toyal Europe	Fabrice MORVAN Norbert GOMEZ
MOTUL	Didier CROUZET

RTD performer	Contact Name
ITERG	Carine ALFOS
COORDINATOR	Xavier PAGES Julien Verollet
BFB Oil Research S.A.	Dr François VAN DIEVOET Vincent BOUILLON

2 Workpackage Progress of the Period

2.1 Workpackage 1: Industrial Specifications

Finalised in period 1.
Please refer to First Periodic Report.

2.2 Workpackage 2: Raw Material Characterisation

Finalised in period 1.
Please refer First Periodic Report.

2.3

Workpackage 3: Standolisation Process Development

Starting: Month 1
Partners involved:

Partners	Planned effort	Actual total
VdP	12	12,25
Itegr	3	3

Objectives:

The main objective of this workpackage is to proceed to the oil standolisation protocols optimisation in order to reduce significantly the reaction time and the operating temperature. The goal is thus to reduce raw material production costs.

Task 3.1: Lab-scale standoils synthesis (ITERG and VDP-OLEO)

Finalised in period 1.

Task 3.2: Produced standoils characterisation (ITERG)

Finalised in period 1.

Task 3.3: Process transfer to pilot-scale (ITERG and VDP-OLEO)

The most powerful process was transferred to the VDP-OLEO pilot-scale in order to optimise the scale transfer inherent operating parameters. 4 Standoils were synthesised at pilot scale taking into account the results obtained in task 2.2 and 3.2. (The better results concerning acidity, reaction time and colour are obtained with the mixture of rapeseed, linseed and soyabean oil.)

In order to get the best Standoils for future transformation at ITERG, VDP chose to work under nitrogen vacuum. They have also decided to work with some amount of glycerine in order to limit the acidity increase during the reaction of polymerisation. The aim of process optimisation was to reduce as much as possible the acid value and the colour of the Standoil. A low acid value is the only way to get a good lubricant base stock (low sodium content) and to control the global cost process (limitation of waste)

Different raw material composition was used to make the process transfer. We started with a 100% raw linseed standoil. The second standoil was made from refined linseed oil. The comparison between these two pilot productions has shown that the use of refined oil is necessary to get a low acid value. The third pilot production used dehydrated castor oil as raw material. The last pilot standoil production was made from a blend of linseed oil, soybean oil and rapeseed oil. The results showed that the last pilot production is more adapted for a lubricant application because we have reached the right value of iodine index with a very low acid value.

VdP is now able to produce standoils with the required specifications at the pilot scale. VdP can control the acidity easily, the viscosity and thanks to the catalyst VdP optimised the reaction time.

Iterg has analysed this standoil and showed that the content of dimer is sufficient.

Also, when the acidity is low Iterg has less difficulty during the esterification and costs are reduced (smaller amounts of Trysil are required). That is why VdP developed a special process in the Stanlub project to produce standoils with very low acidity (0.13%).

The low Iodine value is an advantage to give more oxidation stability at the lubricant.

So, thanks to the pilot trials made at VdP, Iterg was able to produce dimer esters to provide to the lubricant partners for testing them.

Deliverables:

D7: Report on the lab-scale used operating protocols and comparative table on the obtained standoils and the current commercialised standoils characteristics (VDP-OLEO)
Achieved in May 2005

D8: Report on standoils characterisation and comparison to others standoils produced with the classical process (ITERG) The impact of the new process will be clearly described.
Achieved in May 2005

D9: Report on the definitive process once the scale transfer is carried out (VDP-OLEO)
Achieved in July 2005

2.4 Workpackage 4: Development Of The Standoils Transesterification And Distillation Of The Dimers/Monomers Fractions Processes

Starting: Month 4

Partners involved:

Partners	Planned effort	Actual total
VdP	3	3,25
Itegr	9	9.48

Objectives:

This workpackage includes two steps :

- Transesterification of the standoils
The objective is to perform at ITERG the fabrication of methyl esters from standoil at lab scale and also the analysis of the derivatives obtained. The process will also be transferred to pilot scale to produce large quantities of product.
- Distillation of the methylic esters obtained
The goal is to develop the distillation process of the resulting standoils methyl esters. In this step, ITERG will perform the process at lab scale and pilot scale. The analysis on the products resulting from the distillation will be done at ITERG: monomers, dimers and monomers-dimers mixtures..

Task 4.1: Methyl ester fabrication process optimisation and validation (ITERG)

Concerning WP4 Task 4.1, Itegr showed that all triglycerides and polymers of triglycerides can be transformed into monomers, dimers and polymers of methyl esters. Yields of reactions are near 98%.

Itegr proved that the ratio of catalyst, sodium methoxide, could be decreased to 0.6% + 0.19*OA% (vs. 1.5% + 0.19*OA initially) without impacting the quality of the final product. The catalyst was diluted in methanol before its addition to avoid a sudden heating of the mixture.

During WP4, treatments of transesterified standoils were adapted to the type of distillation (molecular distillation or classical distillation). In the case of molecular distillation, the only treatment is the total removal of methanol. As molecular distillation is expensive and implies the loss of the high polymer fraction containing soaps, Itegr decided to carry out a classical distillation. It implies that treatments of the transesterified standoils must be adapted to a classical distillation. Therefore, Itegr tested several treatments.

The best solution was to use Trisyl, an amorphous silica gel adsorbent for the refining of vegetable oils. Trisyl enables an easy neutralisation of the catalyst. Its use replaces the water washings and consequently reduces effluents. Without water washings, there is no risk of creating emulsions during treatments. An other advantage of using Trisyl is to reduce the

sodium content by adsorbing sodium salt and a few soaps. Trisyl is easy to handle and its filtration is fast.

In November 2005, Vandeputte Oleochemicals provided Itegr a new standoil made at pilot scale (80 L). This standoil had a lower acidity (0.5%) compared to previous ones (near 2%) to reduce fatty soaps/acids in the final product and a lower viscosity to reduce the amount of polymers (30 Poises at 20°C instead of 50 Poises). Before the scale-up, a synthesis was successfully carried out at lab-scale using the new standoils and the corresponding ratio of catalyst.

Task 4.2: Analysis methods finalisation and analysis of the 4 standoils selected (ITERG)

All products were analysed thanks to HPLC analysis. The ratios of monomer/dimers/trimers and polymers were determined and results were similar with those obtained in WP3. Acidity of transesterified standoils was also determined.

In September 2006, analytical parameters were transferred to VdP. The analyses can be made thanks to the material currently used by VdP.

Task 4.3: Analytic protocols and know-how transfer (ITERG and VDP-OLEO)

Two trials at pilot scale were carried out in a reactor of 30 litres. It enabled to produce 36 kg of transesterified standoils. Yields were near 98%. The analyses of the transesterified standoils showed that oleic acidity was very low (0.2%). The results of HPLC analyses (polymer of triglyceride content) of the pilot trial were identical to the results obtained on the standoils which were transesterified at analytical scale. It proved that synthesis was successfully carried out.

In September 2006, the process was transferred from Itegr to Vandeputte Oleochemicals. The goal is to produce 1 tonne of lubricant base at semi-industrial scale. Therefore, Mr Deherripon from Vandeputte Oleochemicals came to Itegr for an entire week to follow the entire process and the analytical characterisation. The raw material used for this last synthesis was a standoil with very low acidity (0.13% - see WP3). The ratio of Trisyl was reduced to the minimum (0.42%) because the cost of Trisyl is not negligible in the process. Analytical parameters were transferred to VdP. It was concluded that the process is easily transferable to semi-industrial scale.

Task 4.4 : Optimisation of the distillation process (ITERG)

Molecular distillations were replaced by classical distillation (see Year 1). The distillation consists in separating monomers from the dimers and polymers under vacuum (1 mbar) and heating (between 160°C and 210°C). During Year 2, several batches of transesterified standoils (obtained in Task 4.3) were distilled in order to obtain 5 litres of monomers for Toyal Europe and 500 mL for Unikalo (see Task 5.2). The resulting dimers and polymers of methyl were used to produce lubricant bases (see Tasks 6.1 and 6.3).

Properties of the lubricant bases (determined in Tasks 6.4, 6.6 and 7.1) greatly depend on the distillation process. It was shown that lubricant bases made of dimers and polymers of 2ethylhexyl (samples TH08, TH09 and THP01) were too viscous. So distillation was modified in order to have a precise ratio of monomers in the dimer fraction : distillation of

monomers is therefore a partial distillation. Lubricant bases obtained from this new dimer fraction (sample FORM01) have a more suitable viscosity according to lubricant manufacturers.

Task 4.5: Distillation products analytical characteristics : monomers, dimers and monomers-dimers mixtures (ITERG)

Several analyses were performed on dimers :

- dimer content by HPLC (IUPAC 2.508)
- dimer content by GC (ITERG method)
- iodine index (NF EN ISO 3961)
- acid index (NF EN ISO 660)

The analyses showed that dimer fractions containing monomers have a lower iodine index and viscosity. They contain 30% of monomers, 46% of dimers and 24% of trimers.

Several analyses were performed on monomers :

- monomer content by HPLC (IUPAC 2.508)
- methyl ester composition and content by GC (NF T60-703)
- iodine index (NF EN ISO 3961)
- viscosity at 40°C (ISO 3104)

The analyses showed that monomers are very pure (>97%). They contain a few dimers (2%<). Concerning the iodine index, it was greatly reduced (85) thanks to the use of new raw materials for standolisation (mixture of soya, linseed and rapeseed oils). NB : according to 1st year results, tung monomers had an iodine index of 155 and monomers coming from a mixture of linseed oil 50% & soya oil 50% had a iodine index of 98. Monomers with a low iodine index are preferred because they reduce yellowing in paints.

Deliverables:

D10: Operating protocol on methyl esters synthesis from standoils (ITERG)
Achieved in November 2005.

D11: Analysis report on the 4 methyl esters and comparative study (ITERG)
A comparative study will be performed to highlight the potential applications (paint, foundry, bio-lubricants) as far as required criteria are concerned.
Achieved in November 2005.

D12: Operating protocol on methyl esters synthesis from standoils at pilot scale due to scale transfer and characterisation of these products compared to those produced at lab scale (ITERG)
Achieved in November 2005.

D13: Standoils at pilot scale provided to ITERG (VDP-OLEO)
Achieved in November 2005.

D14: Operating parameters after optimisation of the distillation process at lab scale (ITERG)
Achieved in July 2005.

D15: Report including the whole realised distillation tests and the analytical follow-up (ITERG)

Achieved in November 2005.

2.5

Workpackage 5: Industrial Specifications

Starting: Month 10

Partners involved:

Partners	Planned effort	Actual total
Unikalo	3.5	3,5
Toyal	5	1,17
Iteerg	1	1,11

Objectives:

The objective is to upgrade monomers resulting from the 4 selected standoils in the coating field as “reactive bio-solvent” in comparison with traditional linseed methyl esters.

Task 5.1: Comparative drying tests on beck koller bench (ITERG)

The objective was to compare the drying of the monomers synthesised at pilot scale to several methyl esters. The agrosolvent to test was beforehand formulated as a paint. A reduced formulation of paint was used to simplify the formulation. This formulation contains no pigment, no thickener and no antifoaming agent. These products does not change the drying properties of the paint.

The results showed that the drying of the “monomer solvent” is very satisfying compared to the solvents using methyl esters of oils (linseed, rapeseed and sunflower) and to petrochemical solvent (white spirit).

Task 5.2: Monomers tests as bio-solvents in paints formulation (UNIKALO and TOYAL)

After performing trials during the 2nd quarter of the project (01/01/05 to 30/06/05), Toyal Europe focused on completing the study and producing the Deliverable #17. The first trials (DT 1325 & DT 1338) allowed to select one potential candidate to be used as a grinding solvent: Linseed/Soy/Rapeseed based standoil monomer (Monomer M). In another study (DT 1395), this monomer was used as grinding solvent in comparison with other “green solvents” (methyl laurate and methyl cocoate) and with classical grinding medium (white spirit + oleic acid). The impact of using the standoil monomer was evaluated on different milling parameters (milling safety, milling efficiency, solvent recycling possibility, etc.) but also on the properties of paint film containing the so-obtained aluminium pigments (drying properties, adhesion properties, humidity resistance, colorimetry, etc.).

In November 2005 and June 2006, Unikalo received two other samples of bio-solvents: Rapeseed/linseed/soya monomers and modified oleic sunflower/linseed/soya monomers. They have tested them in the same formulation of a white gloss paint using two different proportions of D40/monomers, all D40 replaced by bio-solvent or a mix D40/monomers 70:30 in order to respect the 2010 legislation concerning VOC for such class of paint (300g/L). These following properties have been studied: viscosity, drying, film hardness, film yellowing and gloss values.

Monomers used as 100% solvent do not permit keeping the same characteristics as the paint with D40 and induce:

- A yellowing too high.
- A hardness too weak with no increase even after several days of drying.
- Drying is slightly long but it could be improved.

Better results are obtained using a mix D40/Monomers in the ratio 70:30 especially considering Persoz hardness.

Yellowing is still important compared to the standard D40 but lower values can be reached with Linseed-soya, Rapeseed/linseed/soya or Modified oleic sunflower/linseed/soya monomers.

Plus the improvement of hardness, resistance to yellowing into the darkness, drying times even better than the standard, the study with the mix D40/monomers allows to respect the CEPE directive for reducing VOC.

In spite of these encouraging points, Unikalo can not use a formulation with the mix D40/monomers to replace these we use actually because Persoz hardness remains too low to keep best qualities of the paint's film in this type of application.

Deliverables:

D16: Comparative table on the methyl esters and the monomers drying ability (ITERG)
Achieved in January 2006

D17: Report on the monomers used as a grinding medium for aluminium pigments production (TOYAL)
Achieved in August 2006

D18: Report on the monomers used as solvents into paint formulations (UNIKALO)
Results will be presented along with some paint starting formulations
Achieved

2.6

Workpackage 6: Setting-Up & Development Of Lubricants “Dimers” Approach

Starting: Month 7

Partners involved:

Partners	Planned effort	Actual total
PeWas	3	3
Baraldi	4.5	4
Motul	2.5	5
BfB	7	8
Itegr	6	6.39

Objectives:

The objective is to produce bio-lubricants from distilled methyl esters, that is to say dimers fractions and monomers-dimers mixtures fractions in order to upgrade standoils in this field in expansion. 2-ethyl hexyl alcohol dimerates resulting from rapeseed seed or sunflower dimers have a real market at the moment and will be the commercial reference in this program.

Task 6.1: Lab scale synthesis (ITERG)

The objective was to transesterify the dimer fraction or a mixture of monomer / dimer with 2ethylhexanol to obtain dimers of 2ethylhexyl. The raw materials are dimer fractions produced in WP4.

The best catalyst is sodium methoxide. A ratio of catalyst of 0.65% w/w of dimers (i.e. 0.37% w/w raw materials) is sufficient to have a high conversion rate. An excess of 66% of 2ethylhexanol is necessary to reach a conversion rate higher than 90%. At the beginning of reaction, a temperature below 100°C is desirable to avoid a strong boiling of methanol. Then temperature must be rapidly raised to at least 110°C, ideally 120°C, to have a fast kinetics.

Neutralisation of catalyst with concentrated acids is difficult (analyses must be done before the addition) and dangerous (exothermic reaction). Neutralisation of catalyst with diluted acids may sometimes imply problems of emulsion and large amounts of acids. Therefore catalyst was neutralised with Trisyl.

Treatments consist in one treatment with Trisyl (initially at 3% w/w of dimer, i.d. 1.8% w/w of raw material) and one distillation to remove the remaining solvent 2ethylhexanol. These treatments can easily be transferred at pilot scale.

In September 2006, Itegr and VdP collaborated to optimise this step for a future scale-up at semi-industrial scale. The use of Trisyl was reduced to 0.57% w/w of raw material (instead of 1.8%). It greatly reduces the cost of the final product and properties of the final product are quite similar if the dimer fraction comes from standoils with a low acidity. At industrial scale, it is easier to use liquids rather than solids or powders. Therefore, sodium methoxide in a powder form was replaced by sodium methoxide diluted in methanol at 30% w/w. The use of this liquid catalyst was validated at lab-scale and just implies the removal of methanol during heating (ideally under vacuum).

Monomers of 2ethylhexyle were also produced to test their performances as fluid lubricant bases (or additives). The process is quite similar with the one used for dimers. Filtration step is easier because monomers have a low viscosity compared to dimers.

As observed in WP4, the “dimer fraction” from the distillation can contain some monomer. Different ratios of monomers in dimer fractions were tested. Anyway, this parameter has no negative impact on the process.

Task 6.2: Finalised products characterisation (ITERG)

GC analysis separates the different dimers : bis methyl / methyl- 2ethylhexyl / bis-(2ethylhexyl) dimers. HPLC analysis give the ratios of polymers, dimers, monomers and 2ethylhexanol. From these 2 analyses, the different products contained in the lubricant bases can be described. These analyses were optimised at Iterg and carried out on most of the trials (NB: for monomers of 2ethylhexyle GC analysis is not necessary because there is nearly no dimer).

Viscosity at 40°C and at 100°C, alkalinity and oleic acidity were also determined for the samples sent to the lubricant manufacturers. Iodine indexes of the final lubricant bases were also determined if the mixture of oils used to produce them had changed (i.e. the choice of raw materials for standolisation – see WP3).

Task 6.3: Synthesis tests at pilot-scale (ITERG)

A reactor of 10 litres was used at pilot scale. Heating at 120°C was slower and implied a longer reaction time. The solution of this problem was found : catalyst must be added in two times to maintain a fast kinetics and avoid a deactivation of the catalyst during reaction.

If filtration of Trysil is difficult, centrifugation of the reaction mixture enables a fast separation of Trysil from the liquid phase. Filtration is still necessary to remove traces of Trysil but it is quite easier. Removal of excess 2ethylhexanol is easy thanks to a heating under vacuum (80°C - 100°C under 1 mbar for example).

Several samples were sent to the lubricant manufacturers. Samples TH08, TH09 (Deliverables 19 & 20), THP01 were dimers of 2ethylhexyl that contains trimers and polymers of 2ethylhexyl. These products are characterised by a high viscosity (between 100 and 150 cSt at 40°C). Lubricant manufacturers asked for lubricant bases with other viscosities. That is why Iterg produced sample FORM01 (viscosity near 53 cSt at 40°C) and TH11 and TH12 (see Deliverables 19 & 20).

Task 6.4: Formulation of the esterified dimer acids (BARALDI, PeWaS, MOTUL)

Please refer to Deliverable D23.

Task 6.5 : Study on the compatibility with additives (BFB)

It was initially expected the study on the compatibility of the raw materials with additives. Some tests were selected to be able to check additive selection :

- compatibility,
- stability,
- filterability after additives and base oil mixture,
- evaluation of performance of formulated oils.

The work of performance evaluation of formulated oils is described in task 6.6 and with deliverables 24.

At the beginning of the Stanlub project, the ester from standoil were supposed to be used in formulations like hydraulic fluids and gear oils. Taking into account some base stocks used in this type of lubricants as polyalphaolefins (PAO) or polyinternalolefins (PIO) which present a very poor solubility with some additives, the compatibility has to be evaluated.

During the project, due to the raw material characteristics, the SME were more interested by other types of lubricants like release agent for die-casting of aluminium alloys, railway switch lubricant, straight oils and soluble oils for many metalworking operations and deformation oils. As the base oils used in these types of formulations are not synthetic ones, it was not usefulness to evaluate the compatibility anymore. SME and Research centres decided to perform more performance tests and not carry out compatibility tests.

Task 6.6 : Evaluation of performance laboratory tasting (BFB)

It was initially expected the evaluation of performance laboratory tests on formulated oils. Depending of their applications, some tests were selected :

- thermal stability,
- oxidation characteristics,
- seals compatibility,
- painting compatibility,
- shear stability,
- volatility,
- air release value,
- demulsibility,
- foaming characteristics,
- rust preventive characteristics and corrosion tests.

Due to the change during the project of the types of lubricants, some performance tests have been replaced by most relevant tests relative to their applications.

The work done is the following :

The objective is to produce bio-lubricants from the more convenient raw materials relating to the type of lubricant. Lab scale synthesis will permit to optimise the molar ratio of reagents, catalyst nature or consumption, reaction parameters, treatment after reaction and purification and yield. The reaction will be transferred to a pilot scale to produce a quantity of raw materials necessary to formulations. After blending, the formulations will be evaluated according to a test selection agreed by SME. Some physico-chemicals characteristics will be carried out as well as performance tests.

Description of raw materials

From standoils produced by VDP-OLEO, ITERG performed some synthesis to obtain following raw materials; these raw materials will be compare to a commercial base produced by Oléon.

- TH05 : ester (dimer) of 2 ethylhexyl from refined linseed standoil (BfB 52297),
- TH06 : ester (dimer) of 2 ethylhexyl from a standoil mixture of 50% soya oil and 50% refined linseed oil (BfB 52296),
- TH07 : ester (dimer) of 2 ethylhexyl from tung standoil (BfB 52600),
- TH08 : ester (dimer)of 2 ethylhexyl from rapseed, linseed and soya standoils (BfB 58208),
- THP01 :ester (dimer) of 2 ethylhexyl from rapseed, linseed and soya standoils (BfB 61122),
- TH11&12 : ester (monomer) of 2 ethylhexyl from rapseed, linseed and soya standoils (BfB 61122),
- Form 01 (mixture THP01 and TH13): ester (dimer + monomer) of 2 ethylhexyl from rapseed, linseed and soya standoils (BfB 62478),
- TH14 : ester (monomer/dimmer (85/15)) of 2 ethylhexyl from rapseed, linseed and soya standoils (BfB 63702),
- Radialube 7121 from Oléon (BfB 53524).

Characterisation of raw materials done by BfB

Some physico-chemicals and performance tests have been selected to characterize and compare the raw materials to a commercial bio-lubricant base Radialube 7121.

Analysis	Standardized methods
Kinematic viscosity at 40°C	ASTM D 445
Kinematic viscosity at 100°C	ASTM D 445
Viscosity index	ASTM D 2270
Acid number	ASTM D 664
IR spectrum	NF ISO 660
Elementary analyses C, H, N	ASTM D 5291
Pour Point	ASTM D 97
Sulfur content	ISO 14596
Noack volatility 1 hour at 250°C	ASTM D 5800
Metals content by ICP	ASTM D 5185
Rotating Pressure Vessel Oxidation Test (RPVOT)	ASTM D 2272
Baader stability	DIN 51554

Discussion on the results

The results are in deliverables 24

Kinematic viscosity at 40°C and 100°C ASTM D445 and VI ASTM D 2270

In comparison with a lot of base fluid used in formulation of industrial oils, the viscosities of the dimerates are quite high; it should be interesting to have products with lower viscosity corresponding to ISO grade 32 and 46 which represents the market demand. One way to obtain lower viscosity grade is of to decrease the molecular weight of the dimerates and to use methanol (bio if possible) instead of 2 ethylhexanol. Moreover, if it is permitted in some formulations, a mix of esters from monomer and dimer will reduce the viscosity even more since the ester from monomer content will be high. In any case the tested esters can be used as viscosity booster.

The viscosity index are quite high which is positive; the VI is higher for commercial Radialube product.

Influence of the proportion esters monomer / dimer of 2ethylhexyl on viscosity at 40°C

A small amount of monomer will decrease significantly the viscosity of the mixture. A grade ISO 46 will be obtained with approximately 35%(w/w) of monomer and a ISO 32 grade with 50/50 (%w/w) monomer/dimer which is quite similar to the proportion monomer / dimer, trimer and polymer of linseed, soya and rapeseed standoil. The selection of the proportion of monomer / dimer can be determined during the process at distillation step.

Acid number ASTM D 664

The acid number of the demerates produced by ITERG show a very low acidity. The base number which is very high on TH05, TH06 and TH07 after synthesis and lower than 0,05 mg KOH/g on Radialube 7121 is due the possible residual presence of alkali and the soap (carboxylates).

Iterg has set up a new protocol conducting to a reduction of soap and alkali (TH08); the base number decrease at 0.5 mg KOH/g but the free fatty acids and the acidity of standoil give an acidity of 0.87 mg KOH/g.

IR spectrum

In correlation with the base number and sodium content by ICP spectrometry, it is important to note the presence of a significant peak at 1565 cm^{-1} in demerates produced by ITERG (TH06), non existing in Oleon dimerates. It indicates the presence of carboxylates.

The new production of raw material (TH08) show a severe reduction of this carboxylate peak. The commercial product, Radialube 7121, show a fingerprint similar to the raw materials.

Elementary analyses C,H and N ASTM D 5291

The hydrogen carbon ratio is around 0,160; it is slightly higher than the corresponding oil due to the presence of two ester functions instead of three in the triglyceride structure.

A higher H/C ration indicates a lower polyunsaturated fatty acid content; the Radialube 7121, which is also a 2 ethylhexyl dimerate shows the lowest polyunsaturated content.

A lower H/C ratio indicates higher unsaturation or presence of polymers.

Pour point ASTM D 97

The 2 ethylhexyl dimerates give better pour point properties than related vegetable oils. The results of the three tested dimerates produced by ITERG are similar. Nevertheless, the Radialube 7121, which has a similar structure, shows a lower pour point. The pour point is negatively affected by the presence of unsaturation and polymers.

Sulfur content ISO 14596

The esterification and distillation process give a low sulfur content as expected.

Noack volatility 1 hour at 250°C ASTM D 5800

The volatility of the dimerates produced by ITERG are on line with the expected value. The lower volatility of the Radialube is due to the presence of high amount of trimers and absence of monomers.

Metals content by ICP ASTM D 5185

There is no significant presence of metals excepted the small amount of silicium due to trisyl and a large presence of sodium coming from the catalyst; this sodium has been reduced to 279 ppm after the new Iterg's synthesis; even if carboxylates (soap) are reduced, in comparison with the Radialube 7121, the remaining sodium concentration is significant.

Rotating pressure oxidation test (RPVOT) ASTM D 2272

The RPVOT results of dimerates are quite similar to the base oil and there is no significant improvement after trans-esterification process. The RPVOT on the Radialube seems slightly higher but not significantly with regards to this method. It will be necessary to find the right antioxidant additives. This raw material should be used in applications where temperature is not too high.

Baader stability DIN 51554

It was determined in previous workpackage that Baader test performed on tung oil lead to product extremely viscous to a gel; when performed on the dimerates, better results are obtained despite the fact that it must be improved in complete formulated lubricants. The refined linseed oil and the mixture of linseed oil and soja show better results than the corresponding dimerates. In comparison with the Radialube, the acid number increase is quite similar but the viscosity increase of dimerates produced by Iterg is significantly higher; this could be due to the presence of unsaturation, uncontrolled polymerisation or presence of carboxylates.

After the new synthesis, TH08 presents results better than previous samples and closest to Radialube 7121. The TH08 acidity after Baader test is lower than Radialube 7121 maybe due to residual alkalinity but the viscosity increase is higher.

Conclusion on raw materials

The first syntheses using the standoils (TH05, TH06 and TH07) presented a high amount of carboxylates; this has been reduce after the new synthesis.

The oxidation resistance has been also considerably improved.

The presence of trimers and polymers doesn't change most of the product properties.

The acidity of the product remains high and the pour point should be lower.

The viscosity is high but the mixture with monomers permitted to produce a base oil at the convenient ISO grade to SME.

FORMULATIONS

Baraldi

Formulation

Baraldi company is interested in the formulation of release agent for die-casting of aluminium alloys which the main properties should be :

- a very good thermogravimetric properties,
- no residue after burn off,
- good release properties,
- low smoke,
- high flash point,
- low friction coefficient,
- good anti-corrosive properties on non-ferrous metals (Al, Mg,...)
- low surface tension,
- low impact on environment,...

Test selection

In agreement with SME, following tests have been selected and performed:

- Thermogravimetric analysis with thermogravimetric curve
- Kinematic viscosity at 40°C ASTM D445
- Kinematic viscosity at 100°C ASTM D445
- Viscosity index STM D2270
- Acid number ASTM D664
- Elementary analysis carbon, hydrogen and nitrogen content ASTM D5291
- Cloud point ASTM D2500
- Pour point ASTM D97
- Sulfur content by wavelength dispersive X-ray fluorescence spectrometry
- Noack volatility, evaporation loss at 250°C during 1 hour ASTM D5800
- Total Base number ASTM D4739

- Metals content by ICP spectrometry
- IR spectrum
- Rotating Pressure Vessel Oxidation Test (RPVOT) ASTM D2272
- Baader ageing DIN 51554

Test description

The tests are described in deliverables 24.

Results, discussion and conclusion

The characteristics of TMP-O lubricant base cod. 5501 which is used by Baraldi (BfB 60494) has been compared to the ester from rapeseed / linseed / soya standoil TH 08 (BfB 58208) and Radialube 7121 produced by Oléon (BfB 53524).

The results are included in deliverables 24

Some results show properties at least identical or better with TH08 than the TMP-O base oil used by Baraldi mainly in oxidation resistance (Baader test).

Nevertheless, despite an IR fingerprint similar to TMP-O, the ester from rapeseed / linseed / soya standoil TH 08 has a relatively low VI, a higher volatility and poorer thermo-gravimetric properties which is for Baraldi the main property.

For this reason and after confirmation of the poorer thermo-gravimetric results in comparison with TMP-O using different mixture of monomers, dimmers and polymers of standoil, Baraldi found the base from standoil inconvenient for its field of application.

Pewas

Formulation

Pewas company is interested in the formulation of railway switch lubricant which the main properties should be :

- water resistance,
- viscosity stability at low temperature,
- low pour point,
- rust-preventing characteristics,
- high surface tension,
- anti-wear properties,
- oxidation stability,
- low impact on environment,...

The objective was to find a new formulation using the base oil from standoils in replacement of the raw material used in the actual Pewas formulation which is the High Oleic Sunflower Oil (HOSO).

Some data will be given to compare the raw materials.

The actual switch point lubricant formulation is labelled BioCon PP40.

The composition of BioCon PP40 (BfB 59890) formulation is indicated in deliverables 24.

The results on BioCon PP40 are mentioned in III.2.4 results and discussion of deliverable 24.

According to Pewas, due to oxidation resistance properties poorer in the formulation with complete substitution of HOSO by TH09 and Form01, only 10 % in mass of HOSO is substituted by TH09 or Form01. This has conducted to the following switch point lubricating oils formulations :

The composition of SO TH09 (BfB 63829) formulation is indicated in deliverables 24.

The composition of SO FORM01 (BfB 63828) formulation is indicated in deliverables 24.

Test selection

In agreement with SME, following tests have been selected and performed :

- Kinematic viscosity at 40°C ASTM D445
- Kinematic viscosity at 100°C ASTM D445
- Kinematic viscosity at low temperature (-20, -10 and 0 °C) ASTM D445
- Kinematic viscosity stability 72 hours at -10°C (ASTM D445)
- Viscosity index STM D2270
- Acid number ASTM D664
- Cloud point ASTM D2500
- Pour point ASTM D97
- Density at 15°C ISO 12185
- Iodine index ASTM D1959
- Noack volatility, evaporation loss at 250°C during 1 hour ASTM D5800
- Evaporation loss ASTM D972
- Hydrolytic stability according to ASTM D 2619
- Rotating Pressure Vessel Oxidation Test (RPVOT) ASTM D2272
- Baader ageing DIN 51554

- Water separability according to ASTM D1401

Test description

The tests are described in deliverables 24.

Results, discussion and conclusion

The results are included in deliverables 24

The SO TH09 and SO Form01 have been used in the formulations in a concentration of 10% (w/w).

In comparison with the actual formulation BioCon PP40 (BfB 59890), the SO TH09 and SO Form 01 based formulations show some similar properties : the viscosity at 40°C and 100°C, the viscosity index (a little bit higher for SO Form 01 based formulation), the acid number, density, pour point and cloud point.

The iodine index of SO TH09 and SO Form 01 based formulations are higher (71 cg I/g) due to more unsaturated compounds; the BioCon PP40 (BfB 59890) has an iodine index of 64 cg/g.

The RPVOT is slightly better for BioCon PP40 (BfB 59890) but a difference of 7 minutes in this test is not really significant.

Although the results are acceptable for formulations based on SO TH09 (BfB 63829) and SO Form 01 (BfB 63828) with an acidity increase of 0.2 mg KOH/g and a viscosity increase less than 5%, The BioCon PP40 (BfB 59890) shows better results with a slight decrease of acidity (-0.08 mg KOH/g) due to a small additives consumption and an unchanged viscosity (< 1%).

Considering the poorer oxidation properties, only a part of High Oleic Sunflower Oil was substituted by SO TH09 and SO Form 01.

The water separability after 30 minutes shows the presence of an emulsion.

Taking into account the field tests results conducted by Slovak Railway (Deliverables 23) the SO TH09 and SO Form 01 based formulations can be used as switch lubricating oils.

Zerowaste

In this project and after the characterisation of the raw materials, Zerowaste company is interested to use the esters from standoils in some applications :

- Soluble oil : the name given to soluble oil is “Stabilis 820”; this polyvalent high performance soluble oil is prepared by dilution to form bio-stable emulsions. It can be used for many metalworking operations by sharp tools and for rectification of all ferrous and non-ferrous metals.
- Straight oil : the name given to the straight oil is “Supraco 2030”; this light-coloured entire metalworking fluid is formulated without organo-chlorides additives. This high

performance product is dedicated to ferrous and non-ferrous turnings removal in difficult metalworking operations.

- Deformation oil : the name given to this oil is “Supraco 1506”; this light-coloured high quality deformation/lubricating oil is used to draw out steel tubes, steel alloys rods (special stainless steel).It is recommended to use it in strong deformations. This product has an high additives content but without any organo-chlorides additives and chemically active compounds.

Formulation

The company Zerowaste is intended to replace a base oil used in their actual formulation by the standoils esters produced by Iterg from Vandeputte Olechemicals standoils.

For each types of oils described above, Motul sent the following samples :

- the actual product
- the formulation with standoils esters (dimerate, Form 01, Monomer of 2EH and monomer of ethyl)
- the actual ester used in the formulation 100%

: The samples received by Zerowaste are listed below; the BfB code, the name and the reception date are mentioned:

Zerowaste/ Motul		
59896	Stabilis 820 ester based 100%	09/02/2006
59897	Stabilis 820 conc from dimérate	09/02/2006
59898	Stabilis 820 conc batch n° 77194	09/02/2006
59899	Supraco 2030 ester based 100%	09/02/2006
59900	Supraco 2030 from dimerate	09/02/2006
59901	Supraco 2030 batch n° 76367	09/02/2006
59902	Supraco 1506 ester based 100%	09/02/2006
59903	Supraco 1506 from dimerate	09/02/2006
59904	Supraco 1506 batch n° 74697	09/02/2006
63822	Supraco 1506 E (Form 01)	20/06/2006
63823	Stabilis 820 (Monomer of 2 EH)	20/06/2006
63824	Supraco 1506 E (Monomer of 2 EH)	20/06/2006
63825	Supraco 2030 (Monomer of 2 EH)	20/06/2006
63826	Supraco 2030 (Form 01)	20/06/2006
63827	Stabilis 820 (Form 01)	20/06/2006
64039	Supraco 1506 E (Monomer of Ethyl)	30/06/2006
64040	Stabilis 820 (Monomer of Ethyl)	30/06/2006
64041	Supraco 2030 (Monomer of Ethyl)	30/06/2006
64326	Supraco 2030 (SO Form01 ester)	13/07/2006
64327	Supraco 2030 (Ester from Motul)	13/07/2006

Test selection

These tests have been selected by SME and performed by BfB :

- Kinematic viscosity at 40°C ASTM D445
- Kinematic viscosity at 100°C ASTM D445
- Viscosity index ASTM D2270
- Sulfur content by wavelength dispersive X-ray fluorescence spectrometry
- Ash content ASTM D482
- Density ISO 12185
- Stability at 0°C and 50°C IP 311
- Anti-wear properties using 4-balls test machine ASTM D4172 mod.
- Extreme pressure properties with welding load CNOMO D55-1136 and ASTM D2783
- Gumming tendency CNOMO D 65-1663
- Corrosion on non-ferrous metals CNOMO D 63-5223
- Corrosion on ferrous metals CNOMO D 63-5200
- Anti-wear properties using Reichert DBL 6570
- Mist from oil CNOMO D 65-1649
- Oxidation stability IP 280

Test description

The test methods are described in deliverables 24

Results, discussion and conclusion

The results are indicated in deliverables 24

Supraco 1506 : light-coloured high quality deformation/lubricating oil is used to draw out steel tubes, steel alloys rods (special stainless steel).

Formulated products using Form 01 (BfB 63822), monomer of 2 EH (BfB 63824) and monomer of Ethyl (BfB 64039) have been sent by Motul. Some performance testings have been carried out and do not show differences between the products for anti-wear properties.

Soluble oil Stabilis 820 : polyvalent high performance soluble oil is prepared by dilution to form bio-stable emulsions. It can be used for many metalworking operations by sharp tools and for rectification of all ferrous and non-ferrous metals.

The first products sent by Motul were used to evaluate the stability at 0°C and 50°C according to IP 311, gumming tendency and corrosion on non ferrous metals. If stability tests and corrosion on non-ferrous metals show similar good results, there is a big difference for gumming tendency evaluation; the Stabilis 820 batch 77194 (BfB 59898) used at 8% (v/v) concentration has a tendency to gum while dimerate formulated product (BfB 59897) pass the test.

A new series of Stabilis 820 products were constituted by a formulated product with Form 01 (BfB 63827) and with monomer of 2 EH (BfB 63823). After testing anti-wear properties

using the four balls machine, the Form 01 formulated product presents better results with a big difference of wear scar diameter at 80kg (0,40 mm for BfB 63827 and 2,53 mm for BfB 63823).

A formulated product with monomer of Ethy was also sent to be tested. There are no result difference between the three formulations against corrosion on non-ferrous metals tests; we noticed a slight tarnish on aluminium. Corrosion on ferrous metals according to CNOMO D63-5200 give good results for the three formulations.

The Reichert anti-wear test seems to be not applicable for these diluted products because there were no discrimination between the products and water.

Supraco 2030 : light-coloured entire metalworking fluid formulated without organo-chlorides additives. This high performance product is dedicated to ferrous and non-ferrous turnings removal in difficult metalworking operations.

Taken into account the first formulations, the welding load of the dimerate formulated product (BfB 59900) is slightly better than formulation with batch 76367 (BfB 59901) and the load-wear index is significantly better for dimerate formulated product.

Some performance properties have been compared on Supraco 2030 formulations with Motul ester (BfB 64327) and ester Stanlub Form 01 (BfB 64326) :

- The tendency to form mist from oil : similar results.
- The oxidation stability test according to IP 280 : the remaining Total Oxidation Product (TOP) is higher on Motul ester formulated product; it means that the oxidation resistance properties are better with ester Stanlub Form 01 formulated product as well for total sludge as soluble and volatile acidity.
- The Reichert test shows no significant differences.
- The Extreme Pressure properties were determined using the welding load results according to ASTM D2783; the ester Stanlub Form 01 formulated product shows slightly better result than Motul ester formulation.

Based on these performance tests the Motul ester can be replaced favourably by Stanlub Form 01 ester.

Task 6.7: Evaluation of biodegradability and ecotoxicity lubricant properties (BFB)

In order to put into evidence the environmental characteristics of vegetable oil based products, tests have been performed to evaluate the persistence of the products in the environment and their toxicity on aquatic organisms (algae, daphnia and fishes). The selected tests meet the OECD guidelines but the preparation mode of poorly soluble substance has been applied for toxicity tests as it is used in the European ecolabel determination.

Results

At the beginning of this project, the biodegradability and toxicity evaluation of raw material was not planned. After consultation with SME, it appeared obvious that these tests have to be done. The first tests were the comparison of commercial base oil produced by Oléon (Radialube 7121) labelled BfB 53524 with the dimmer ester of 2 EH (rapseed / linseed / soya) labelled BfB 58208.

Further tests have been performed on other base oil :

- ester (dimer + monomer) of 2EH which is called Form 01 and labelled BfB 62748,
- ester (monomer) of 2 EH labelled BfB 61123,
- a mixture (50/50) by weight of BfB 61123 and BfB 62478.

Three formulations will be also tested to evaluate their biodegradability as well as their toxicity on the three organisms (algae, daphnia and fishes).

Conclusion

The correlation between the biodegradability tests on raw materials is very good. The ester from rapeseed, linseed and soya standoil TH08 is not biodegradable with a result of 27 %; this result has been confirmed twice. We have also carried out the test on the commercial product from Oléon, Radialube 7121 which is chemically similar to our TH08; the results obtained is 14 % which is lowest than our raw material. These types of ester are not biodegradable probably due to presence of dimer and trimer giving a very high molecular weight.

Consequently we decided to test the following three raw Stanlub base oils :

- ester (dimer + monomer) of 2EH which is called Form 01 and labelled BfB 62748,
- ester (monomer) of 2 EH labelled BfB 61123,
- a mixture (50/50) by weight of BfB 61123 and BfB 62478.

The biodegradability results show a direct correlation with the presence of dimer; the product composed only by monomer is easily biodegradable with 77% while the BfB code 62748 reach a plateau at 38%; the mixture at 50/50 (w/w) give an intermediate result of 63 % and can be considered a biodegradable.

SME decided to use Form 01 in their formulation.

The both formulations of Zerowaste using Form 01 and their own ester have biodegradability results of 31 and 36% within the repeatability of the test.

Pewas used the Form 01 to formulate a railway switch lubricant labelled BfB 63828; the results of 76% obtained on this formulation is good.

Concerning toxicity results, taking into account the water accommodated fraction as preparation mode, all the base oil tested as well as the three formulations show no toxicity (> WAF 100 mg/l) on algae, daphnia and fishes.

Deliverables:

D20: Characterisation of the different products obtained at lab scale compared to commercial ones and final products characterisation (ITERG)

Achieved in January 2006.

D21: Operating optimised and validated at a pilot-scale synthesis protocol (ITERG)

This protocol will be validated and optimised for the 2-ethyl hexyl alcohol dimerates and monomerates derivatives.

Achieved in June 2006.

D22: Analysis report on the products made at pilot-scale (ITERG)
Achieved in June 2006.

D23: Report on the formulation of new biodegradable oil (PeWaS)
Achieved September 2006

D24: Report on performance laboratory testing (BFB)
Achieved September 2006

D25: Report on biodegradability and ecotoxicity lubricant properties (BFB)
Achieved September 2006, please refer to task 6.7

D26 : Report on compatibility of additives with esters derivatives from standoils (BFB)
Achieved September 2006

2.7

Workpackage 7: Industrial validation

Starting: Month 19

Partners involved:

Partners	Planned effort	Actual
PeWas	1	1
Baraldi	2	2
Unikalo	1.5	1,5
Motul	2.5	2,5
Zerowaste	2	2

Objectives:

The objectives of this work package is to validate the characteristic of the products obtained in the WP5 and WP6 by testing them according to the different application fields

Task 7.1: Validation by the lubricants manufacturers for the targeted applications (BARALDI, PeWaS, ZW, MOTUL)

BARALDI:

During die filling, excess amounts of release agents develop gas causing casting porosity and can cool excessively the die during heating transient increasing the number of scraps. At production start up, when the die is in Warm-Up phase the optimum solution is to use release agents with specific low heat and high lubrication capacity and to be able to change the spray time during production in function with die temperature variations when the machine is in full operation. During production the die temperature should remain constant on all the surface area and at the same cycle time, but in reality it is conditioned to the down times due to various reasons and to variations due to outside factors such as: metal temperature, cooling water temperature and in some cases also environmental conditions. The use of die thermo regulators has increased but the excess quantity of 250 Kcal to be extracted from the die per Kg. of cast alloy is removed by the release agents sprayed on the die surface. The cooling channels in the die have geometrical restrictions due to the shape of the cavity, presence of ejectors and need of not passing near the cavity surface to avoid premature breaking of the inserts. To obtain fast production cycles there must be high cooling capacities therefore high fluid flows at low temperature but this can cause breaking due to the temperature gradient. Hot steels with 5% Cr used for inserts are bad heat conductors therefore the temperature difference between the surface in contact with the cast metal and where the cooling channels slide generates stretching due to thermal expansion. The most critical phase of the die life is during cooling when the water based release agents are atomized on the hot surface of the cavities because of strong stress tractions due to contraction of superficial layers respect to the underlying part which cools much slower for the reduced thermal conductivity. It is known that the traction breaking load is less compared to compression and fatigue strength. This shows that die pre-heating is important to speed up production but has a limited effect on the surface breaking due to thermal fatigue. Another important factor is the effect of the die temperature on the casting quality and it is evident how die thermoregulation units are not very efficient because the fluid temperature is adjustable but not the die surface temperature.

Thermocouples can be fitted directly into the die but unless they are very close to the surface, causing mechanical resistance, they have a great hysteresis and the correction effect given by the fluid temperature variation is restrained and with a very high time variable. Using water limits the fluid temperature to 120°C (pressurized circuits) whereas thermal fluids that can reach a temperature of 350°C have a specific heat which is half the value of water therefore are not suitable to remove great heat quantities in short periods. The simulation models used, allow to make precise simulations of the die thermal dynamics with different geometries of the cooling channels, therefore we can say:

- Constant die temperature is necessary for product quality and for die life
- The cavity surface temperature is the most important because it is subject to important thermal cycles
- The most important factor for removing heat from the die is to spray release agents and to keep a thermal balance.

These trials have confirmed our laboratory tests and our expectation, so we can conclude as first result that our lab tests and in particular the TGA analysis are very effective in predicting the behaviour of a lubricant base with respect to a process in which it has to perform a separating antisoldering function at very high temperature. Our product made with FORM 01 showed a lower thermal resistance than the standard one, and consequently a not enough releasing and anti-soldering power between die and injected alloy at the registered temperature.

The obtained sample FORM 01, so as the product previously sampled are not suitable for the application as synthetic base in the formulation of releasing in the field of high pressure die-casting of aluminum. This aspect doesn't affect its usefulness as lubricant for others particular or special purposes.

PeWaS

The switch points lubricant oil made from TH09 sample was prepared by substitution of HOSO oil in the original formula of BioCon PP40 oil by TH09 oil. However, oxidation tests results proved antioxidant properties of the formula to be insufficient, so part of HOSO oil was consequently substituted by supplied oils (TH09, FORM 01). Composition of SOTH09 and SOFORM 01 switch points lubricating oils is listed in the tables here below .

Table: Composition of SOTH09

Component	% mass
HOSO	55,0
Syntolubco 4111	30,0
TH09	10,0
Additine 7115	3,0
Lubrizol 5186	1,5
Lubrizol 7785	0,5

Table: Composition of SOFORM 01

component	% mass
HOSO	55,0
Syntolubco 4111	30,0
FORM 01TH09	10,0

Additive 7115	3,0
Lubrizol 5186	1,5
Lubrizol 7785	0,5

Physico-chemical characteristic of Switch Oils

Table: 1 Physico-chemical characteristics of Switch Oils

Property	method	BioCon PP40	SOFORM 01	SOTH09
Viscosity at 40°C	ASTM D-445	min. 24,02	35,01	40,10
Viscosity at 100 °C			7,383	7,470
Viscosity index	ASTM D - 2270			
Viscosity grade ISO VG	ISO 3448	22	32	46
Pour Point °C	ASTM D-97	-30	-38	-37
Flash Point C.O.C. °C	ASTM D- 92	>185	250	254
Density kg/m ³	ASTM D-941	cca 920	921,0	920,0
R BOT , min.	ASTM D -2272	n.a.	n.a.	n.a.
4 Balls wear, 75 °C, 1200 rpm, 40 kg, 1 hr, mm	ASTM D -4172	0,50		n.a.
Acid number, mgKOH/g	ASTM D-974	0,1	0,22	0,22
Cu corrosion test /3h/100 °C	ATM D-130	1a	1a	1a
Corrosion test-steel Steel/3h/100 °C	ASTM D-665 B	neg.	Neg.	Neg.
Biodegradation %	CEC L 33-A-93	85		
Noack %	CEC L-40-A-93	n.a.	n.a	n.a

In EU there are no uniform standards for switch point lubricants. Practically every railway operator has developed its own specifications for switch point lubricant.

Therefore, we have based the oil formulation on available information and particularly on more than 8 years of development and application of oils for switch points lubrication in Slovak Railways.

We consider oil which meets the following criteria a suitable one for the stated purpose:

Table: required parameters of a switch points lubrication oil

Parameter	Required specifications
biodegradability CEC-L-33-A93	> 80 %
resistant to oxidation <ul style="list-style-type: none"> PeWaS screening test - Ageing behaviour of lubricants in a ferrous dish Oxidation test DSC , onset temperature Rancimat :AOCS Official Method Cd 12b-92 	min. 110 h min. 210°C min. 60 hour
Application Temperature Range	- 30 to + 80 °C
Good corrosion prevention , STN ISO 2160	1a
Viscosity at 40 °C min STN EN ISO 3104+AC	Min. 20 mm ² /s
Pour point °C STN 656072	Max. -30°C
Flash point °C STN 65 6212	Min. 200 °C
Acid number STN 65 60 70	max . 0,1 mg KOH /g

The lubrication oil of the stated features will ensure failure-free operation of classical as well as modern electromagnetic switch points of the following utility properties:

- Lubrication interval 3 – 14 days according to operation and atmospheric conditions
- Lubricant consumption for 1 m² is cca 1 liter for 15 - 25 m²

Consumption of oil (Liter/year/switch)

Lubricant consumption at both of the switch points was evaluated by weight – vaporisator was weighed before and after application. The results within the period were following:

Table: Application of lubricant SOTH09 on switch point #1 on the railway station

date	Consumption of SOTH09 /g
28.04,2006	81
01,05.2006	73
06.05.2006	87
09.05.2006	72
23.05.2006	75
27.05.2006	81
31.05.2006	80
04.06.2006	78
08.06.2006	92
12.06.2006	97
17.06.2006	78
consumption	894
Number of lubrications	11
Date of lubrications	28.04 – 16,06 2006
Consumption per year	: 6,53 kg
Period of lubrication	3 – 5 days

Table : : Application of lubricant SOTH09 on switch point #3

date	Consumption of SOTH09 /g
28.04. 2006	81
7.05. 2006	78
17.05. 2006	80
27.05. 2006	70
6.06. 2007	75
17.06. 2006	73
Consumption completely	479 g
Number of lubrications	6
Date of lubrications	28.04 – 17.06 2006
Consumption per year	3,33 kg
Period of lubrication :	9 – 11 days

Table: Application of lubricant SOFORM 01 on switch point #2

date	Consumption of
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	SOFORM 01/g
8.mája 2006	83
11. may 2006	83
14. may 2006	88
17. may 2006	77
21. may 2006	76
24 may 2006	80
28. may 2006	79
2. june 2006	75
5. june 2006	78
9. june 2006	79
13. june 2006	75
17. june 2006	75
Consumption completely	948 g
Number of lubrications	12 x
Date of lubrications	8.05 – 17.06 2006
Consumption per year	6,39 kg
Period of lubrication :	3 -4 days

Table: Application of Lubricant SOFORM 01 on switch point #4

date	Consumption of SOFORM 01/g
8. may 2006	78
16. may 2006	75
26. may 2006	73
9. june 2006	75
17. june 2006	76
Consumption completely	377 g
Number of lubrications	5 x
Date of lubrications	8.05 – 17.06 2006
Consumption per year	3,44 kg
Period of lubrication :	8 - 14 days

Summary

- consumption of oil (liter /year/switch) and interval time of lubrication

Table: Lubrication of switch point with SO TH09

Parameter	Switch point no.1	Switch point no. 3
Date of lubrication	28.04.2006 – 17.06. 2006	28.04 2006 – 17 .06 2006
Total days of lubrication	50	50
Amount of applications	11	6
Interval time lubrication	3- 4 days	9 – 11 days
Consumption of oil –single shot	81,2 grams	76,2 grams
Consumption of oil per year	6,53 kg/switch point	3,33 kg/switch point

Table: Lubrication of switch point with SO FORM 01

parameter	Switch point no.2	Switch point no.4
Date of lubrication	8.may – 17. june 2006	8.may- 14.june 2006
Total days of lubrication	40 days	40 days
Amount of applications	12	5
Interval time lubrication	3- 4days	8- 14 days
Consumption of oil –single shot	79,0 grams	75,4 grams
Consumption of oil per year	6,39 kg/switch point	3,44 kg/switch point

- application method – with spraying devices
- visual control of switches by digital camera

Zerowaste/Motul:

They performed several formulation tests, all reported in D23, however the validation of the applications couldn't be performed by know since to high volumes were requested (over 200L).

Task 7.2: Validation by the paints manufacturers for the targeted applications (UNIKALO,TOYAL)

No paints were used for industrial validation since none of the initial products matched sufficient criteria. The different results obtained on the study of the use of bio-solvents in replacement of D40 in one of UNIKALO's alkyd white gloss paint formula showed that all properties of the paint's film under these conditions are not as well performed as the standard one with D40 especially for the yellowing into the darkness and the Persoz hardness.

The mix D40/monomers in the ratio 70:30 permitted to improve the hardness of the film but yellowing remains too high compared to the value reached with D40. Lower values were obtained with Linseed/soya, Rapeseed/linseed/soya, Modified oleic sunflower/linseed/soya monomers.

In spite of these encouraging points, Unikalo cannot use a formulation with the mix D40/monomers to replace their actual formulation because Persoz hardness remains too low to keep best qualities of the paint's film in this type of application. Unikalo could try to compare the characteristics obtained with the mix D40/biosolvent to another standard of paint for wood trimmings.

The last week of June 2006, Unikalo began the study of two samples of non leafing aluminium pastes of Toyal Europe (one in the white spirit 17%, the other in bio-solvent C12) in two of their paints, an alkyd gloss decorative paint and an acrylic solvent based paint. To determine the consequences of this substitution, we carried out a series of tests such as the viscosity, drying, persoz hardness, gloss value, tack, aspect of the film applied.

The results put into evidence that they could replace in their alkyd gloss decorative paint, the standard aluminium paste in WS17% by an aluminium paste in C12 without modifying any final characteristics of the paint. But it is not possible to use the "bio-solvent paste" in the acrylic solvent based paint because of a residual aspect of tack.

Deliverables:

D26: Results of testing bio-lubricant in the different applications
Achieved September 2006

D27: Results of testing bio-solvents and their use in coating industry
Achieved September 2006

2.8

Workpackage 8: Project Management

Starting: Month 1

Partners involved:

Partners	Planned effort	Actual
Iterg	4	4,54

Objectives:

The objective of this work package is to ensure a good co-ordination of the work-packages and work carried out in the frame of the project, and to allow a good project progress and management. It will enable the partners to correctly follow up the progress of the project and understand the scientific, technical and economic elements of the project. Then they may use all results in the best possible manner.

Iterg as coordinator was permanent contact point for all partners, both on scientific and administrative level. Common goals were set from the start of the project but regular fine tuning was needed to keep the project on track, by organising some conference calls, technical meetings and steering committee meetings every 6 months. All meetings had minutes and action plans that were followed-up.

Deliverable templates were prepared, due dates reminded to partners and all drafts validated before further diffusion. Specific actions were clarified with some partners as to define precisely to expected results.

Iterg also organised first and second period reporting, and contract amendment. Please refer to part 3 of this report here below.

3 Consortium Management

Iterg as coordinator of the consortium initiated and organised, together with the hosting institutions, 18 month meeting on January 23rd and 24th February in Gembloux, Belgium at BfB. Final meeting was organised in July 2006 at TOYAL, in Accous, France.

Scientific and technical progress were discussed, the up-coming periods prepared, EC requirements explained and reporting documents prepared. Minutes of all meetings were prepared as well.

For the reporting, as in the precedent period Iterg helped all partners by preparing specific guidelines and assisting the partners with the completion of the documents.

Iterg managed the deliverables, to be sure they were produced in time and in respect of the excellence required. All deliverables were obtained in time and are available for all partners on Prodigé for free and secured download.

Communication between the consortium members occurs mainly through e-mail and Prodigé, however regular telephone contact occurs as well for partners being active on the same tasks or having a cooperation to prepare.

4 Other Issues

ITERG, coordinator of the STANLUB project had already several experiences of craft projects and its research is industry oriented. BfB, has also close relationships with companies and thus the work performed by both institutions is specifically applied to the needs and requirements of the other project partners.

One can notice this by the way the research has been planned. The first WP consists effectively in the analysis by the RTD performers of the actual status of knowledge owned by the companies and their best practices. All input has been analysed and summarised in deliverable 2. At the same time ITERG has been analysing the raw material available for their work, in order to base their research on the products that are really available in the consortium.

BfB, by its knowledge of the final products (lubricants especially) and all standardization processes and requirements offer the SMEs in invaluable source of knowledge and studies of the best possibilities, always considering actual market conditions and competitive prices. These aspects are also constantly taken into account by ITERG while choosing raw material or production pathways.

Partners are also regularly contacted in order to track progress and receive several samples to test.

Iterg employed also on a private basis a company to assist the coordinator in its administrative and financial tasks, which makes it also an advantage for the entire consortium who can contact the company and be informed of the exact status of the project (budget, deliverables, up-coming plans, next meetings, minutes of the meetings). It assures well shared information which is a real asset for the consortium.

The other participants in the project, namely Motul and Toyal, as bigger companies, share their market visions and have specific know-how, which enables further testing and evaluation of the developed products. Although no real active role was planned in this first period for Motul, Toyal has already assisted Unikalo in the identification of its requirements and performed first test on the samples sent by ITERG.

To conclude, all requested were closely monitored and there have been several back and forwards between SMEs and RTD performers, in order to comply exactly with their requests. Personnel from VDP has also spent a week at ITERG for training purposes. However as each scientific project, not all initial hypothesis are always successful. As it appears in Stanlub, successful applications have been found for Standoils for the lubricant producers but not yet for paint applications. Nevertheless the project had still his interest for all partners and everyone is satisfied.