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SSOG DIVISION

Biolubricants formulations: what the market offers as antioxidant additives

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Introduction

Lubricanting oils: are formulated products made by Base oils + Additives

Vegetable oils and synthetic esters basestocks for environmentally friendly lubricant formulation.

THE KEY POINT FOR A LUBRICANT APPLICATION: OXIDATIVE STABILITY
Particulary Vegetable Oils have poor thermal and oxidative stabilities that strongly effect their use in industrial in life-service. Oil degradation after an oxidation process drastically influence the lubricating function due to the tendency to form deposits, sludge and corrosive byproducts.

The antioxidant additives can prevent or delay the oil degradation. For this reason we asked to Additive Manufacturers antioxidant package, targeted to vegetables and esters basestocks.

This paper presents the improvement of the oxidation stability with the synergic effect of different commercial antioxidant additives available on the market.

Materials: base oils

The tests were performed in this work on a series of vegetables oils, synthetic esters and one base mineral oil

Vegetable Base Oils: three different oils were used as basestocks

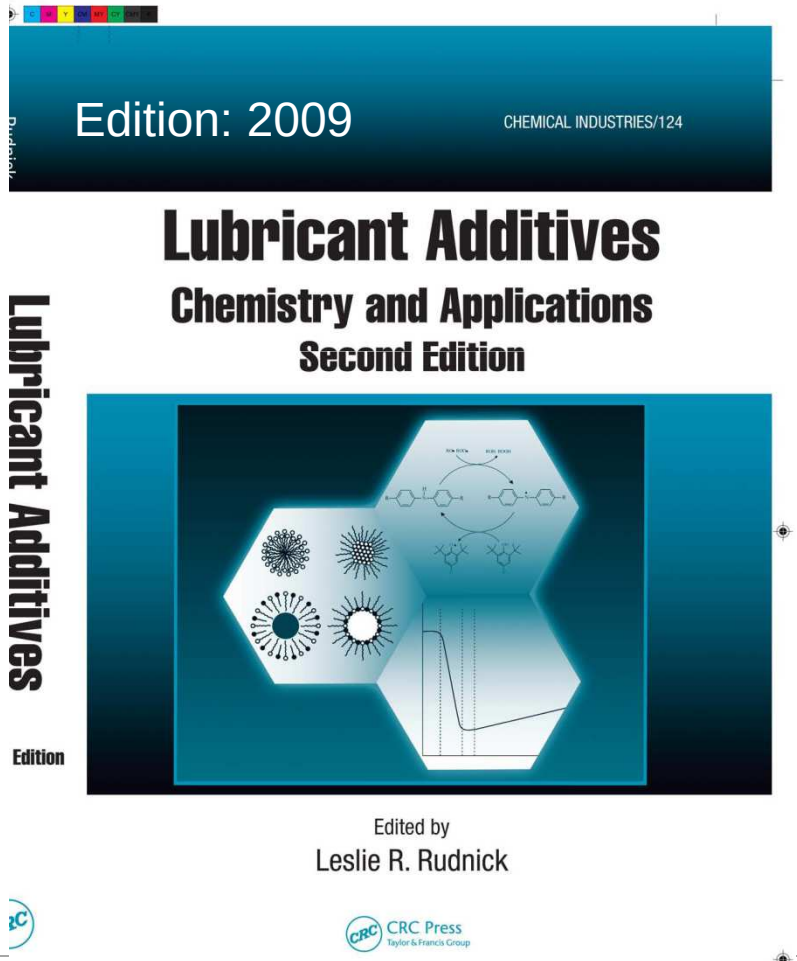
- High oleic sunflower oil (HOSO)
- Hazelnut oil
- Safflower oil (Carthamus oil)

HOSO and Halzenut oil were selected for their content of oleic acid (> 85%, consequently lower level of polyunsaturated fatty acids); Carthamus oil was suggested by a specific Supplier as a new and interesting oil available on the market

Esters base: three different TMP-46 esters were tested, coming from different Suppliers

Mineral Oil: SN 150 (petroleum reference oil)

The relationship between the biobased oils and the response to added antioxidants was done by testing antioxidants additives supplied by SEVEN different Companies Most of the additives are in the list of the Commercial antioxidant mentioned in these pages of the book *"Lubricant additives"*

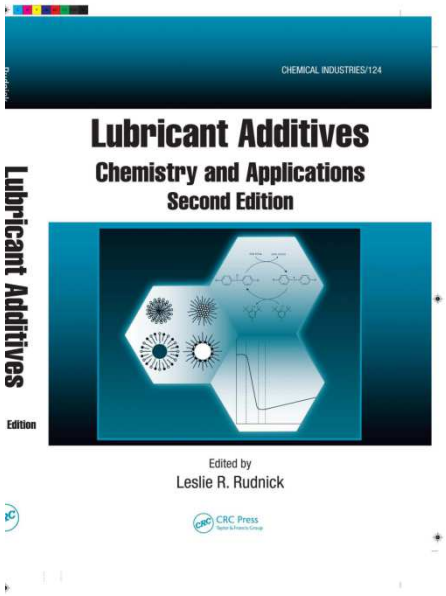


Chapter 1.15 Commercial Antioxidants

Product	Company	Chemistry
Ethanox® 310	Albemarle	Tetrakismethylene (3,5-di-*t-butyl-4-hydroxyhydrocinnamate)methane*
Ethanox 323	Albemarle	Nonylphenol disulfur oligomer
Ethanox 376	Albemarle	3,5-Di-*t-butyl-4-hydroxy-hydrocinnamic acid, C18 alkyl ester*
Ethanox 4701	Albemarle	2,6-Di-*t-butyl phenol*
Ethanox 4702	Albemarle	4,4′-Methylene bis(2,6-di-*t-butyl phenol)*
Ethanox 4703	Albemarle	2,6-Di-*t-butyl-alpha-dimethylamino-p-cresol*
Ethanox 4716	Albemarle	3,5-Di-*t-butyl-4-hydroxy-hydrocinnamic acid, C7–C9 alkyl ester*
Ethanox 4733	Albemarle	Mixture of mono-, di-, and tri-*t-butyl phenols*
Ethanox 4735	Albemarle	Mixture of *t-butyl phenols*
Ethanox 4755	Albemarle	Boron containing derivatives of Ethanox 4702
Ethanox 4872J	Albemarle	Multiring *t-butyl phenol, 53% active*
Ethanox 4827J	Albemarle	Multiring *t-butyl phenol, 30% active*
Ethanox 4777	Albemarle	Alkylated diphenylamine
Additin® 7010	Rhein Chemie	Oligomerized 1,2-dihydro-4-trimethylquinoline
Additin 7130	Rhein Chemie	Phenyl-alpha-napthylamine

Continued

Product	Company	Chemistry
Additin 7110	Rhein Chemie	2,6-Di-*t-butyl-p-cresol*
Additin 7120	Rhein Chemie	2,6-Di-*t-butyl phenol*
Additin 7115	Rhein Chemie	Phenol derivative sterically hindered
Additin 7135	Rhein Chemie	Styrenated diphenylamine
Naugalube® 15	Chemtura	2,2′-Thiodiethylene bis(3,5-di-*t-butyl-4-hydroxyphenyl)propionate*
Naugalube 16	Chemtura	4,4′-Thiobis(2-*t-butyl-5-methyl phenol)*
Naugalube 18	Chemtura	2,2-Thiobis(4-methyl-6-*t-butyl phenol)*
Naugalube 22	Chemtura	Mixture of *t-butyl phenol*
Naugalube 32	Chemtura	Tetrakismethylene (3,5-di-*t-butyl-4-hydroxyhydrocinnamate)methane*
Naugalube 37	Chemtura	3,5-Di-*t-butyl-4-hydroxy-hydrocinnamic acid, C18 alkyl ester*
Naugalube 38	Chemtura	3,5-Di-*t-butyl-4-hydroxy-hydrocinnamic acid, C13–15 alkyl ester*
Naugalube 531	Chemtura	3,5-Di-*t-butyl-4-hydroxy-hydrocinnamic acid, C7–C9 alkyl ester*
Naugalube 438	Chemtura	Dioctyl diphenylamine
Naugalube 438L	Chemtura	Dinonyl diphenylamine
Naugalube 635	Chemtura	Styrenated diphenylamine
Naugalube 640	Chemtura	Butylated-, octylated-diphenylamine
Naugalube 680	Chemtura	Octylated-, styrenated-diphenylamine
Naugalube AMS	Chemtura	Alpha-methystyrenated DPA
Naugard® PANA	Chemtura	Phenyl-alpha-napthylamine
Naugalube APAN	Chemtura	Alkylated PANA
Naugalube TMQ	Chemtura	Oligomerized 1,2-dihydro-4-trimethylquinoline
Naugalube 403	Chemtura	*N,N′-di-sec-butyl-p-phenylenediamine*
Naugalube TPP	Chemtura	Triphenyl phosphite
Irganox® L 01	Ciba	Dioctyl diphenylamine
Irganox L 06	Ciba	Octylated PANA
Irganox L 57	Ciba	Butylated, octylated diphenylamine
Irganox L 67	Ciba	Dinonyl diphenylamine



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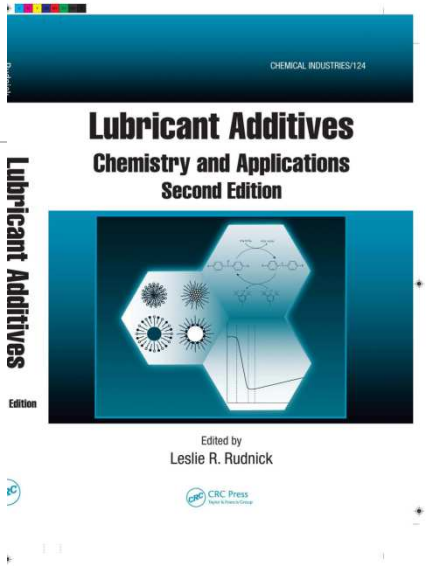


Product	Company	Chemistry
Irganox L 67	Ciba	Dinonyl diphenylamine
Irganox L 101	Ciba	Tetrakismethylene (3,5-di-*t-butyl-4-hydroxyhydrocinnamate)methane*
Irganox L 107	Ciba	3,5-Di-*t-butyl-4-hydroxy-hydrocinnamic acid, C18 alkyl ester*
Irganox L 109	Ciba	Hindered bis-phenol
Irganox L 115	Ciba	2,2′-Thiodiethylene bis(3,5-di-*t-butyl-4-hydroxyphenyl)propionate*
Irganox L 118	Ciba	High MW liquid hindered phenolic with thioether
Irganox L 135	Ciba	3,5-Di-*t-butyl-4-hydroxy-hydrocinnamic acid, C7–C9 alkyl ester*
Irganox E 201	Ciba	Liquid di-alpha-tocopherol (vitamin E)
Irgaphos® 168	Ciba	Tri-(di-*t-butylphenyl) phosphite*
Vanlube® AZ RT	Vanderbilt	Zinc diamyldithiocarbamate in oil
Vanlube EZ RT	Vanderbilt	Zinc diamyldithiocarbamate and diamyl ammonium Diamyldithiocarbamate
Vanlube NA RT	Vanderbilt	Nonylated, ethylated diphenylamine
Vanlube PCX RT	Vanderbilt	2,6-Di-*t-butyl-p-cresol*
Vanlube RD RT	Vanderbilt	Oligomerized 1,2-dihydro-4-trimethylquinoline
Vanlube SL RT	Vanderbilt	Octylated, styrenated diphenylamine
Vanlube SS RT	Vanderbilt	Octylated diphenylamine
Vanlube 81 RT	Vanderbilt	Dioctyl diphenylamine
Vanlube 7723 RT	Vanderbilt	Methylene bis(dibutyldithiocarbamate)
Vanlube 869 RT	Vanderbilt	Zinc dithiocarbamate/sulfurized olefi n blend
Vanlube 8610 RT	Vanderbilt	Antimony dithiocarbamate/sulfurized olefi n blend
Vanlube 887 RT	Vanderbilt	Tolutriazole compound in oil
Vanlube 887E RT	Vanderbilt	Tolutriazole compound in ester
Vanlube 9317 RT	Vanderbilt	Organic amine in synthetic ester
Vanlube 961 RT	Vanderbilt	Butylated, octylated diphenylamine
Vanlube 996E RT	Vanderbilt	Methylene bis(di-butyl-dithiocarbamate) and tolutriazole derivative

Materials: antioxidant additives

Our specific request to the seven Additive Companies was:

"What they have in their portfolio products as the best antioxidant additives targeted for vegetable oils and polyester bases"

As we are not specialist in this sector, we completely relied on their advice and tips for the best use in the formulation

At the request of some of these additive Suppliers we were not authorized to use the commercial name of the products delivered.
So the name of additives used in this work were identified with fantasy name…and categorized in classes, in function of their chemistry

Materials: antioxidant additives

Company	Additive name	Chemistry	Class AntiOX
Fantastic Four	REED Richards	Octylated-butylated di phenilamine	aminic
	SUSAN Storm	Tetrakis(3-(3,5 di tert butyl 4 hydroxyphenyl propionate)pentaerythtol	phenolic
	JOHNNY Storm	3,5 Di-t-butyl-4-hydroxy-hydrocinnamic acid,C7-C9 alkyl ester	phenolic
	BEN Grimm	Bis(3(3,5 di tert butyl 4hydroxyphenyl) propionate) of tiodietilene; benzenamine, N phenyl, reaction products with 2,4,4 trimethylpentene	blends (aminic+phenol)
Hero 1	SPIDERMAN	Complex mixture phenol and amine	blends (aminic+phenol)
The Incredibles	Mr INCREDIBLE	2,6-Di-tert.butylphenol	phenolic
	ELASTICGIRL	diphenilamine derivative	aminic
	VIOLETTA	2,6-Di-tert.butyl-4-methylphenol (BHT)	phenolic
	FLASH	Substituted aromatic amines	aminic
	JACK JACK	Tolytriazole	Copper Deactiv.
Hero 2	SUPERMAN	Alkyl Aryl ammine mixture, Aryl triazole alkyl amine	blends (aminic+phenol)
Hero 3	CAPITAN AMERICA	Not described (antiox blend)	Blends???
Heros 4	BATMAN	3,5-di-tert-butyl-4-hydroxyhydrocinnamicacid, C7-9 branched alkyl esters	phenolic
	ROBIN	Alkylated phenol mixture	phenolic
Heros 5	IRONMAN	Butylated hydroxy-hydrocinnamate (3,5-bis(1,1 Dimethylethyl)-4-hydroxybenezenepropanoic acid branched alkylC7-9 ester	phenolic
	ICEMAN	Tolutriazole compound in ester	aminic

Methods for thermal and oxidative degradation

The method used to evaluate the oxidation stability was:

ROTATING PRESSURE VESSEL OXIDATION TEST (RPVOT - ASTM D 2272)

The choice of this method was because:

- promote measurable oils breakdown in a relatively short time
- it's an automatic method
- suitable for investigating the effectiveness of antioxidant additives
- good repeatable results

Rotating Pressure Vessel Oxidation Test - RPVOT

Originally know as RBOT or rotating bomb oxidation test, was originally designed to evaluate the oxidation stability of new and in service turbine oils having the same composition (basestock and additives)

This test can also be used to characterize other types of industrial lubricants

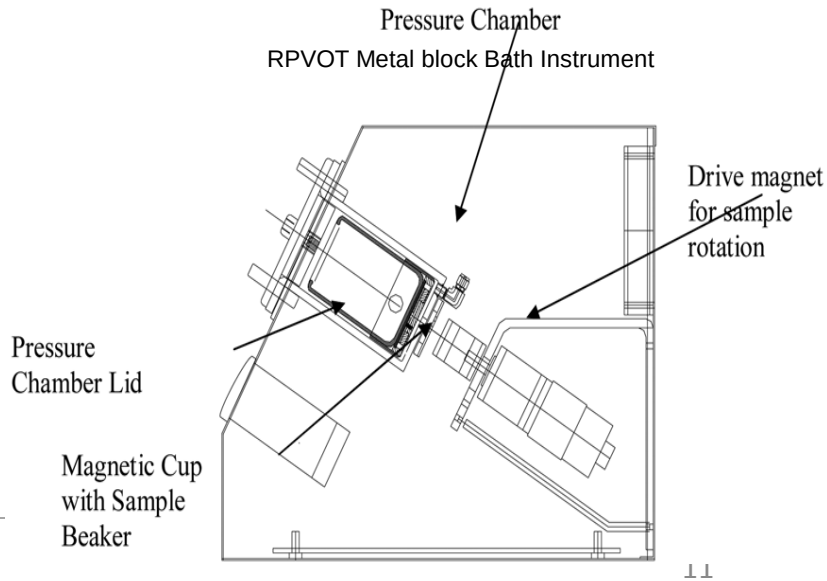
Our laboratory uses it as a rapid test to compare the oxidation stability of different additives and bases

3.0 Summary of Test method ASTM D2272

3.1 The test oil, water, and copper catalyst coil, contained in a covered glass container, are placed in a vessel equipped with a pressure gauge. The vessel is charged with oxygen to a gauge pressure of 620 kPa (**90 psi**, 6.2 bar), placed in a constant-temperature oil bath set at 150°C or **dry block taken to 150°C**, and rotated axially at 100 rpm at an angle of 30° from the horizontal.

3.2 The number of minutes required to reach a specific drop in gauge pressure is the oxidation stability of the test sample.

9.4 The test is completed after the pressure drops more than 175 kPa (**25.4 psi**, 1.75 bar) below the Maximum pressure. This is the life of the sample



Results

Base oils	High Oleic Sunflower Oil	Refined safflower oil (Carthamus Oil)	Refined Hazelnut oil	TMP 46- 1	TMP 46 -2	TMP 46 - 3	SN 150
RPVOT (minutes)	30	27	30	29	29	29	69

		High Oleic Sunflower Oil	Refined safflower oil (Carthamus Oil)	Refined Hazelnut oil
Iodine number	gI2/100	87,7	129,2	90,3
Palmitic acid	C16:0	3,8	6,58	5,6
Palmitoleic acid	C16:1	0,1	0,15	0,16
Stearic acid	C18:0	3,16	3,18	2,03
Oleic acid	C18:1	81,14	35,23	82,51
Linoleic acid	C18:2	9,57	53,79	8,94

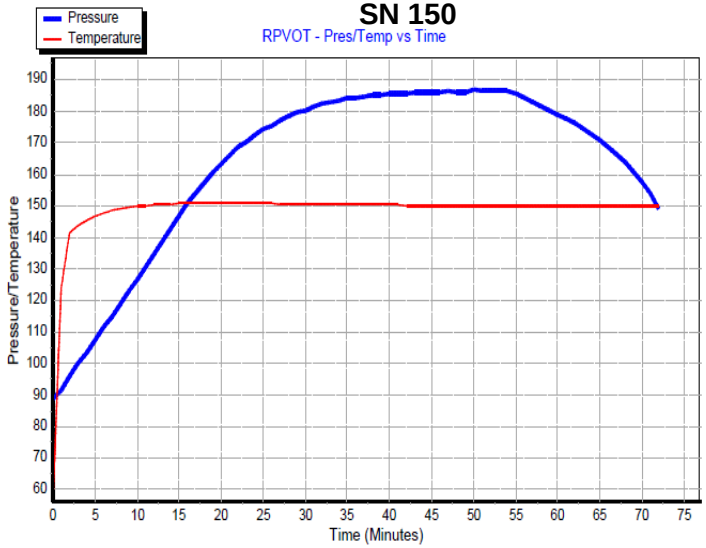
Vegetale oils: the oxidation stability is dipendent on the fatty acids composition

TMP46 1 = TMP46 2 = TMP 46 3 (Even if their iodine number was different: 81.2/ 78.8/ 89.0 $gI_2/100$. Data from the lots of production)

Mineral oil: the stability is twice compared to vegetable oils

Results

SN 150



Break Option: 25.4 PSI Drop
Break Time: 30 Min

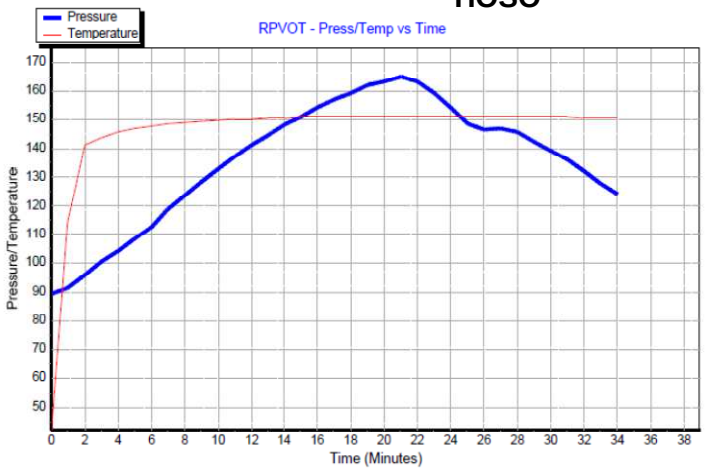
Maximum Pressure: 165.3
Oxidation Index: N/A

Halzenut Oil

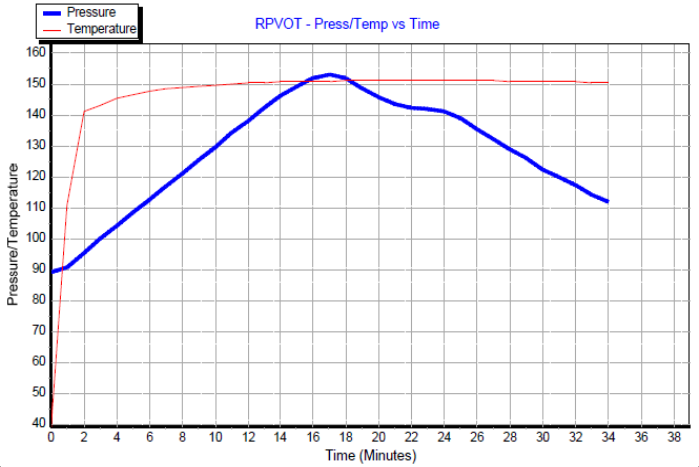
Break Option: 25.4 PSI Drop
Break Time: 29 Min

Maximum Pressure: 153.8
Oxidation Index: N/A

HOSO



TMP 46 - 1



RESULTS from Spiderman - Hero 1

Blend: (aminic+phenol)

RPVOT (minutes)	High Oleic Sunflower Oil	Refined safflower oil (Carthamus Oil)	Refined Hazelnut oil	TMP 46 - 1	TMP 46 -2	TMP 46 - 3	SN 150
SPIDERMAN 3%	244	59	238	226	220	200	653

Best results for HOSO and hazelnut oil.

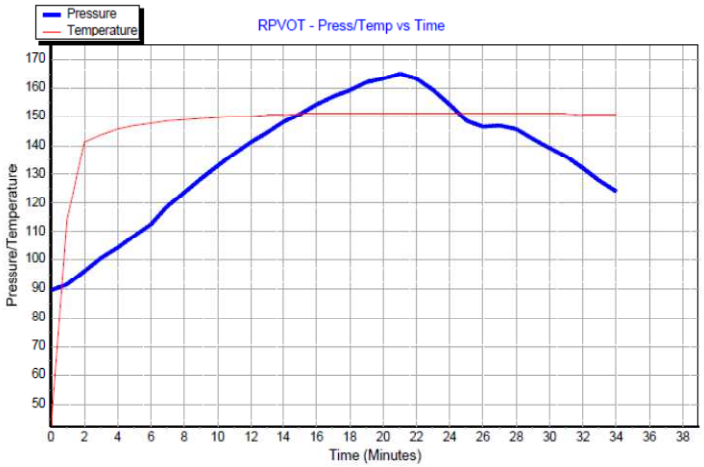
The stability of vergetable oils can be improved through the correct choice of the base oils. Spiderman improve ten time more the stability of HOSO and hazelnut oil

SN 150+Spiderman: its stability is three time greater than HOSO and Hazelnut and ten time more than the mineral oil base

The oxidation stability of TMP esters are more or less similar to HOSO and Hazelnut oil

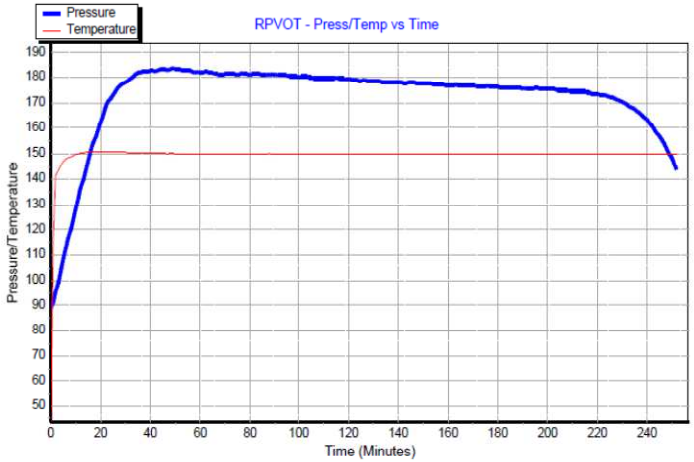
Results: RPVOT diagrams with Spiderman

HOSO

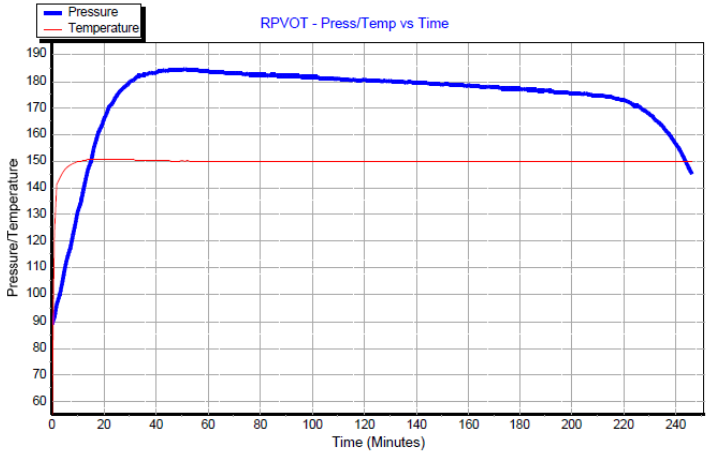


Halzenut Oil

HOSO 3% Spiderman



Halzenut 3% Spiderman



Break Option: 25.4 PSI Drop
Break Time: 244 Min
Maximum Pressure: 183.7
Oxidation Index: N/A

Break Option: 25.4 PSI Drop
Break Time: 238 Min
Maximum Pressure: 184.6
Oxidation Index: N/A

RESULTS from Spiderman - Hero 1

Blend: (aminic+phenol)

RPVOT (minutes)	High Oleic Sunflower Oil	Refined safflower oil (Carthamus Oil)	Refined Hazelnut oil	TMP 46 - 1	TMP 46 -2	TMP 46 - 3	SN 150
SPIDERMAN 3%	244	59	238	226	220	200	653
SPIDERMAN 5%	308	93	301	305			

If you increase the amount of additive, the formulated product increase the oxidation stability.

To meet the performance requirements typical of classical lubricants vegetable oils and ester bases need more additive

TMP 46-1: we choose it for the other tests to reduce the costs of the analysis (high price of the copper coins the are new in each test)

RESULTS From Fantastic Four

RPVOT (minutes)			High Oleic Sunflower Oil	Refined Hazelnut oil	TMP 46 - 1	SN 150
ADDITIVES	added in	Class				
JONNY	1%	phenol	53			156
BEN	1%	Blend	101			313
REED+JONNY	2%	aminic+phenol	102	67	66	
REED+BEN	2%	aminic+blend	106	75	67	

Synergic effect of aminic and phenolic antioxidants
Best results for HOSO; hazelnut oil is equal to TMP 46
Mineral oil: as previously, tripled the stability respect to HOSO
BEN at 1%: it' a promising additive

RESULTS From Fantastic Four

Innovazione e ricerca

Bases Suppliers gave us an estimation of prices (september 2014)

Costs of base oils (industrial uses)	High Oleic Sunflower Oil	Refined safflower oil (Carthamus Oil)	Refined Hazelnut oil	TMP 46 - 1
	1,20-1,50€	2,00-2,20 €	3,00 €	2,00 €

Taking into account the
- RPVOT results,
- the costs of base oils
the additives were evaluated only with High Oleic Sunflower Oil

In this table Fantastic Four results are summarized:

Added in	Aminic	Phenol		Blend (Aminic+phenol)			
	REED	SUSAN	JOHNNY	BEN	REED+SUSAN	REED+JOHNNY	REED+BEN
1%	39	68	53	101	140		
2%						106	102
3%					227		
0,2%					55		

Best results: REED+SUSAN and BEN
Synergic effect (aminic+phenol) antiOX

Results: HOSO and The Incredibles

The incredibles Company		Aminic				
High Oleic Sunflower Oil Hoso	added in	**Flash**	Blend (Aminic+phenol)			
	0,35%	70	**Violetta+ Elasticgirl**	**Mr Incredible+ Elasticgirl**	Blend (Aminic+phenol+copper deactivator)	
	(0,2+0,2)%		38	41	**Violetta+ Elasticgirl+ Jack Jack**	**Mr Incredible+ Elasticgirl +Jack Jack**
	(0,2+0,2+0,02)%				63	87

Results show a short life time of the formulations, even if the additives amount suggested is very low
Interesting result of Flash
synergic effect (double time) of the copper deactivator

Results: HOSO and Batman & Robin

Company Hero 4	Added in	Phenolic + Stabiliser
High Oleic Sunflower Oil	(3+0,05)%	**Batmann & Robin**
		79

High concentration of additive with mediocre result

Results: HOSO and Superman

Company: Hero 2		Blend (Aminic+phenol)
High Oleic Sunflower Oil	Added in	**Superman**
	1,2%	48
	1,8%	59
	4,0%	95

To get good results Superman must be used at high concentration

Results: HOSO and Capitan America

Company Hero 3	Added in	Phenolic + Stabiliser
High Oleic Sunflower Oil		**Capitan America**
	5%	40

Capitan America is not a so good Hero!

Results: HOSO and Heros 5

Company: Heros 5	Added at	Phenolic	Aminic
High Oleic Sunflower Oil		**Ironman**	**Iceman**
	2%	69	43

Company	Additive name	Additive R phrases	Formulated product R phrases	Suggested application
Fantastic Four	REED Richards	R52/53	NO	Synthetic industrial lubricants
	SUSAN Storm	NO R clauses	NO	Synthetic industrial lubricants
	JOHNNY Storm	R53	NO	Industrial lubricants, engine oils
	BEN Grimm	R52/53	NO	Industrail lubricants, engine oils, metalworking fluids
Hero 1	SPIDERMAN	R38, R50/53	R51/53	Environmentally compatible additive for vegetable oils and synthetic esters
The Incredibles	Mr INCREDIBLE	R38, R50/53	NO	Natural and syntetic esters
	ELASTICGIRL	R52/53	NO	Hydraulic fluid (High temperature application)
	VIOLETTA	R50/53	NO	Natural and syntetic esters
	FLASH	R22, R43, R50/53	R52/53	Industrail lubricants, engine oils, metalworking fluids
	JACK JACK	R22 R52/53	NO	Lubricant additive
Hero 2	SUPERMAN	R43/66, R50/53	R51/53 R52/53	Petrolchemical industries: hydraulic industry
Hero 3	CAPITAN AMERICA	NO R clauses	NO	Industrial lubricant
Heros 4	BATMAN	R53	NO	Antiossidant additive
	ROBIN	R22,R35,R43, R50/53		Methylesters stabilizer
Heros 5	IROMAN	R53	NO	Lubricant additive
	ICEMAN	NO R clauses	NO	Lubricant additive

Before drawing conclusion about the RPVOT results we must observe that in the the safety data sheet:

IRONMAN = JHONNY= BATMAN (THE SAME CHEMISTRY = the same R clauses) They are used in different amount as was suggested by each additives Company:

Additive	Added at	RPVOT
JHONNY	1%	53 minuti
IRONMAN	2%	69 minuti
BATMAN	3%	79 minuti

- Only three additives (green colours) have not R phrases. Only these three antiOX could be used for ecolabel formulation because are eco-toxicologically harmless

- Three formulated products are in red colour because they have Hazards identification:

- *R51/53: toxic to aquatic organism, may cause long term adverse effects in the aquatic environment*

-R52/53: harmful to aquatic organism, may cause long term adverse effects in the aquatic environment

- From the data sheet only three additives have as application “natural and syntetic esters”……as the target required

- Spiderman works properly: It's recommended for environmentally compatible additve BUT, at the end, ……has R51/53 hazards risks

- R phrases have an important impact on the allowed treat levels of antiOX additives. R phrases are the discriminating parameter for their applicability as biolubricant. In this contest REED and SUSAN additives are interesting to be studied further

- Even if RPVOT is a "drastic test", for the purpose of this work it has been used as first screening to categorize the effect of antiOX additives. As a matter of fact other tests are used to evaluate the oxidation stability:
the standard ISO 15380 for categories HETG (hydraulic fluid, triglycerides), indicates ISO 4263-3 and Baader test (95°C is the temperature for both of them). Obviously these tests are manual and too long, even if are more suitable per evaluate the real life time of biolubricants

RPVOT: data from the available biolubricants

RPVOT data from products available on the market and selled as biolubricants:

Product – 22: 81 minutes
Product – 46: 112 minutes
Product – 46: 743minutes
Product – 46: 81 minutes
Product – 46: 141 minutes
Product – 46: 38 minutes
Product – 68: 135 minutes
Product – 68: 45 minutes
Product – 68 762minutes
Product - 68: 172 minutes
Product - 68: 29 minutes
Product - 68: 727 minutes
Product - 68: 242 minutes
Product - 68: 190 minutes
Product – 100 79 minutes

Mainly hydraulic fluids, selled as bio….eco….lubricants
RPVOT Value from 29-762 minutes!!!!!

CONCLUSIONS

Vegetable oils and esters bases need more antiOX to meet the performance requirements set for mineral oil based lubricants. Most of the additive packs tested have shown an improvement but no one was able to reach the performance of the petroleum base reference.

Envirnonmentally friendly lubricants need to use additives that satisfy biodegradation and ecotoxicity requirements. The development of new biodegradable antiOX may be needed.

For different reasons, antiOX suitable for mineral oils are not always suitable for vegetable oil or synthetic ester-bases. Hystorically, the unsucces of the use of vegetable oils in industrial application was because the new lubricants were misformulated by using the additives for petroleum-base lubricants.

Conventional petroleum antiOX additives have solubility problems in these biobased stocks. Often the carrier fluid for a multicomponent additives package is usually mineral oil….

CONCLUSIONS

The daunting task for Oleochemical industries is to market a gamma of ester-bases stocks, more stable and at competitive prices

☺ Wonder no more to the nature as regards the supply of vegetable oils

The daunting task for additives Company is to specialize in this particular application, where the chemistry of the additives has to be combined with ester-bases fluids (syntetic and natural).

The goal must be: antioxidant additives, without R phrases, environmentally compatible, effective with biobase stocks, effective in the formulation and working in service application!

THANK YOU VERY MUCH FOR YOUR ATTENTION

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