Government of Saskatchewan
Ministry of Agriculture

ADF Project Final Report

1. Project title and ADF file number
Industrial Products from Vegetable Oils, 20160110.

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4. Abstract/ Summary: *An outline on overall project objectives, methods, key findings and conclusions for use in publications and in the Ministry database (Maximum of 500 words or one page in lay language).*

Vegetable oils from Saskatchewan-grown crops, such as camelina, canola, corn, flax and soybean oils, are used in commercial products like paints and epoxy resins. Flax seed oil is the most common base for oil paints, but it is prone to yellow discoloration over time, and other oil bases form cracks. We have developed a process to remove the components in flax oil that causes yellowing. To explore the limit and scope of the sweet flax seed oil in current art supplies market, 20 commercial pigment products were selected for this study. The medium in the pigment was extracted and analyzed for stability and yellowing components using chemical analysis (^{1}H- and ^{13}C-NMR spectroscopy). This showed that existing paints contain oxidized and aromatic compounds that interfere with product stability. The sweet linseed oil has these components removed, as confirmed by the chemical analysis. The visual colour of paints made with sweet linseed oil was characterized by Fiber Optics Reflectance Spectroscopy (FORS) and compared to the FORS database of paint colours. The Titanium White shows more reflectance than typical linseed oil, and the Naples Yellow with sweet linseed oil has a unique second peak in reflectance at 650 nm, giving it a red hue. The performance of the dried paint was observed using scanning electron microscopy (SEM) images, which showed that the sweet linseed oil paints form smooth layers without pores or cracks, except for Lead White and Titanium White, which developed pores < 5 μm in size. This issue was mitigated by adding turpentine to the paint. The new product made from sweet linseed oil is now commercially available as a paint supply.

Further work on vegetable oil-based industrial products shows that Saskatchewan oilseed crops are suitable to produce modifiers for epoxy resins and plastics. Epoxidized vegetable oils (EVO) can be used to modify the hardness and flexibility of epoxy resins. This process uses hydrogen peroxide to catalyze the epoxidation reaction and results in a plant-based chemical that is generally recognized as safe. Epoxidized corn oil, soybean oil, canola oil, camelina oil and ultra-pure flax seed oil were prepared. The products were characterized by ^{1}H- and 13C-NMR spectra. A convenient method to quantify the degree of epoxidation based on ^{1}H-NMR was established by calculating the area under the peaks associated with the epoxidized chemicals. The addition of acrylic acid creates acrylated EVO, which are plasticizers that can be used to adjust the flexibility of polyvinylchloride (PVC) plastics. This ingredient would replace phthalates in plastic production. UV and thermal cured coatings were achieved with acrylated EVO product.

Saskatchewan crops are valuable resources of chemical feedstocks for industrial and commercial chemicals. The locally sourced, plant-based materials use green processing technologies, and can be incorporated into existing materials, and manufacturing processes without the need for additional infrastructure. The use of locally sourced feedstocks enables Saskatchewan industry to diversify its feedstocks and avoid supply-chain disruptions. The value-added plant-based materials market adds demand for Saskatchewan-based producers.

5. **Key Messages:** *key outcomes and/or extension messages and their importance for producers/industry (3-5 bullet points in lay language).*
   - A method for ultra-purification of flax seed and camelina seed oils was developed.
   - Ultra-pure "sweet" linseed oil is a water white oil base for paints and coatings, now available for purchase.
   - Ingredients for epoxy resin are derived from vegetable oils from Saskatchewan crops (camelina, canola, corn, flax, soybean). The preparation method uses green chemical processes to make ingredients that modify the hardness of epoxy resin. This has broad application in industrial and consumer applications.
   - Further modification of the resin ingredients produces a material that could replace harmful phthalates in plastics and is biodegradable.

6. **Introduction:** *Brief project background and rationale.*

Globally, significant steps are being taken to move from today's fossil-based economy to a more sustainable bio-based economy. Canadian industry is increasingly viewing chemical and polymer production from renewable resources as an attractive area for investment. Oilseeds represent a growing portion of the total agriculture output of Saskatchewan. Currently, oilseeds are sold primarily for food production. With the aid of cost-effective synthesis technology, tremendous opportunity exists to capitalize on high-value products from vegetable oils. Saskatchewan crops will be considered as platforms to produce precursor molecules for conversion to numerous value-enhanced products. This project is designed to develop a series of chemical processes that Saskatchewan communities can use as a basis to manufacture new products and compete in world markets.

The unsaturated fats such as flaxseed oil, camelina oil, or canola oil can be derivatized catalytically by functionalization, oligomerization, oxidation, or metathesis. Thereby, new functional groups are introduced into the oleochemical substrate. These oleochemical substrates are key building blocks for most of the bio-degradable industry products. The chemistry of these types of polymer-based systems (biolubricants, adhesives, coatings, plastics, etc.) is often tightly controlled and orchestrated by the presence or absence of seemingly minor trace components. The uncontrolled presence of trace additives like these can lead to a cascade of unintended consequences.

Flaxseed oil contains cyclolinopeptides (CLP), which can bind to metal ions and trap free radicals. These properties make the CLP a very good drug carrier, an excellent backbone of organic light emitting devices, an inhibitor in the oligomerization process, and a catalyst poison in metal-catalyzed functionalization and metathesis processes. The Lipid Quality and Utilization (LQU) Chair and his research group have developed an efficient approach to recover these valuable peptides and produce ultra-pure flaxseed oil (sweet flaxseed oil). The process also removes indole compounds from camelina oil. These highly refined camelina and flaxseed oils are ideal starting materials for making high quality bio-degradable industry products.

7. **Objectives and the progress towards meeting each objective.**

Objectives (Please list the original objectives and/or revised objectives if Ministry-approved revisions have been made to original objective. A justification is needed for any deviation from original objectives)	**Progress (e.g. completed/not completed)**
a) Develop methods for improving the physical and chemical properties of flaxseed and camelina oil	Completed

b) Determine the yellowing of flaxseed and camelina based oil paints produced with ultra-pure oils	Completed
c) Develop processes for improving the chemical and physical properties of canola and rapeseed oil	Completed

Please add additional lines as required.

8. **Methodology:** *Specify project activities undertaken during entire project period. Include approaches, experimental design, methodology, materials, sites, etc.*

Preparation of ultra-pure flax seed and camelina seed oils.
Flax seed oil (1000 L) was extracted with 200 L of 70% (v/v) aqueous ethanol at 20 ºC, using a pilot scale reactor, for 12 h. The flax seed oil was then removed from the reactor by gravity separation and then concentrated using a pilot rotary evaporator to remove residue ethanol water. This refined flax seed oil was heated up to 50ºC and further purified by charcoal treatment to yield the colorless ultra-pure flax seed oil for this project.
Camelina seed oil (1000 L) was extracted with 200 L of 70% (v/v) aqueous ethanol at 20 ºC, using a pilot scale reactor, for 12 h. The camelina seed oil was then removed from the reactor by gravity separation and then concentrated using a pilot rotary evaporator to remove residue ethanol water. This refined camelina seed oil was heated up to 50ºC and further purified by charcoal treatment to yield the colorless ultra-pure camelina seed oil for this project.

Characterization of oil and epoxy chemical properties.
All ^{1}H-NMR spectra were acquired with a Bruker Avance III Ultrashield 500 MHz NMR spectrometer using CDCl3 as solvent and residual protons as internal reference (7.26 ppm). Spectra were recorded at room temperature with 65536 data points and 32 scans at a spectral width of 5000 Hz, relaxation delay of 1 s, and acquisition time of 6.55 s. Exponential line broadening (0.30 Hz), automatic phase correction, and baseline correction (degree of polynomial equal to 5) were applied to each spectrum.
All ^{13}C-NMR spectrum was recorded on a Bruker (Karlsruhe, Germany) spectrometer operating at 13C frequencies of 125 MHz. Spectra were recorded at concentrations of 5-20% w/v (25-100 mg of lipid in 0.5 mL of chloroform-d) using 5-mm NMR tubes. In addition, spectra were recorded at controlled temperatures of 30 ºC to obtain the best chemical shift and relaxation rate reproducibility. The full 13C-NMR spectrum was recorded over 4000 scans using a 200 ppm spectra width, 16 K data points, a 0.37-s acquisition time, a relaxation delay of 5 s, and a 45o pulse width. The free induction decay (FID) was transformed with zero filling up to 32 K data points to yield a digital resolution of 0.05-0.08 Hz/point. All FIDs, prior to Fourier transformation, were filtered using an exponential multiplication for sensitivity enhancement.

Characterization of oil paint colour
Fiber Optics Reflectance Spectroscopy (FORS) has been established as a powerful tool for the identification of pigments. A FORS spectrum shows for each wavelength, the ratio between the intensity of the reflected light and the incident light, measured with respect to a standard white reference. This ratio is called reflectance and is given as a percentage (%). New or unknown paint coatings are identified by comparison to existing libraries of known pigments. Spectra were collected in the UV-vis range: 200-1000 nm, which includes the region measured in the spectra of the FORS database.

Characterization of oil paint performance.
Scanning electron microscopy (SEM) was used for quantitative and qualitative assessment of the surface quality and the paint coating. Criteria included surface roughness, components surfacing in the paint surface and volumetric layers, and paint coating coverage. Surface microscopic examination before and after paint coating application was carried out with a Hitachi Su8010 SEM in detecting secondary electrons mode at accelerating voltages from 0.5 to 2 kV and Quanta 200 in low vacuum mode with an accelerating voltage of 11kV. The study of the paint coating substrate border line and paint composition surfacing in the paint surface and volumetric layers was carried out based on SEM-images of cross-sectional samples.

Synthesis of epoxidized vegetable oil (EVO)
A solution of vegetable oil (100 g) and glacial formic acid (13.97 g) was heated at 45-55°C. Sulfuric acid (0.5 mL) was then added into the solution, followed by the slow addition of 116.98 g of 30 %wt H_2O_2 solution from a dropping funnel. This solution was reacted at 45, 50 and 55°C for 1-7 h. The molar ratio of vegetable oil : formic acid : hydrogen peroxide was 1 : 2.64 : 8.9. The crude product was filtered and washed with distilled water repeatedly until a pH of 7.0 was obtained. The oil phase was dried with anhydrous sodium sulfate then filtered. Residual water was removed using a rotary evaporator, under vacuum, at 45-50°C.

Synthesis of acrylated epoxidized vegetable oil (AEVO)
A mixture of epoxidized linseed oil (ELO) (25 g) and acrylic acid (5 g) containing 0.5 % hydroquinone was stirred at 75 °C for 20 min. Triphenylphosphine (2 g) was then added to the mixture and stirred for 1 h at 60 °C. A final addition of acrylic acid (4 g) was added to the mixture at 60 °C and incubated for another 1 h. The molar ratio of ELO epoxy groups and acrylic acid in the mixture was 1:1. The consumption of acrylic acid during the acrylation process was confirmed by determining the acid number. The reaction was stopped when an acid number of 50 was obtained. After cooling to room temperature, the unreacted acrylic acid was removed by dissolving the product in diethyl ether and washed several times with 5% aqueous sodium bicarbonate solution until the pH-value was slightly alkaline. The product was washed with saturated sodium chloride solution and dried over magnesium sulphate. The remaining diethyl ether was removed on a rotary evaporator under vacuum at 45 °C for 2 h.

9. **Results and discussion:** *Describe results accomplished during the entire project period under each objective listed under section 6. The results need to be accompanied with tables, graphs and/or other illustrations. Provide discussion necessary to the full understanding of the results. Where applicable, results should be discussed in the context of existing knowledge and relevant literature. Detail any major concerns or project setbacks.*

a) Develop methods for improving the physical and chemical properties of flaxseed and camelina oil
A method was developed to produce ultra-pure flaxseed (sweet linseed) and camelina oils. The seed oil was treated with ethanol, followed by evaporation, and final treatment with charcoal. The resulting seed oil was clarified, and less yellow than the original seed oil. The oils contained fewer peptides (δ = 7-8 ppm), and peroxides (δ = 9-11.5 ppm) after this treatment, as observed by 1H-NMR.

b) Determine the yellowing of flaxseed and camelina based oil paints produced with ultra-pure oils
Sweet linseed oil was used to produce oil-based paint; however the ultra-pure camelina oil has fewer double bonds in the lipid molecules and takes too much time to dry. Camelina oil-based paints were excluded from further research activity for paint products. Further work to improve the physical and chemical properties of camelina oil is described in subsection 9.c, regarding epoxies.

For comparison, oil-based paints from existing manufacturers were characterized by 1H NMR spectroscopy to examine the chemical properties of existing products. New paints were made using traditional pigments and the sweet linseed oil developed in this project. The performance of these paints was characterized using SEM to establish paint quality, and FORS for colour. A local artist produced paintings using this paint, and the sweet linseed oil was developed into a product now sold as an art supply product.

Existing products
High quality coatings of high brilliance and color strength are characterized by a perfect pigment dispersion, optimal pigment particle size, and long-term stabilization of the dispersed particle in the formulation. Linseed oil, walnut oil, poppy oil and safflower oil are common media for pigments, and their properties differ. Linseed oil is the most popular due to its flexibility and resistance to cracking over time. It does have a strong tendency to yellow with age. Walnut oil, poppy oil, and safflower oil are much less likely to yellow and these thin, clear, watery oils are much more prone to cracking.

A sampling of established paint products was selected for characterization and comparison with the oil-based pain products developed under this project. Winsor & Newton is a company based in London that manufactures a wide variety of fine art products since 1832. Reeves is an English artists' supplies firm established by William Reeves (1739–1803) in 1766. Art Spectrum originated as a co-op run by a group of Australian painters who sourced knowledge and machinery required producing materials that would meet the needs of the local art community. Pebeo began to develop ready to use color since 1929 in Marseille, France. Mussini arises from the tradition of Italian painting school and offers an Old Masters palette that dates back over 100 years. The oil composition and quality is summarized in Table 1 and spectra detailed in Appendix A. The presence of oxidized compounds indicate oil instability, and aromatic compounds are associated with paint coatings yellowing over time. The sweet linseed oil developed here has these peptides removed, as verified by NMR spectroscopy, however insufficient time has passed to demonstrate this property on the paintings created with these new paints.

Table 1. Commercial pigment medium NMR analysis results.

Sample Information		**NMR Results**		
Brand	**Color**	**Oxidized Lipids**	**Aromatic Compound**	**Lipids Type**
WINSOR & NEWTON	Permanent Alizarin Crimson	NA	peptide	Pure Linseed Oil
WINSOR & NEWTON	Chrome Yellow Hue	peroxide + aldehyde	dye	Linseed Oil
WINSOR & NEWTON	Lemon Yellow	NA	dye + peptide	Modified Linseed Oil (monoglyceride)
WINSOR & NEWTON	Phthalo Blue	peroxide + aldehyde	dye + peptide	Pure Linseed Oil
WINSOR & NEWTON	Ivory Black	peroxide	peptide	Linseed Oil
WINSOR & NEWTON	Titanium White	peroxide	dye	Safflower Oil
WINSOR & NEWTON	Umbra, Gebrannt	peroxide + aldehyde	peptide	Linseed/Safflower Oils
REEVES	Titanium White	peroxide	NA	Safflower Oils
REEVES	Brilliant Red	peroxide + aldehyde	dye + peptide	Linseed/Safflower Oils
REEVES	Lemon Yellow	aldehyde	dye + peptide	Linseed Oil
REEVES	Phthalo Blue	peroxide + aldehyde	peptide	Linseed Oil
REEVES	Ivory Black	peroxide + aldehyde	NA	Linseed/Safflower Oils
ART SPECTRUM	Yellow Ochre	NA	NA	Pure Alkali Refined Linseed Oil
ART SPECTRUM	Burnt Umber	NA	NA	Pure Alkali Refined Linseed Oil
PEBEO	Yellow Ochre	NA	dye	Linseed/Safflower Oils
PEBEO	Primary Cadmium Yellow Imit	peroxide + aldehyde	dye	Safflower Oils
PEBEO	Burnt Umber	peroxide + aldehyde	NA	Linseed/Safflower Oils

MUSSINI SCHMINCKE	Lemon Yellow	peroxide + aldehyde	dye	Linseed/Safflower Oils

Paint quality

Loss of the paint picture elements is generally caused by open pores on the substrate surface, microcracks and formations with teardrop or round shape. Scanning electron microscopy (SEM) was used to determine the behavior of paints to prolonged exposure to conditions of defined temperature and humidity. These tests provide an indication of the likely performance that can be achieved under different conditions. The coating quality is summarized in Table 2, and the SEM images of the paint coating surface on the packaging materials with different pigments are shown in Appendix B.

Table 2 Coating performance of sweet flax oil with typical pigments, coatings are stable under storage up to 40 days, pores in coatings are reduced by adding turpentine to paint mixtures.

Pigment	Pores	Cracks
Permanent Red	None	None
Permanent Red, 40 days storage	None	None
Naples Yellow	None	None
Hansa Yellow	None	None
Indigo	None	None
Violet Blue	None	None
Titanium White	2-3 µm	None
Lead White	3-5 µm	None
Lead White with Turpentine	None	None

Colour characterization

FORS of the paint made from sweet flax seed oil with different pigments are shown in Figure 28. The Naples yellow with sweet flax seed oil (Figure 1, brown line) shows two characteristic maxima at 400 nm and 650 nm, which is different from any reference in the FORS database which have single maxima in the range of 400-450 nm depending on the binder used (Figure 2a). The titanium white of sweet flaxseed oil can easily be differentiated from other binders (Figure 1, black line) showing a narrower absorption band between 350 nm and 450 nm followed by a stronger and sharper positive slope (Figure 2b). This sweet oil paint reflects more light and appears more white than traditional titanium white with linseed oil.

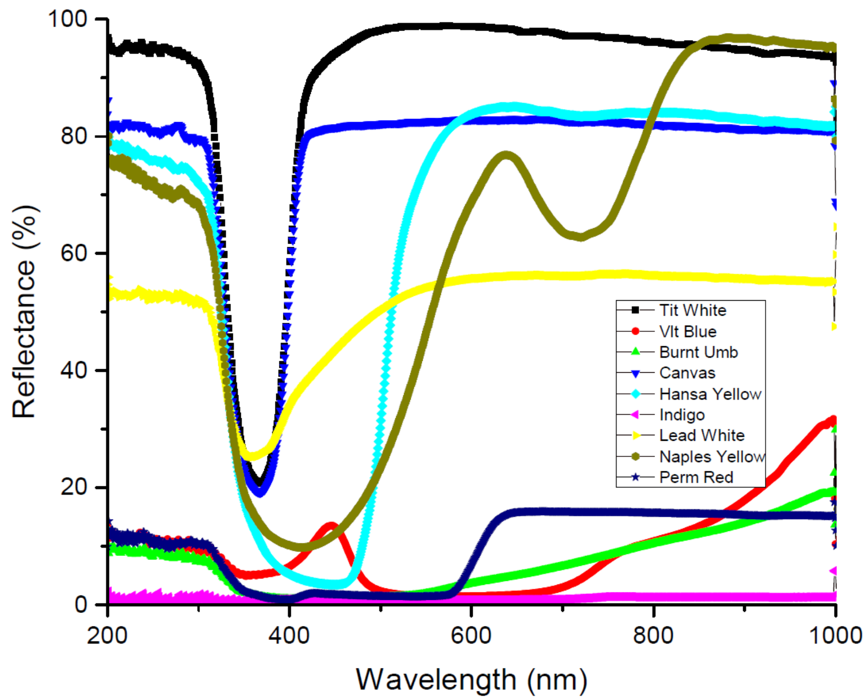

Figure 1 Fiber Optics Reflectance Spectra of paint made from sweet flax seed oil and different pigments

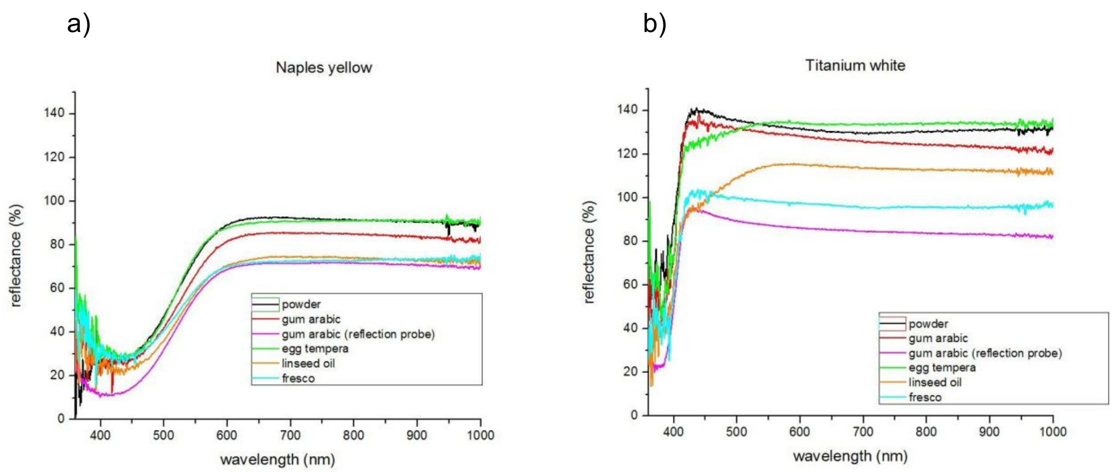

Figure 2. Fiber Optics Reflectance Spectra of naples yellow (a) and titanium white (b) with different binders (FORS database)

Use case

A local artist used paints made with sweet flax seed oil to create two paintings. This demonstrates the effectiveness of the new paint products using the ultra-pure flax seed oil developed under this project.

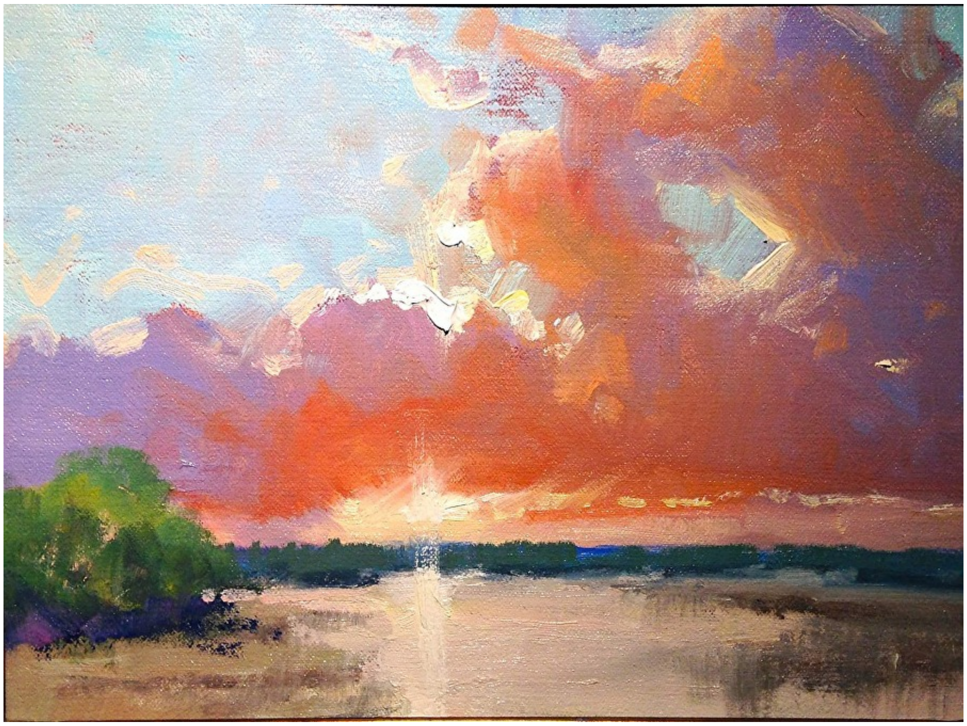

Figure 3. Sunset at Frank Lake by Doug Swinton (sweet flax seed oil painting)

Figure 4. Canada Day by Doug Swinton (sweet flax seed oil painting)

c) Develop processes for improving the chemical and physical properties of canola and rapeseed oil

Two new processes for producing epoxy using vegetable oils (Canola, Camelina, Flax, Corn, and Soybeen oils) were developed. A new NMR method for quantifying the epoxidation of the oil was also developed. This method applies and internal standard for calibration, and calculation of relative peak area to the internal standard. The peaks associated with epoxidized polymers were used to calculate relative peak area, and due to the use of an internal standard, the concentration of epoxidized vs. un-changed polymer was calculated.

Synthesis of epoxidized vegetable oil

Epoxidized vegetable oils can be used as a reactive modifier for epoxy resin systems, as the epoxy groups are available for chemical modification reactions. Epoxidized vegetable oils (EVOs) are currently produced by a conventional epoxidation process (Figure 5) in which the unsaturated oils are converted with percarboxylic acids (e.g. peracetic or performic acid). The percarboxylic acid is generated from H_2O_2 in the presence of a strong mineral acid, *in situ*.

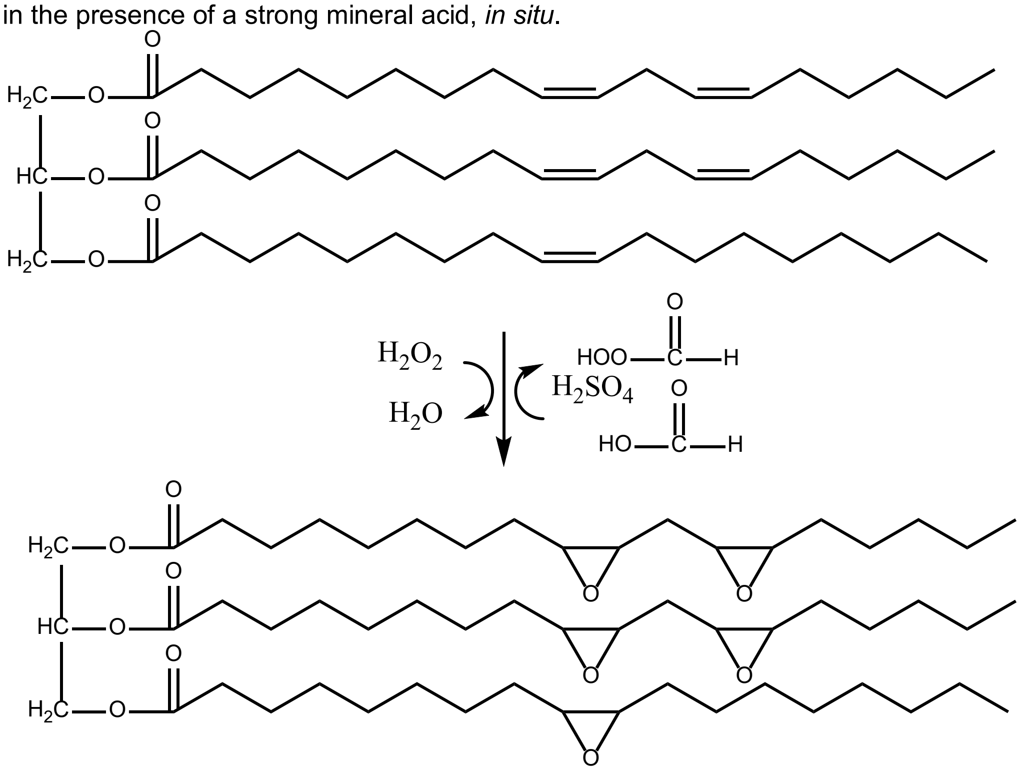

Figure 5. Epoxidation reaction of vegetable oil.

There are enormous advantages in using ultra-pure camelina, canola and flaxseed oil in the development of new products, such as the potential to utilize existing infrastructure in the production of new materials and products. This research provides information that will allow manufacturers to produce useful industrial fluids using these materials with equipment that is presently available in typical production facilities. Corn oil, soybean oil, canola oil, camelina oil and flax seed oil were found to be the most promising oils to produce epoxidized vegetable oils. The desirable quality in these oils is low level of unreactive saturated fatty acid, which leads to a low crosslink density upon cure.

The production of epoxidized vegetable oils was achieved with environmentally friendly, hydrogen peroxide (H_2O_2) as an oxidant. The product was characterized using ^{1}H and ^{13}C NMR spectroscopy (Figures 6, 7).

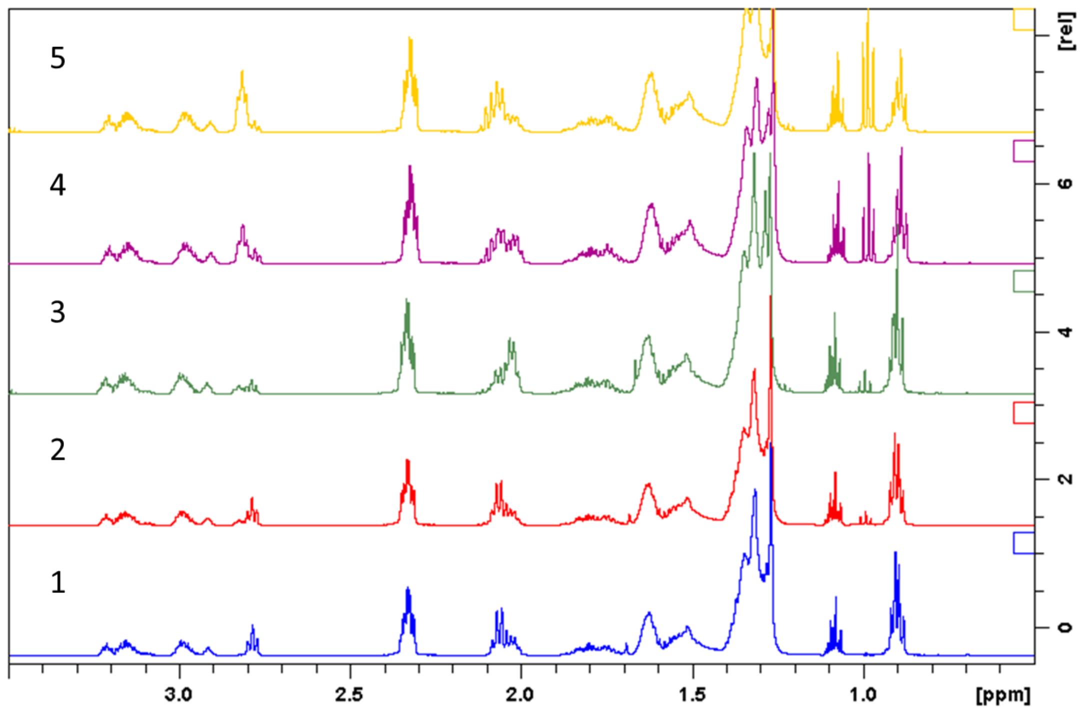

Figure 6. 1H-NMR spectra of the epoxidized vegetable oils (0.5-3.5 ppm). 1 epoxidized corn oil; 2 epoxidized soybean oil; 3 epoxidized canola oil; 4 epoxidized camelina oil; 5 epoxidized ultra-pure flax seed oil.

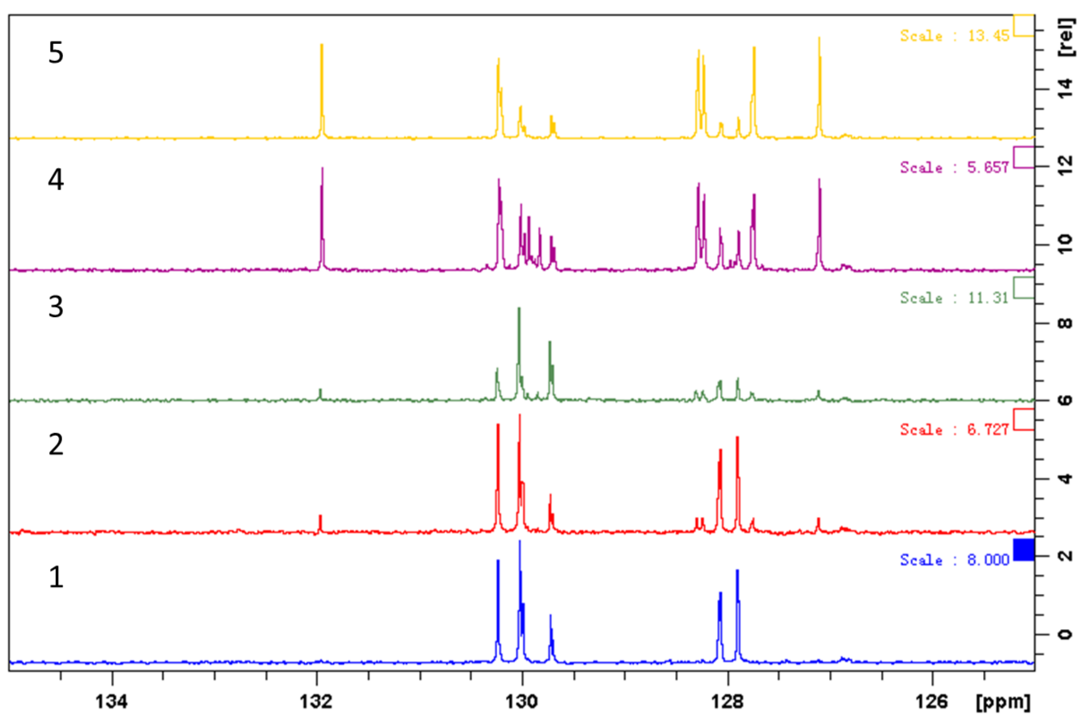

Figure 7. 13C-NMR spectra of the epoxidized vegetable oils (125-135 ppm). 1 epoxidized corn oil; 2 epoxidized soybean oil; 3 epoxidized canola oil; 4 epoxidized camelina oil; 5 epoxidized ultra-pure flax seed oil.

Epoxidized ultra-pure flaxseed oil at different percentages

Oxirane is a cyclic ethylene group that affects the crosslinking density and mechanical/thermal performance of epoxies. To address this, flax seed oil was used to produce epoxies with increasing degrees of epoxidation (50, 80 and 100%). 1H-NMR was used to verify the completeness of the epoxidation process. The ^{1}H-NMR spectra, illustrated in Figure 8, corresponds to (1) flax seed oil epoxidized at 50%; (2) 80%; and (3) 100%. The percentages were calculated from the integrals of double bonds and epoxy ring hydrogen signals. The signals associated to the epoxy group were: -CH- hydrogens (Ha; 2.9 ppm) and -CH- hydrogens, adjacent to epoxy groups (Hb; 1.45 ppm). The ^{13}C-NMR spectra of these products can be differentiated by the signal at 66 ppm (Figure **9**)

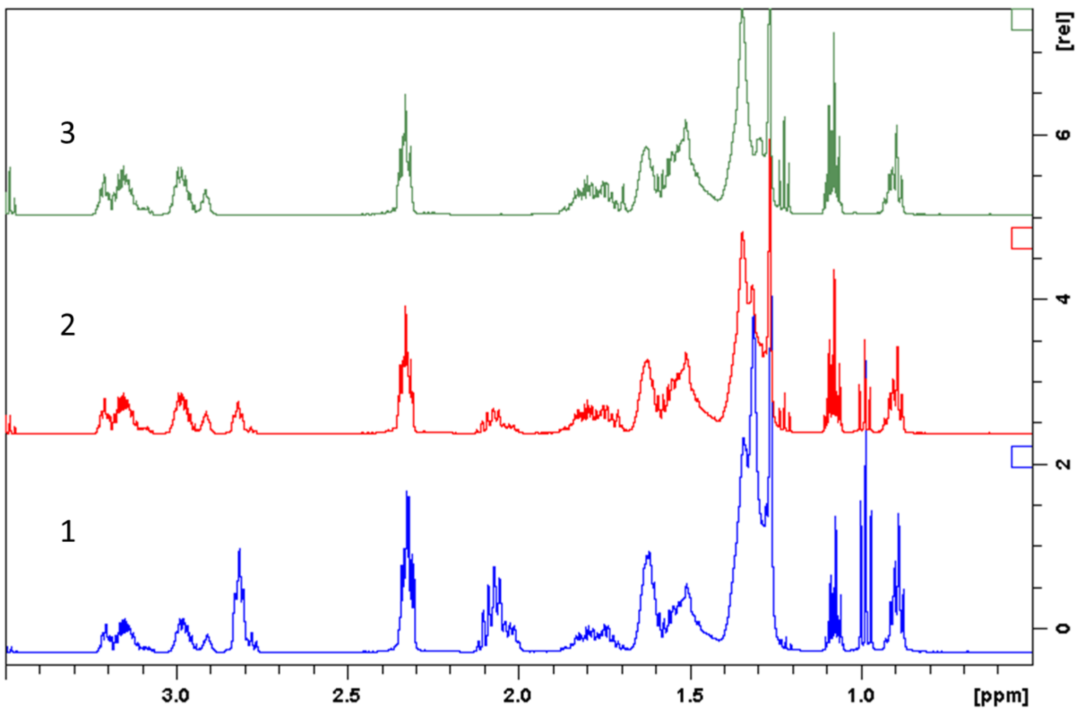

Figure 8. 1H-NMR spectra of the epoxidized ultra-pure flax seed oil at different degree (0.5-3.5 ppm). 1 epoxidation 50%; 2 epoxidation 80%; 3 epoxidation 100%.

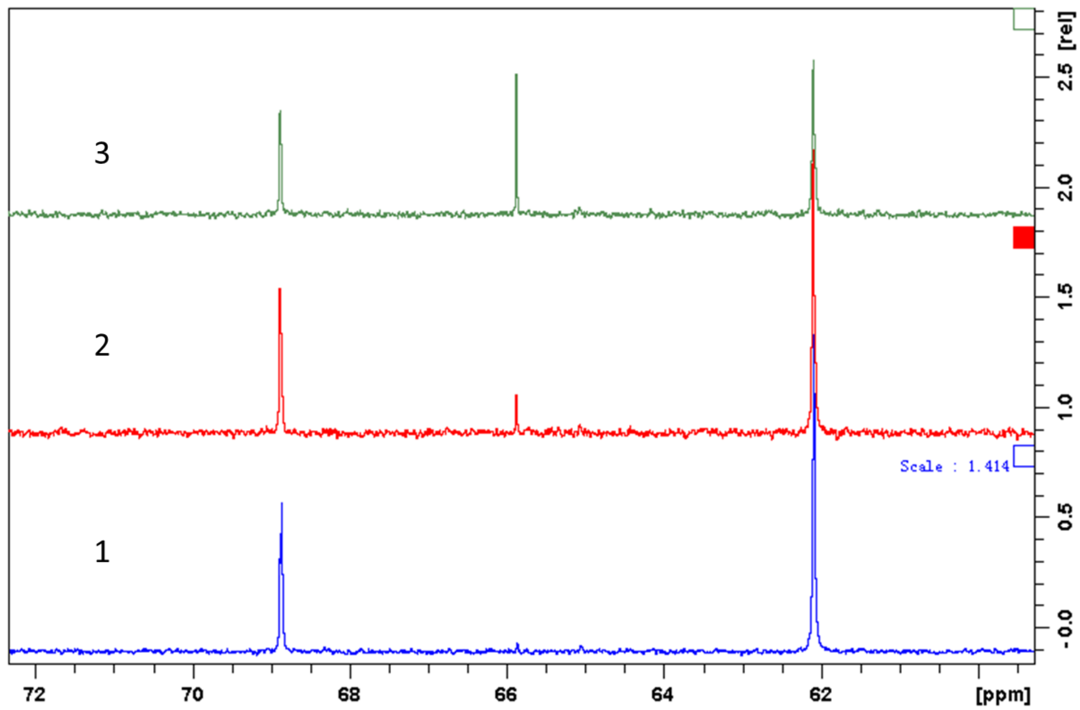

Figure 9. 13C-NMR spectra of the epoxidized ultra-pure flax seed oil at different degree (60-72 ppm). 1 epoxidation 50%; 2 epoxidation 80%; 3 epoxidation 100%.

Synthesis of acrylated epoxidized vegetable oil

Polyvinyl chloride (PVC) is one of the most widely used polymers. These polymers contain additives called plasticizers that improve the flexibility of the plastic. PVC plasticizers, most widely used by the plastic processing industry, are derived from phthalates. Concerns have been raised that these phthalates migrate into contacting materials, which may lead to toxic adverse effects in food applications. These plasticizers can be substituted by ultra-pure epoxidized flax seed oil without the adverse effects. From an industrial point of view, this substitution presents an interesting alternative as epoxidized camelina, canola and flaxseed oils are natural products, generally recognized as safe, and biodegradable.

The introduction of acrylate or methacrylate functions in a polymer or oligomer is generally made with the aim of polymerization or copolymerization of the double bonds leading to network or grafted copolymers. Radiation curable acrylates can be derived from the epoxidized oils discussed above. This work describes the development of vegetable oil-based acrylated UV curable resin which can be beneficial for the surface coating industry. Acrylated epoxidized vegetable oil (AEVO) were prepared using epoxidized vegetable oils and acrylic acid (Figure 10). The product was characterized using ^{1}H-NMR and ^{13}C-NMR spectroscopy (Figure 11, 12). The modified resin samples gave proton signals at 5.5-6.5 ppm, belonging to the vinyl group from acrylation.

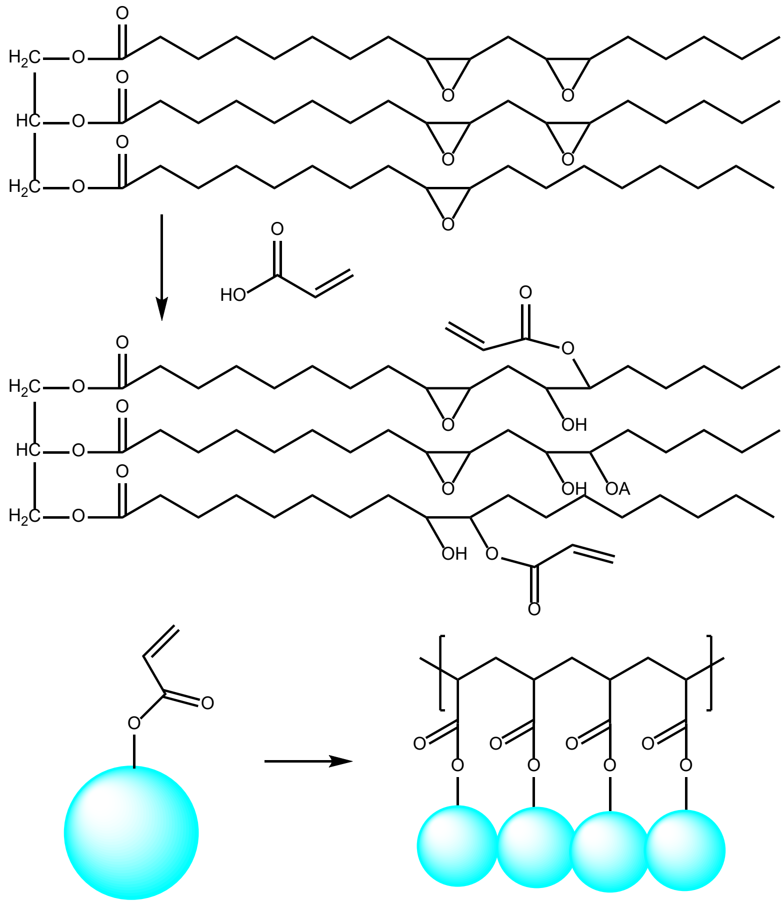

Figure 10. Synthesis of acrylated epoxidized vegetable oil and its crosslinking polymer.

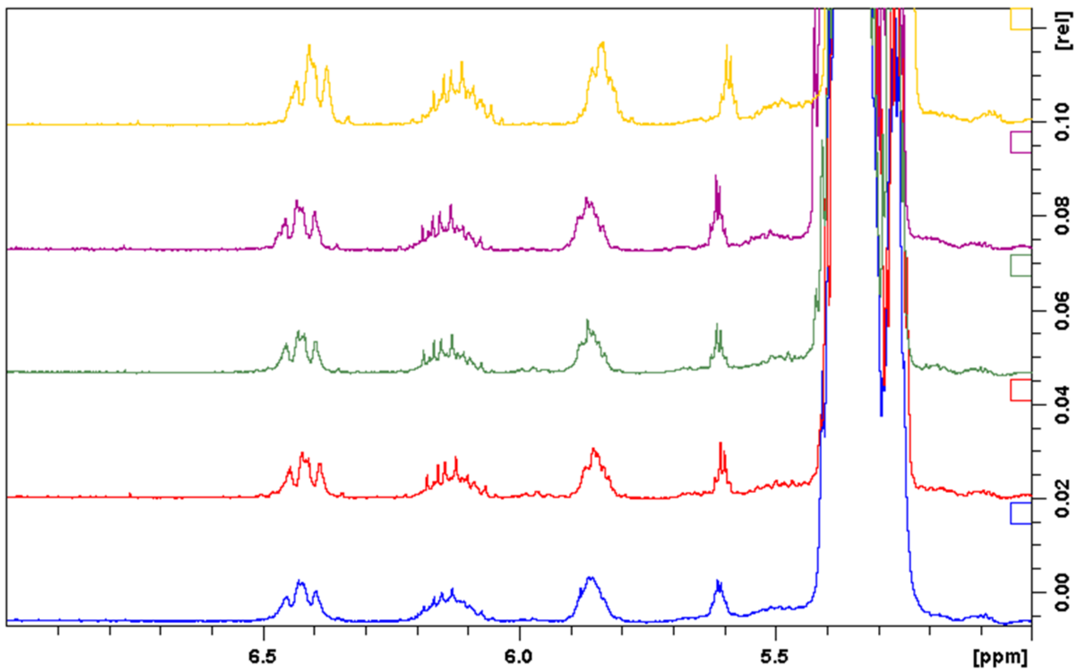

Figure 11 1H NMR spectra of the acrylated epoxidized vegetable oil (5-7 ppm). 1 acrylated epoxidized corn oil; 2 acrylated epoxidized soybean oil; 3 acrylated epoxidized canola oil; 4 acrylated epoxidized camelina oil; 5 acrylated epoxidized ultra-pure flax seed oil .

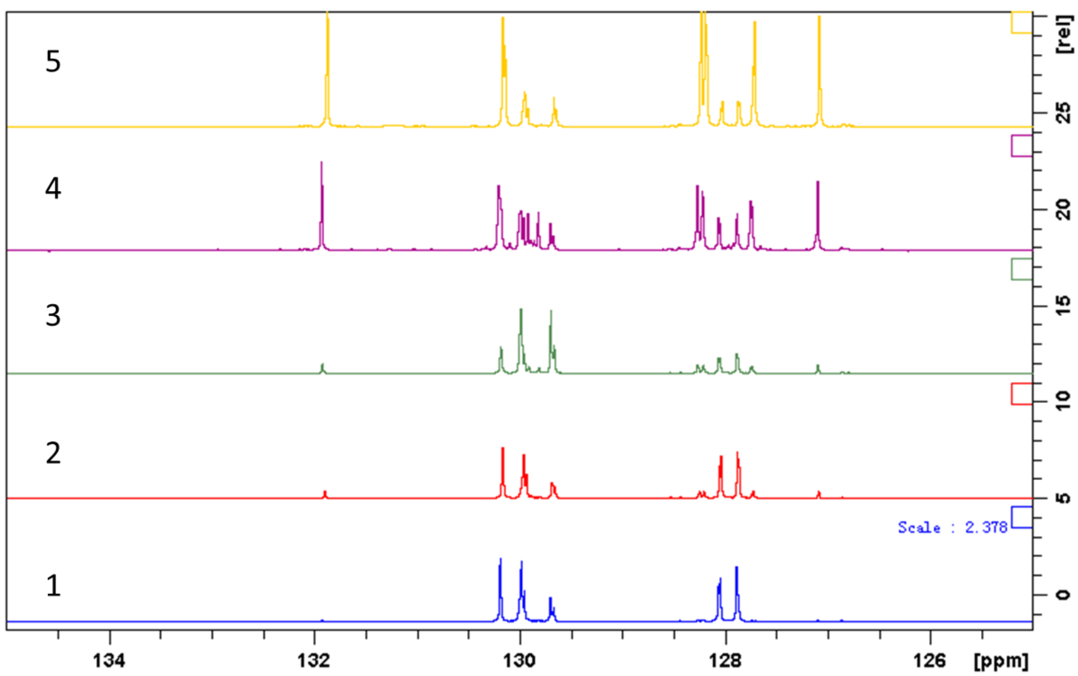

Figure 12. 13C NMR spectra of the acrylated epoxidized vegetable oil (125-135 ppm). 1 acrylated epoxidized corn oil; 2 acrylated epoxidized soybean oil; 3 acrylated epoxidized canola oil; 4 acrylated epoxidized camelina oil; 5 acrylated epoxidized ultra-pure flax seed oil.

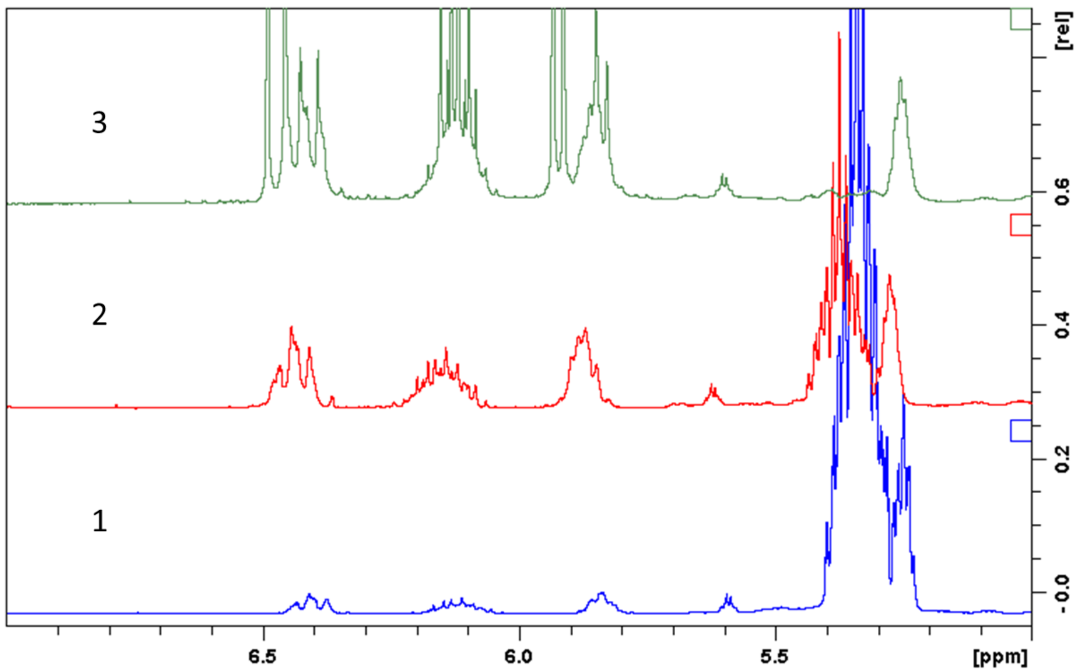

Figure 13. 1H NMR spectra of the acrylated epoxidized ultra-pure flax seed oil at different degree (5-7 ppm). 1 acrylated epoxidation 50%; 2 acrylated epoxidation 80%; 3 acrylated epoxidation 100%.

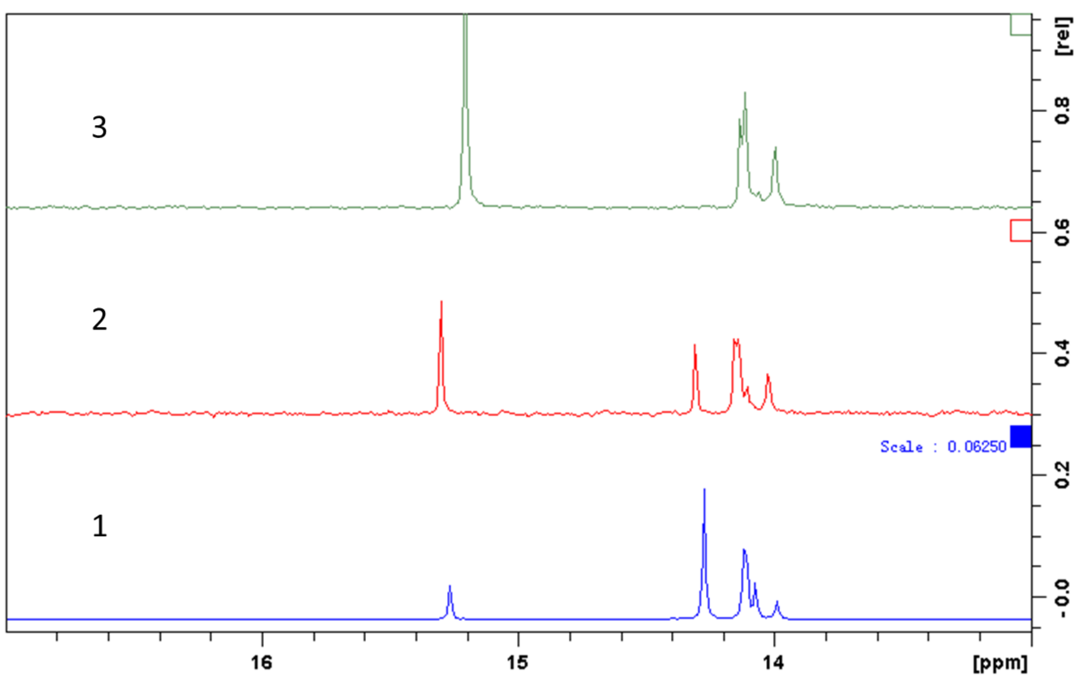

Figure 14. 13C-NMR spectra of the acrylated epoxidized ultra-pure flax seed oil at different degree (13-17 ppm). 1 acrylated epoxidation 50%; 2 acrylated epoxidation 80%; 3 acrylated epoxidation 100%.

10. Conclusions and Recommendations: Highlight significant conclusions based on the findings of this project, with emphasis on the project objectives specified above. Provide recommendations for the application and adoption of the project findings.

a) Develop methods for improving the physical and chemical properties of flaxseed and camelina oil

- ultrapure flax seed oil and camelina oil were produced.
- Sweet camelina oil has a longer dry time and is not suitable for use in paint products.
- Sweet flax seed oil is suitable for oil-based paint products and is investigated further in this report.

b) Determine the yellowing of flaxseed and camelina based oil paints produced with ultra-pure oils

- Linseed oil is the most popular medium in all the commercial products examined; Winsor (100%), Reeves, Art Spec, Mussini (70%), Pebeo (50%); Safflower oil is selected for Titanium White in all commercial paint products examined here. There is an existing market for oil-based paint using flax seed oil.
- The product made from sweet linseed oil is much more stable than commercial products and will not yellow over time due to absence of oxidized lipids and aromatic compounds.
- The paint made from sweet flax seed oil and pigment can form a continuous, even layer without cracks. The layer shows no open pores in most cases.
- The paint made from sweet flaxseed oil and Titanium White shows small open pores (3-5 μm). This can be suppressed with small amount of turpentine.
- The paint made from sweet flaxseed and naples yellow shows an unusual FORS spectrum that is unique compared to naples yellow with other oil paint formulations.
- The paint made from sweet flaxseed and titanium white has a higher reflectance spectrum than that of other titanium white paints made with linseed oil. Whiter whites will still be achieved with non-flax based paint, however the texture and dry time may be more desirable with sweet flax seed oil.
- A new product using sweet flax seed oil for oil-based paints has been created based on this research.

c) Develop processes for improving the chemical and physical properties of canola and rapeseed oil

- Completed the preparation and characterization of epoxidized corn oil, soybean oil, canola oil, camelina oil and ultra-pure flax seed oil acrylation.
- Prepared and characterized the epoxidized ultra-pure flax seed oil at different temperatures for acrylation.
- Completed the preparation and characterization of acrylated epoxidized corn oil, soybean oil, canola oil, camelina oil and ultra-pure flax seed oil for UV and thermal curing.
- Prepare and characterized the acrylated epoxidized ultra-pure flax seed oil at different temperatures for UV and thermal curing.
- A convenient method to quantify the degree of epoxidation based on ^{1}H-NMR was established using integration of double bonds and epoxy ring hydrogen signals.

11. Is there a need to conduct follow up research? Detail any further research, development and/or communication needs arising from this project.

Further research is planned for the compounds that are extracted from the seed oil during the ultra-purification process. The function and purpose of these compounds is poorly understood.

12. Patents/ IP generated/ commercialized products: List any products developed from this research.

- Martin and Paul paint see Martinpaul.ca. This is a water-white painter's medium that has no tendency to yellow.

13. List technology transfer activities: Include presentations to conferences, producer groups or articles published in science journals or other magazines.

- Marambe, H, S Purdy, TJ Tse, **MJT Reaney** (2020) *Flax oil and high linolenic oils.* In Bailey's Industrial Oil and Fat Products, John Wiley & Sons, Ltd., https://doi.org/10.1002/047167849X.bio010.pub2
- **Reaney, MJT**, YY Shim (2019) The upside and downside of flaxseed oil soluble cyclic peptides, *2019 AOCS China Section Conference,* Guangzhou, Guangdong, China. AOCS, November 10, 2019.
- **Reaney, MJT** (2019) Cyclic peptides and lignans of the flax core collection. *Gansu Academy of Agricultural Sciences,* China. June 21, 2019.
- **Reaney, MJT** (2019) Guangdong Saskatchewan Oilseed (GUSTO) Joint Laboratory: Annual review. *Jinan University,* Guangzhou, Guangdong, China. June 17, 2019.
- **Reaney, MJT**, YY Shim (2018) Guangdong Saskatchewan Oilseed (GUSTO) Joint Laboratory: Progress update. *Jinan University,* Guangzhou, Guangdong, China. November 13, 2018.
- **Reaney, MJT**, YY Shim (2018) A portfolio of benefits from flaxseed. *Nutribiotech Co., Ltd.,* Seoul, Korea. November 8, 2018
- **Reaney, MJT** (2018) A portfolio of benefits from flaxseed. *The Embassy of Canada to Korea*, Seoul, Korea. November 8, 2018
- **Reaney, MJT**, YY Shim (2018) Oil chemistry and technology. *Dept. of Food Science and Engineering, Jinan University,* Guangzhou, Guangdong, China. May 16, 2018.
- **Reaney, MJT** (2018) Flaxseed processing and selected products. *Dongguan Fujin Food Co., Ltd.,* Guangzhou, Guangdong, China. March 27, 2018
- **Reaney, MJT**, YY Shim (2017) Guangdong Saskatchewan Oilseed (GUSTO) Joint Laboratory: Research Progress in Saskatchewan. *Dept. of Food Science and Engineering, Jinan University,* Guangzhou, Guangdong, China. April 13, 2017.
- **Reaney, MJT**, YY Shim (2017) Flaxseed product pipeline. *Magtech, Dongguan Songshan Lake Hi-tech Industrial Development Zone,* Dongguan, Guangdong, China. April 14, 2017.
- **Reaney, MJT**, YY Shim (2017) Flaxseed product pipeline. *By-Health Co., Ltd.,* Guangzhou, Guangdong, China. April 6, 2017.

14. List any industry contributions or support received.

- Hues Art supplies has assisted greatly with this research. They have contributed pigments paint and paintings. Numerous paintings available through the web page of painter Nicki Ault (https://www.dailypaintworks.com/artists/nicki-ault-2150/artwork)

15. Acknowledgements. Include actions taken to acknowledge support by the Ministry of Agriculture and the Canada-Saskatchewan Growing Forward 2 bilateral agreement (for projects approved during 2013-2017) or Canadian Agriculture Partnership (For projects approved beyond 2017).

The authors would like to acknowledge Natural Sciences and Engineering Research Council 357 (NSERC) and Agriculture and Agri-Food Canada through the NSERC-AAFC research 358 partnerships program and Saskatchewan Mustard Development Commission, Saskcanola and 359 Milligan BioFuels Inc. for their financial support.

16. Appendices: Include any additional materials supporting the previous sections, e.g. detailed data tables, maps, graphs, specifications, literature cited.

A. NMR-spectra of commercial oil-paint products

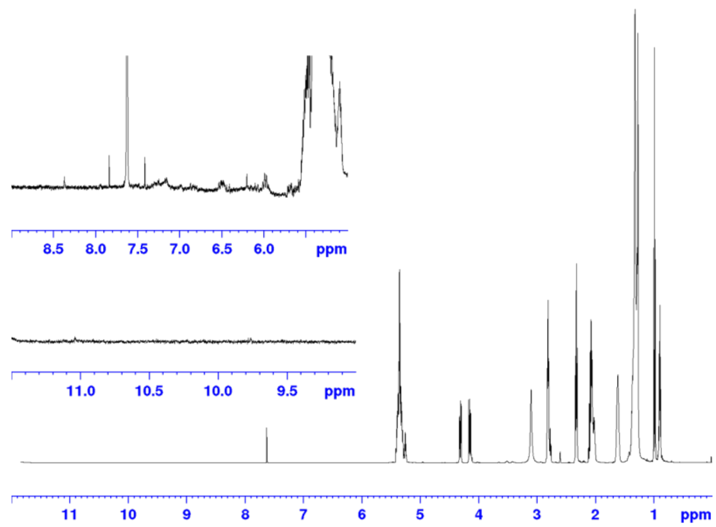

Figure 1. 1H NMR spectrum of WINSOR & NEWTON Permanent Alizarin Crimson, Pure Linseed Oil

The ^{1}H spectrum of Winsor Permanent Alizarin Crimson indicates the medium contains very high level of C18:3 (Figure 1). The alpha linolenic acid level matches the fatty acid profile of pure linseed oil. Trace amount of conjugated fatty acid signals are detected at 6-7 ppm. The signals at 7-8 ppm belongs to the peptide in the linseed oil. No oxidized lipids signal in the region of 9-11.5 ppm.

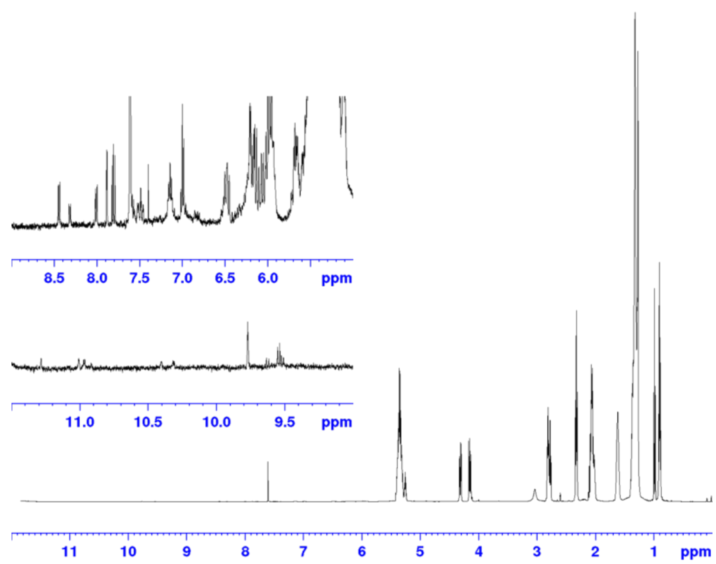

Figure 2. ^{1}H NMR spectrum of WINSOR & NEWTON, Chrome Yellow Hue, Linseed Oil

Winsor Chrome Yellow Hue is made with a mixture of linseed oil and safflower oil. The omega 3 fatty acid ^{1}H signals are less than 50%. The lipid conjugation process is accelerated by lead (II) chromate. Conjugated olefin signals detected at 6-7 ppm. The aromatic proton signals at 7-8.5 ppm belong to the dye protons. Trace amount of peroxide signals (11 ppm) and aldehyde signals (9.5 ppm) were observed due to lipids oxidation.

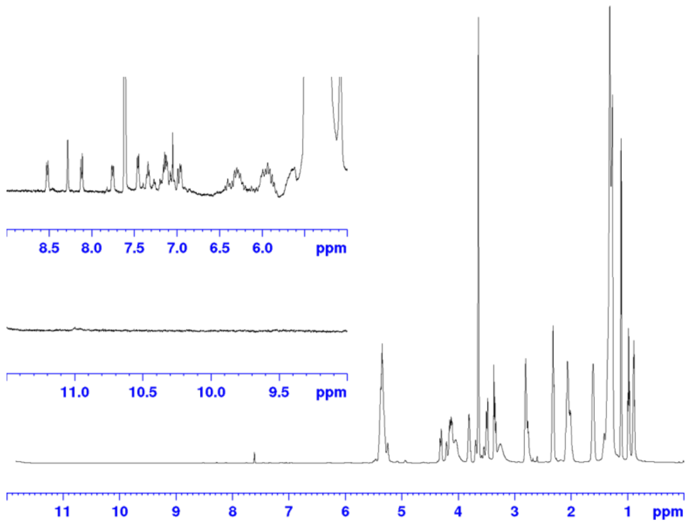

Figure 3. ^{1}H NMR spectrum of WINSOR & NEWTON, Lemon Yellow Modified Linseed Oil

Winsor Lemon Yellow is a mixture of nickel (II) titanate PY53 and linseed oil monoglyceride. Small amounts of conjugated lipids were detected. The aromatic proton signals are coming from the dye and peptides in the mixture. The product is stable to oxidation.

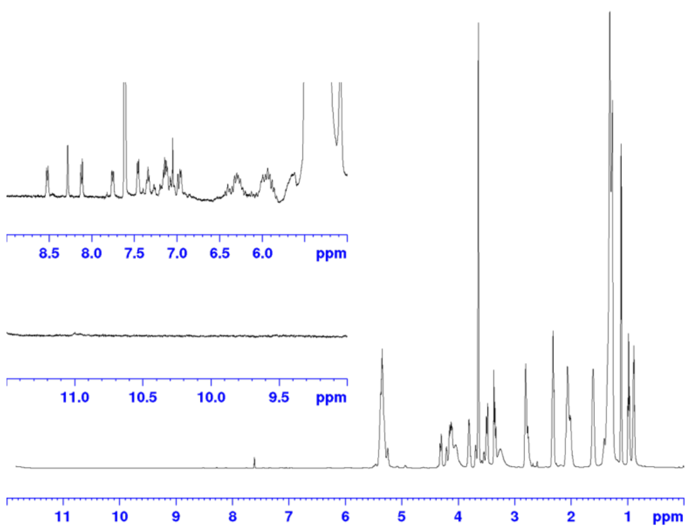

Figure 4. ^{1}H NMR spectrum of WINSOR & NEWTO Phthalo Blue, Pure Linseed Oil

Winsor Blue is made with phthalocyanine dye and pure linseed oil. Conjugated lipids signals were detected. The mixture contains trace amounts of peptides, fatty aldehyde, and fatty peroxide oxidized.

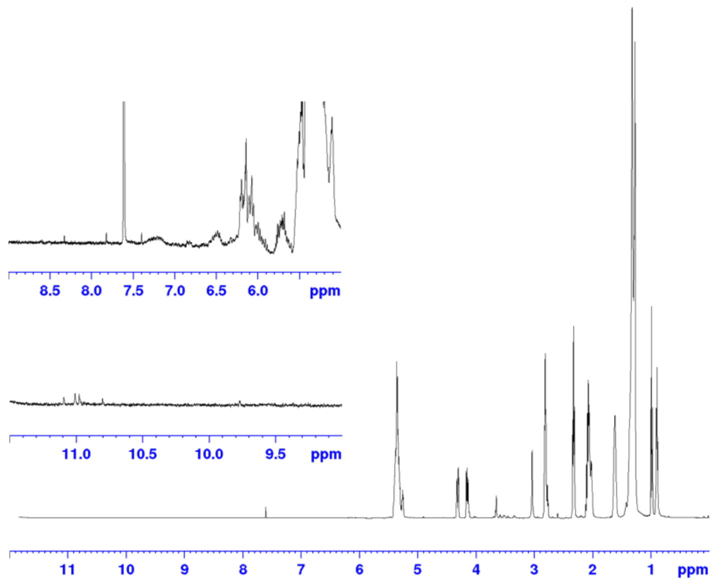

Figure 5. ^{1}H NMR spectrum of WINSOR & NEWTON Ivory Black, Linseed Oil

Winsor Ivory Black is made from 70% linseed oil. The product contains conjugated lipids and trace amount lipid peroxide.

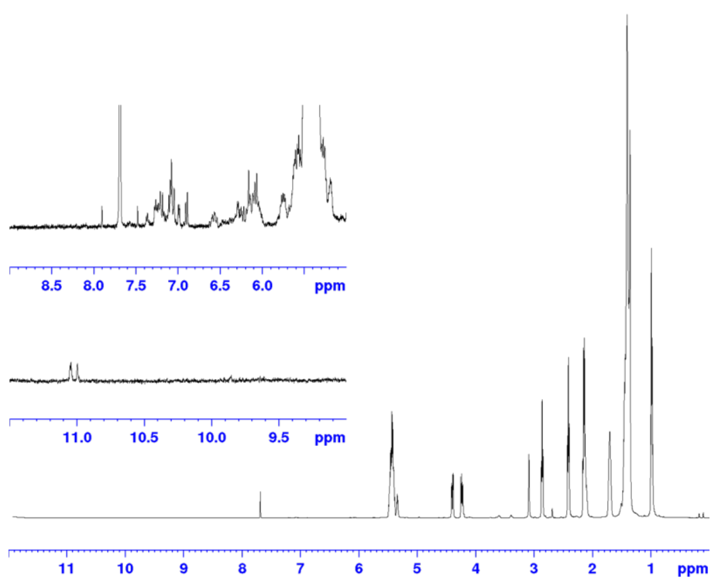

Figure 6. ^{1}H NMR spectrum of WINSOR & NEWTON Titanium White, Safflower Oil

Winsor Titanium White is made from pure safflower oil, as was expected. The mixture contains small amount conjugated lipids and lipid peroxide.

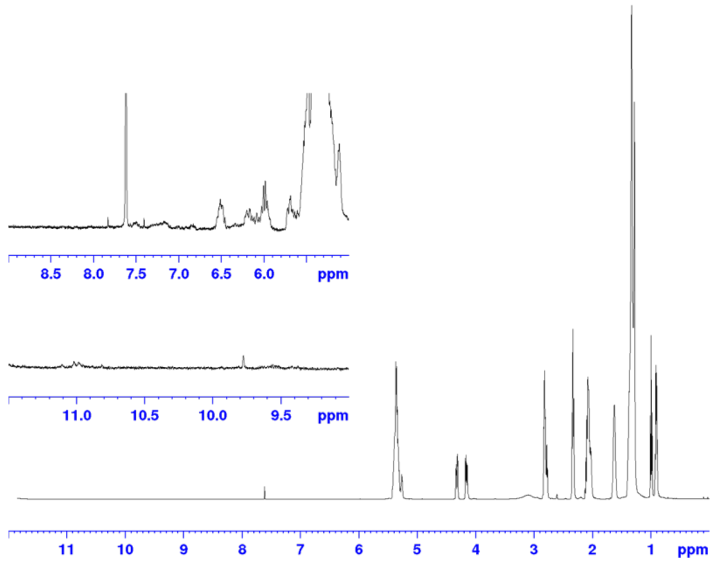

Figure 7. ^{1}H NMR spectrum of WINSOR & NEWTON Umbra, Gebrannt, Linseed/Safflower Oils

Winsor Umbra, Gebrannt is made from 70% linseed oil. The lipid oxidation is catalyzed by iron oxide and manganese oxide. Trace amount of peptide, fatty aldehydes, and fatty peroxides were detected.

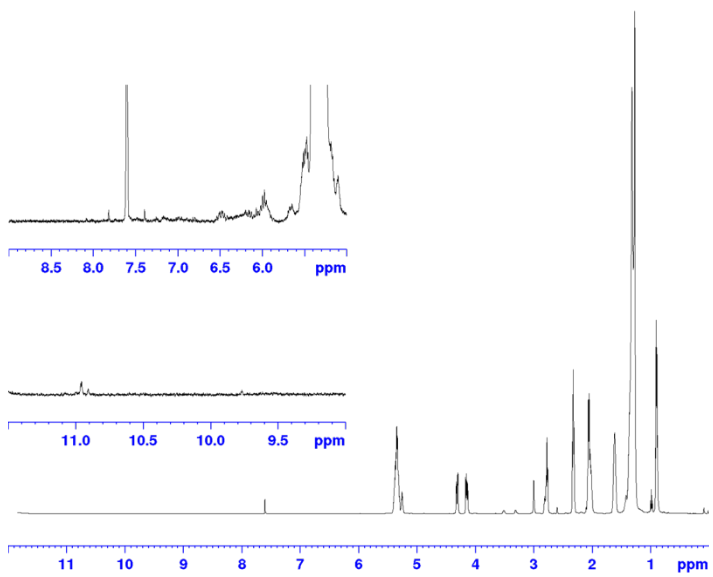

Figure 8. ^{1}H NMR spectrum of REEVES Titanium White

Reeves Titanium White is made from safflower oil as well. Conjugated lipids and trace amount of lipids peroxide presented in the mixture.

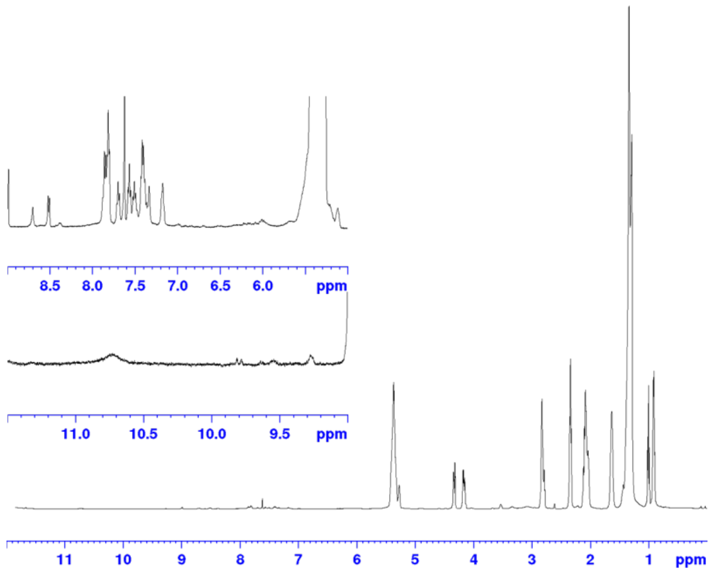

Figure 9. ^{1}H NMR spectrum of REEVES Brilliant Red

Reeves Brilliant Red is made from 70% safflower oil. The aromatic proton signals are mainly contributed by the pyrrole protons from the dye. Trace amount of fatty peroxide and fatty aldehyde were present in the mixture.

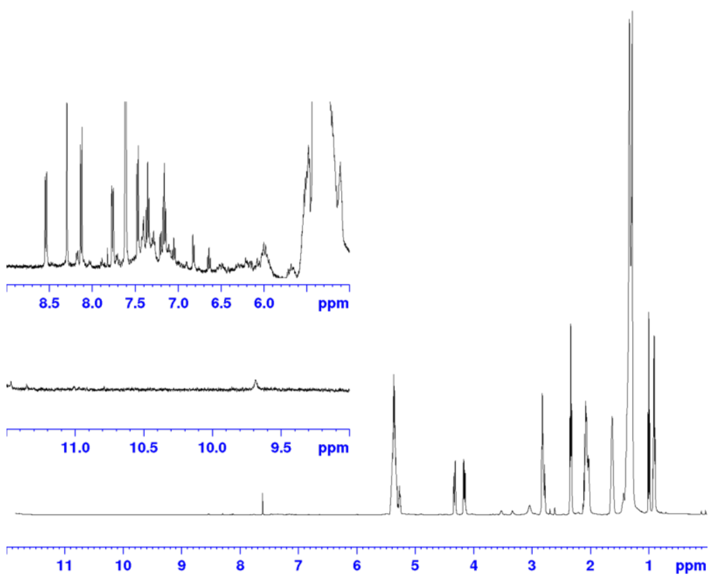

Figure 10. ^{1}H NMR spectrum of REEVES Lemon Yellow

Unlike Winsor and Newton Lemon Yellow, Reeves Lemon Yellow is made from 70% linseed oil triglyceride. The aromatic proton signals are contributed by the dye. The product contains trace amount of fatty aldehyde.

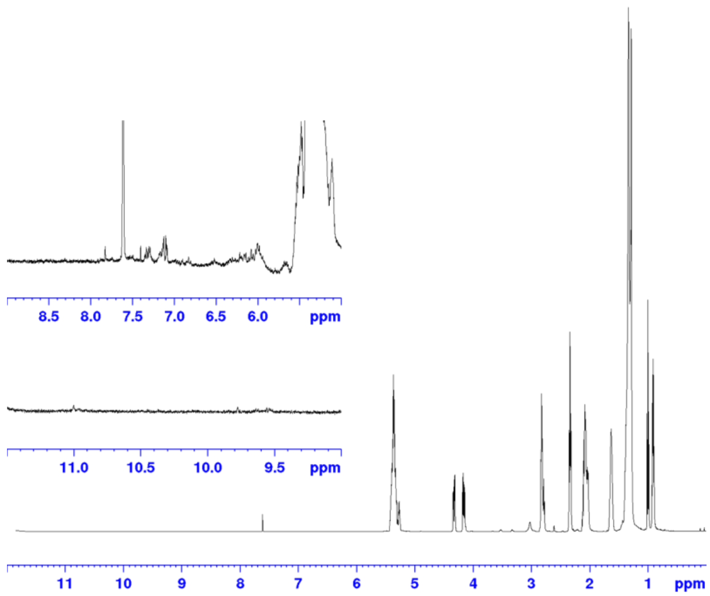

Figure 11. ^{1}H NMR spectrum of REEVES Phthalo Blue

The ^{1}H spectrum of Reeves Phthalo Blue is made from 70% linseed oil. The product contains trace amount of peptide and fatty peroxide.

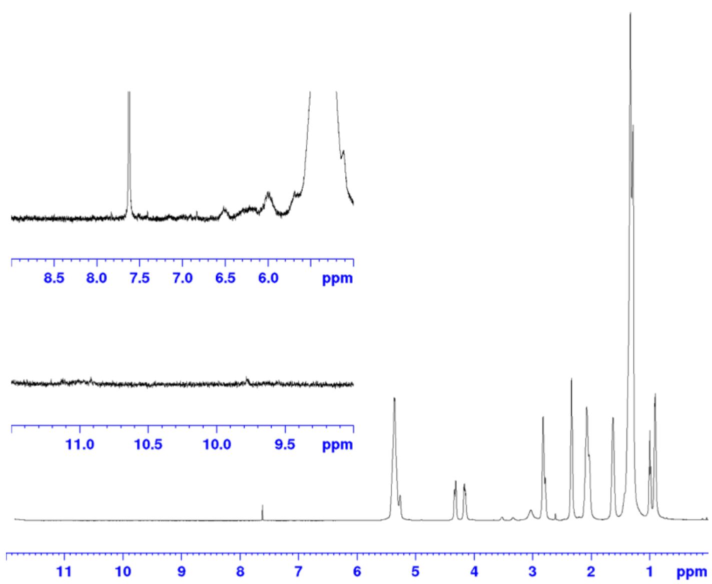

Figure 12. ^{1}H NMR spectrum of REEVES Ivory Black

Reeves Ivory Black is made from 70% linseed oil. The product contains trace amounts of lipid peroxide and lipid aldehyde.

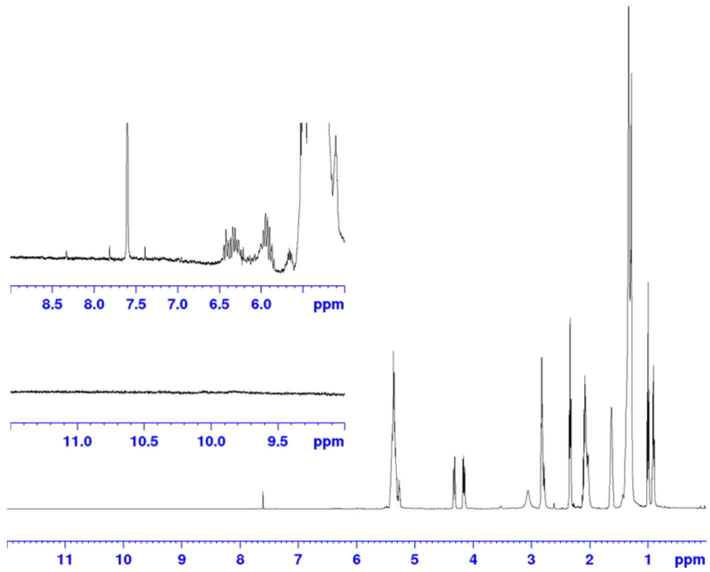

Figure 13. ¹H NMR spectrum of ART SPECTRUM Yellow Ochre, Pure Alkali Refined Linseed Oil

Art Spec Yellow Ochre is made from 70% refined linseed oil. No peptide signals detected in the product. The pigment is stable to oxidation.

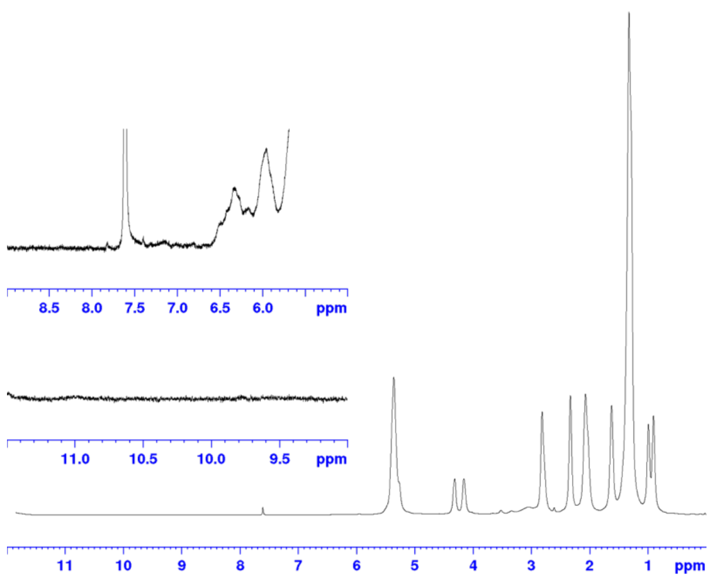

Figure 14. ¹H NMR spectrum of ART SPECTRUM Burnt Umber, Pure Alkali Refined Linseed Oil

Art Spectrum Burnt Umber is made from 70% refined linseed oil as well. No detectable oxidized lipids in this peptide free product.

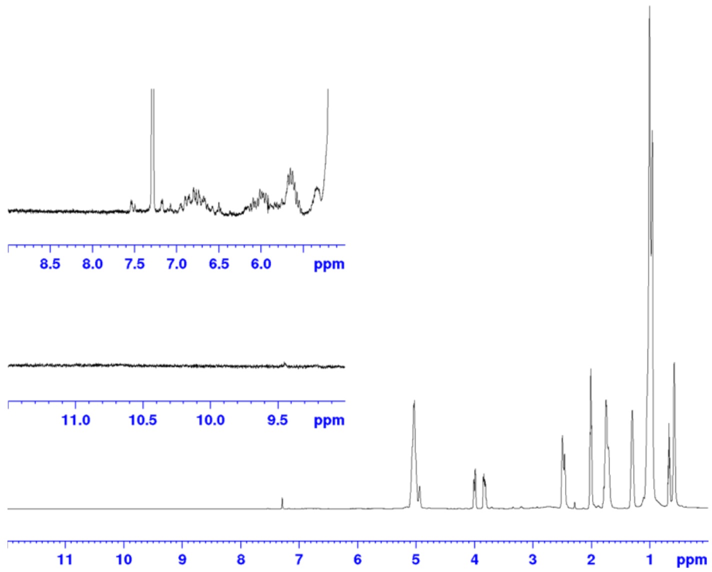

Figure 15. ^{1}H NMR spectrum of PEBEO Yellow Ochre

Pebeo Yellow Ochre is made from 50% linseed oil. The product contains conjugated lipids. No oxidized lipids signals were detected.

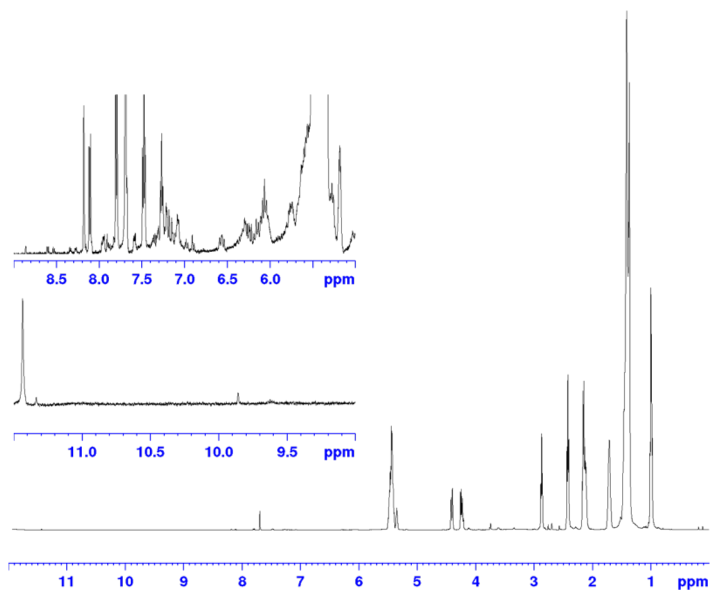

Figure 16. ^{1}H NMR spectrum of PEBEO Primary Cadmium Yellow Imit

Pebeo Primary Cadmium Yellow Imit is made from pure safflower oil. The aromatic proton signals are coming from dye protons. The product contains lipid peroxide and lipid aldehyde.

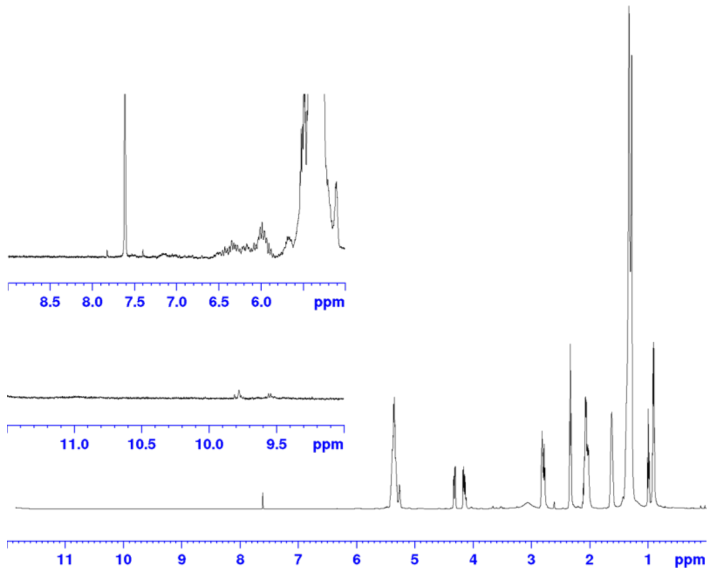

Figure 17. [1]H NMR spectrum of PEBEO Burnt Umber

Pebeo Burnt Umber is made from 50% linseed oil. The product is peptide free. Lipids peroxide signals and lipids aldehyde signals were detected.

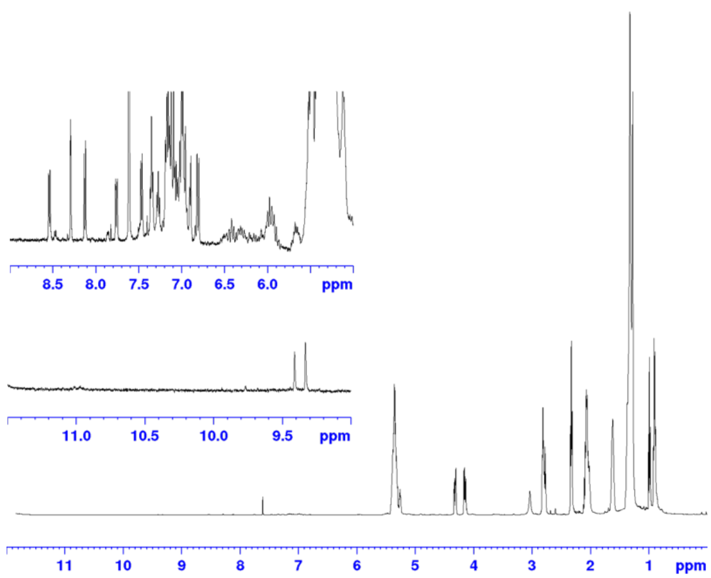

Figure 18. [1]H NMR spectrum of MUSSINI SCHMINCKE Lemon Yellow

Mussini Lemon Yellow is made from 70% linseed oil. This peptide-free product contains trace amounts of fatty peroxides and fatty aldehydes.

B. Coating quality of sweet linseed oil paint

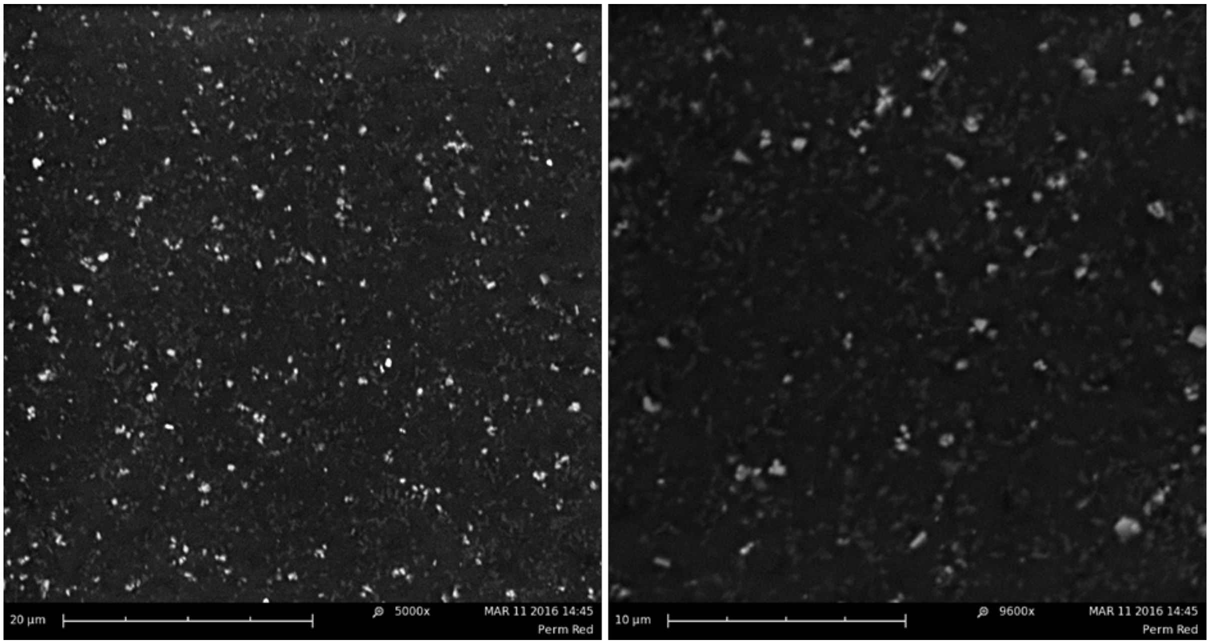

Figure 15. SEM-images of the surface coated with Permanent Red made from sweet flax seed oil

The paint made from sweet flax seed oil and Permanent Red pigment (Figure 23) has a continuous, evenness appearance. No open pores, cracks or fractures are detected.

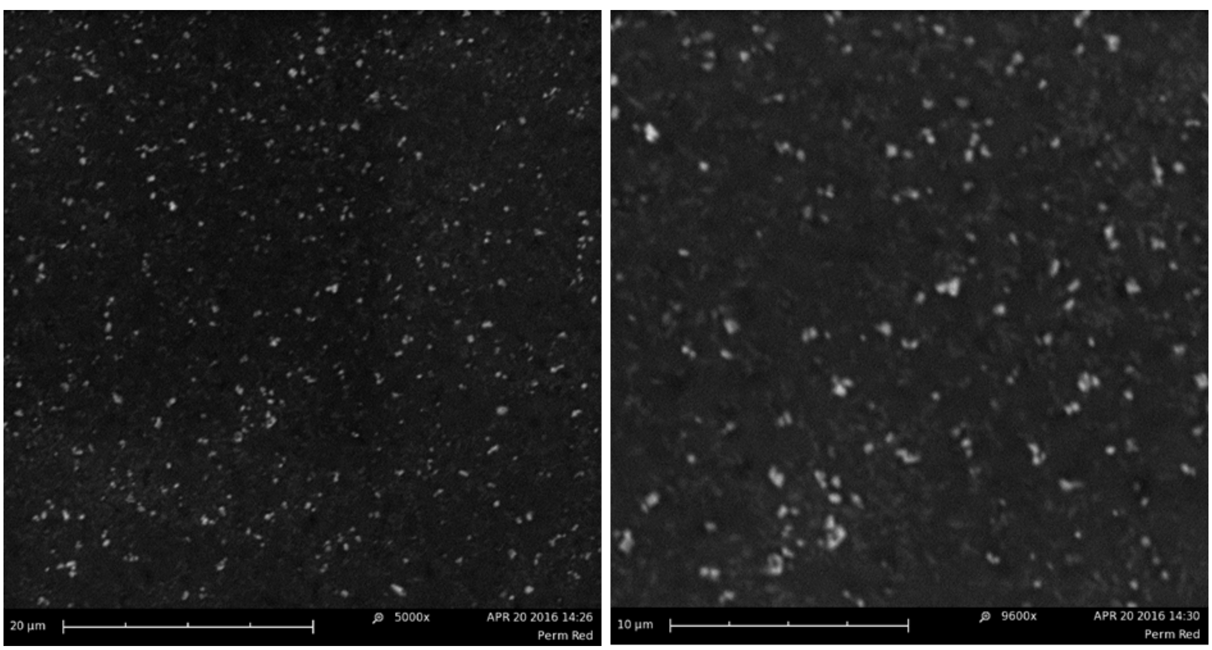

Figure 16. SEM-images of the surface coated with Permanent Red made from sweet flax seed oil after 40 days of storage

The paint made from sweet flax seed oil and Permanent Red pigment after 40 days of storage (Figure 27) has a continuous, evenness appearance. No open pores, cracks or fractures are detected.

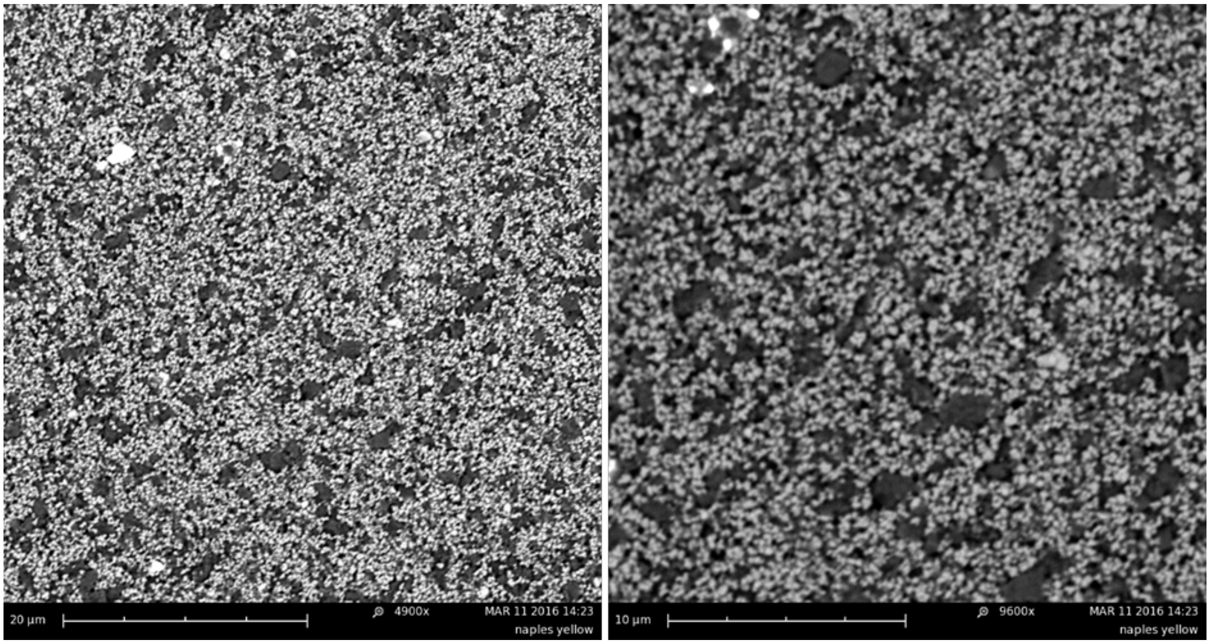

Figure 17. SEM-images of the surface coated with Naples Yellow made from sweet flax seed oil

The paint made from sweet flax seed oil and Naples Yellow pigment (Figure 24) has a continuous, evenness appearance. No open pores, cracks or fractures are detected.

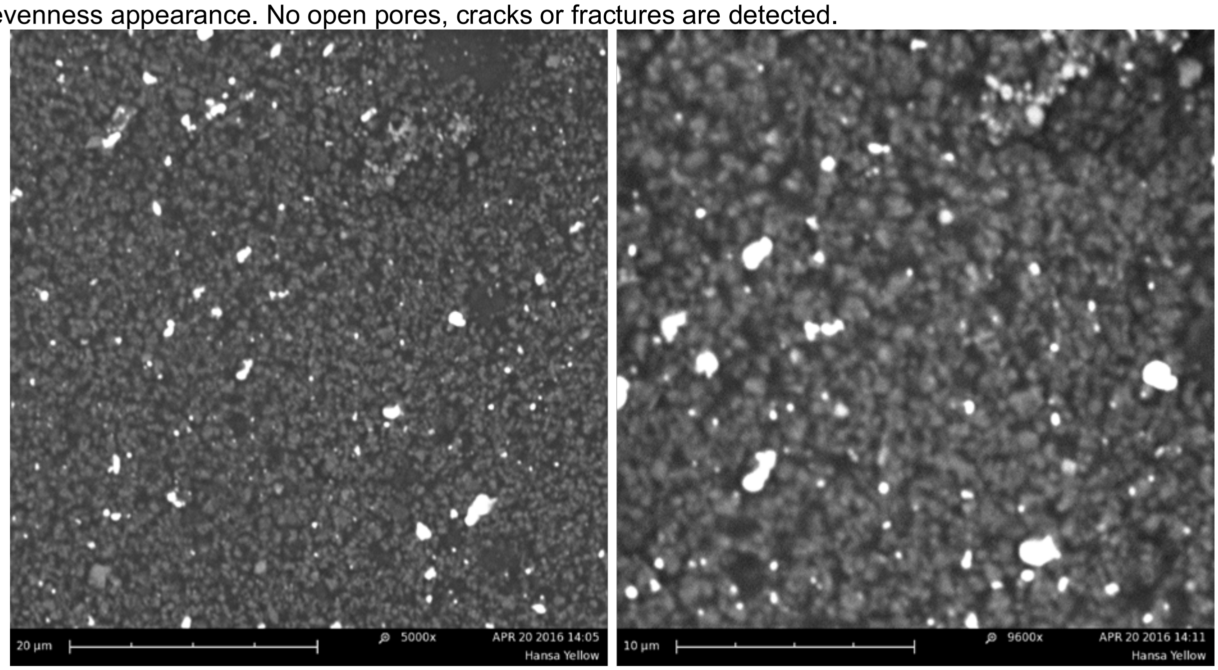

Figure 18. SEM-images of the surface coated with Hansa Yellow made from sweet flax seed oil

The paint made from sweet flax seed oil and Hansa Yellow pigment (Figure 25) has a continuous, evenness appearance. No open pores, cracks or fractures are detected.

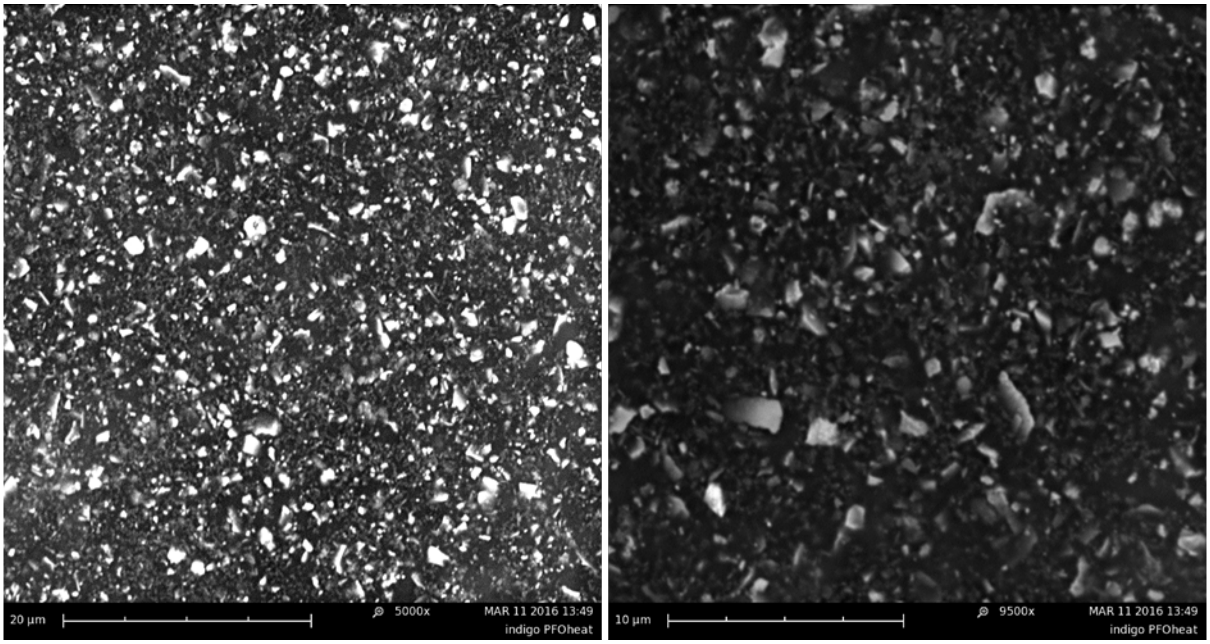

Figure 19. SEM-images of the surface coated with Indigo made from sweet flax seed oil

The paint made from sweet flax seed oil and Indigo pigment (Figure 19) has a continuous, even appearance. No open pores or cracks observed.

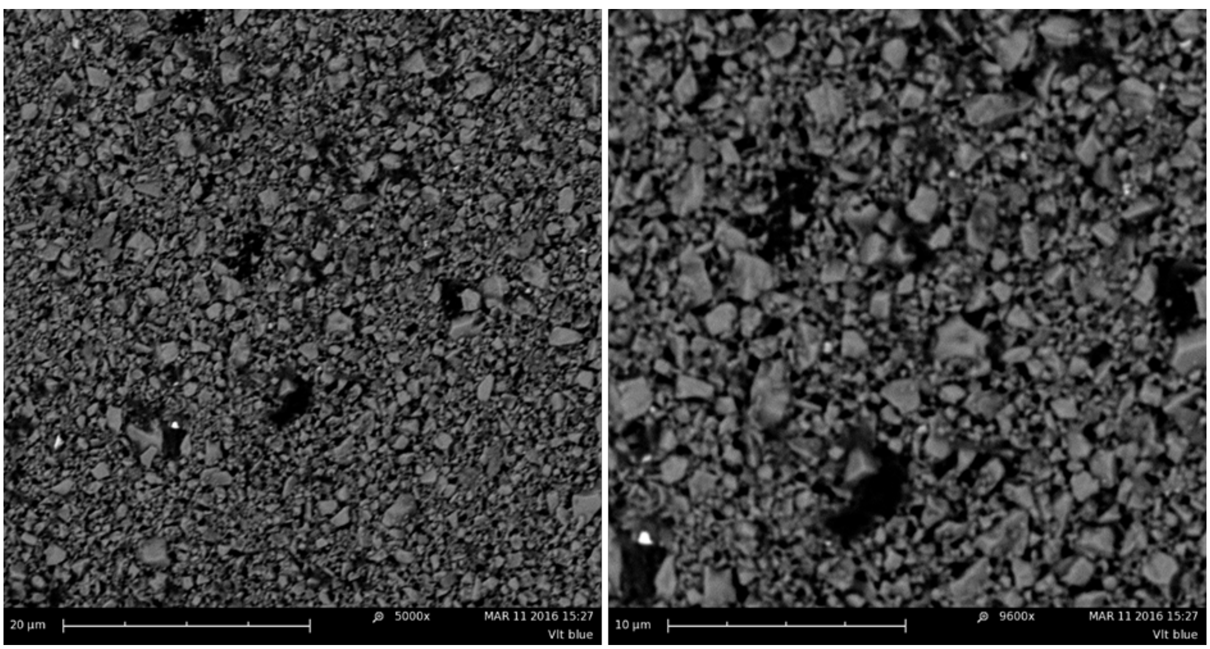

Figure 20. SEM-images of the surface coated with Violet Blue made from sweet flax seed oil

The paint made from sweet flax seed oil and Violet Blue pigment (Figure 21) has a continuous, evenness appearance. No cracks or fractures are detected. Small open pores (2-3 µm) can be observed.

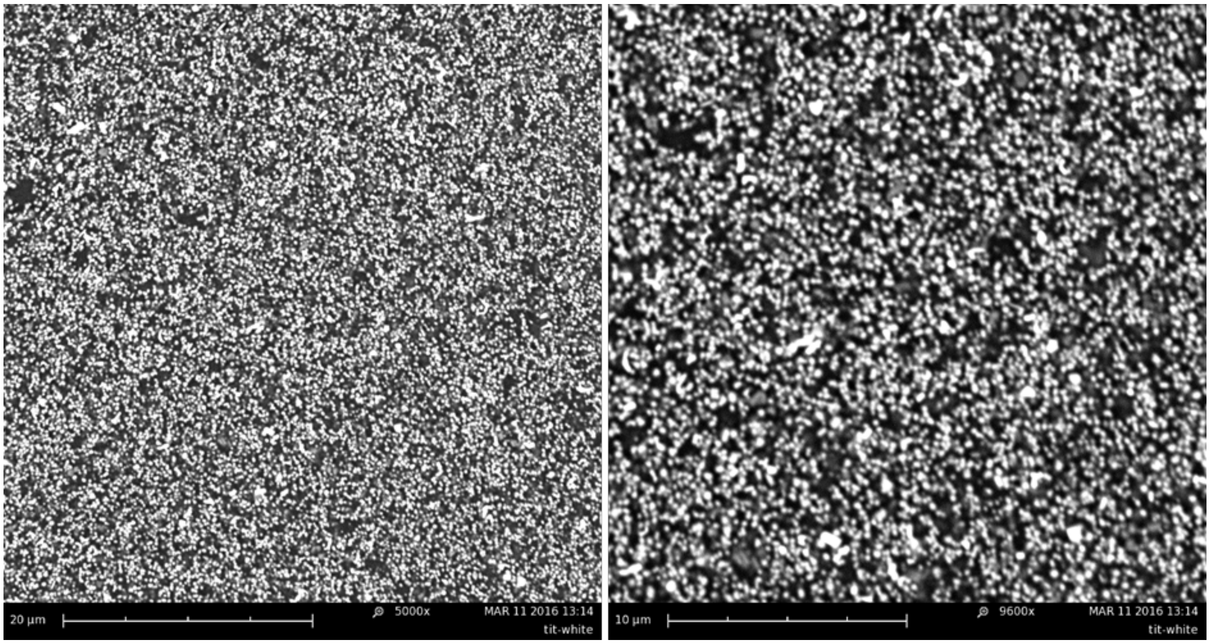

Figure 21. SEM-images of the surface coated with Titanium White made from sweet flax seed oil

The paint made from sweet flax seed oil and Titanium White pigment (Figure 22) has a continuous, evenness appearance. No open pores, cracks or fractures are detected.

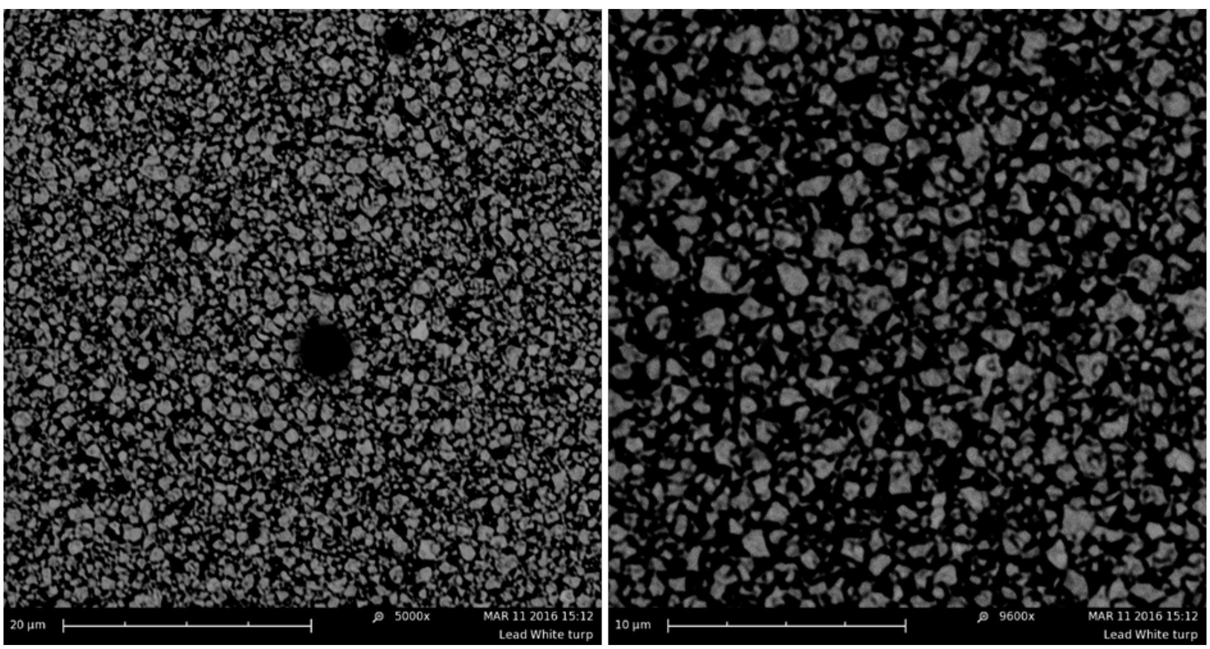

Figure 22. SEM-images of the surface coated with Lead White made from sweet flax seed oil

The paint made from sweet flax seed oil and Lead White pigment (Figure 20) has a continuous, evenness appearance. No cracks or fractures are detected. Small open pores (3-5 µm) can be observed.

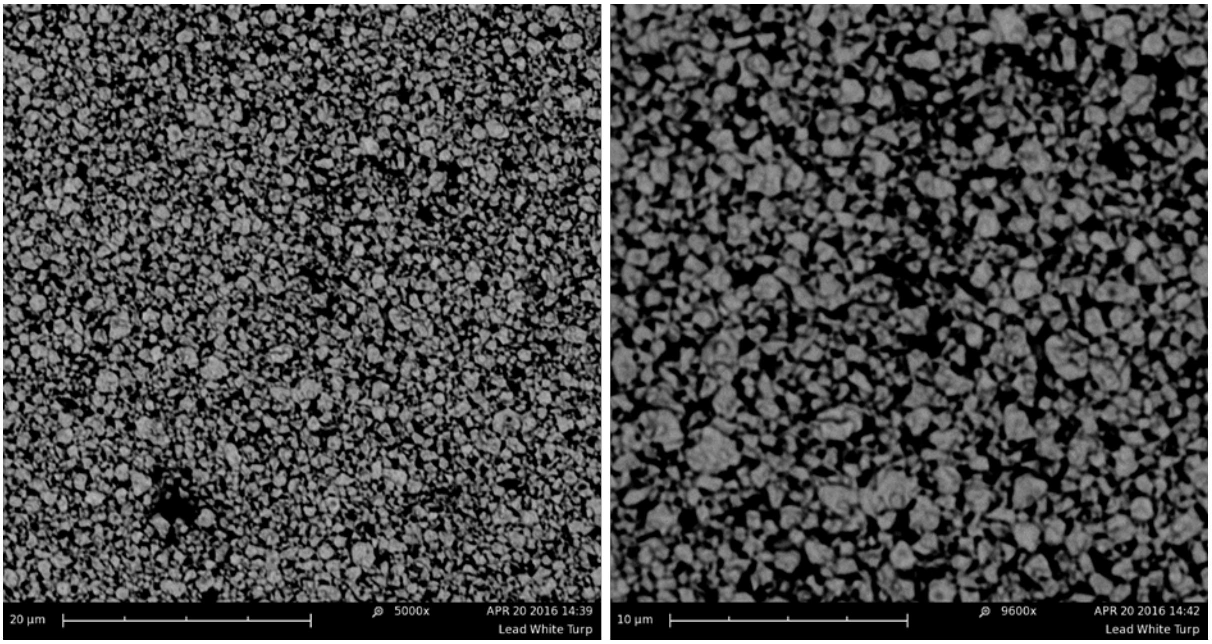

Figure 23. SEM-images of the surface coated with Lead White made from sweet flax seed oil and turpentine

The paint made from sweet flax seed oil, turpentine and Lead White pigment (Figure 26) has a continuous, evenness appearance. No open pores, cracks or fractures are detected. Pore-formed vesicles were suppressed with the addition of turpentine (compare to Figure 20).