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Analysis of Reaction Products (e.g. Chlorohydrins) of ESBO in Poly(vinyl chloride) Type Polymers and Coatings

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Introduction

Epoxidized vegetable oils, such as soybean or linseed oil (ESBO, ELO), are widely used in poly(vinyl chloride) (PVC) and poly(vinylidene)chloride type materials, such as films and coatings. They combine the function of a plasticizer with that of a scavenger to remove hydrochloric acid (HCl) generated during manufacture of the article or coating, as the latter involves heating to temperatures of 160–220°C (HCl must be removed since it catalyzes further degradation). At least at first, reaction of the epoxy group with HCl forms a chlorohydrin function.

Toxicity of ESBO was assessed in 1988 (1). The Scientific Committee for Food (SCF) of the EU proposed a tolerable daily intake (TDI) of 1 mg/kg body weight, resulting in a maximum tolerated migration (for adults of 60 kg) corresponding to the overall migration. On the basis of this, the use of ESBO and ELO as additives was authorized without a specific migration limit (SML) in foods. For plastics, ESBO and ELO were positive listed in the EU Directive 90/128 EEC, for coatings in the Resolution AP 96/5 of the Council of Europe.

Previous work

Castle *et al.* (2) determined the migration of ESBO in a variety of foods after conversion of the triglycerides to methyl esters using sodium methoxide and of the epoxy groups to 1,3 dioxolanes using cyclopentanone. Foods wrapped in PVC films contained around 10 mg/kg of ESBO (maximum 32 mg/kg). The highest migration (85 mg/kg) was found after microwave-heating of peanut biscuits (3). Applying essentially the same method, Hammarling *et al.* (4) determined ESBO in baby foods

packed in glass jars closed with lids containing plasticized PVC gaskets and found concentrations up to 50 mg ESBO/kg (12 mg/kg as an average). For 5 % of the samples, the TDI of 1 mg/kg body weight could have been exceeded for babies.

Gilbert et al. (5–7) studied the transformation products from the reaction of HCl with model compounds, i.e. methyl epoxyoctadecanoate and glyceryl triepoxyoctadecanoate, forming the flophemesyl derivatives of the chlorohydrins. The task showed to be difficult since after heating more than half of the removed epoxy fatty acids did not show up as the expected chlorohydrins. As never more than 10 % of the ESBO was turned into dimers or trimers (experiment with the triglycerides) and bonding to the PVC was not important (max. 2 %), much of the transformation material was left unexplained. Migration (10 d, 40°C) was below 0.1 mg/kg for aqueous simulants and below 1 mg/kg for edible oil.

Intention of the present work

The transformation products of epoxidized fats and oils were of interest again because of the wide use of ESBO and ELO and their rather high migration (easily exceeding 10 mg/kg in some foods). If only 10 % of the ESBO or ELO is transformed, in some foods the sum of the reaction products is likely to exceed 1 mg/kg.

Furthermore, ESBO and ELO seem to be used as substitutes of bisphenol A diglycidyl ether (BADGE) and novolac glycidyl ether (NOGE) in organosol can coatings, for a third time bringing us into the situation that a material is used in organosols the safety of which has not been satisfactorily assessed before the consumers were exposed to it (8).

Recently toxicologists derived a threshold concentration below which chemicals are unlikely to have a significant adverse effect on human health, even if they are highly toxic substances. It tells us that toxicological testing is usually unnecessary when the exposure of the consumers with a migrating substance is below that level. The US-FDA defined the "Threshold of Regulation" (ToR) of 0.5 µg in the diet (9). A compound migrating into food at concentrations below this level is considered a negligible risk, and little information on its toxicity profile is requested before its use is authorized. The International Life Science Institute (ILSI) introduced the "Threshold of Toxicological Concern" (10), defining 1.5 µg in the daily diet of a person as the threshold above which toxicity must be kept under control to grant safety (which corresponds to the 0.5 µg/kg in the diet if 3 kg of food are consumed per day). If, as an explanatory example, foods in contact with ESBO and ELO made up 5 % of the diet (no data is available), the threshold concentration (ToR) corresponded to 10 µg/kg. If migration of ESBO into a food reaches 10 mg/kg, the 10 µg/kg corresponds to a component making up 0.1 % in the migrated ESBO or ELO. It means that food safety can be considered granted only when all the transformation products exceeding 0.1 % in the migrated ESBO or ELO are toxicologically evaluated. So far, however, just the unreacted ESBO and ELO have been tested.

Insufficient attention paid to the reaction products of components migrating from packing materials into foods (as well as of direct food additives) is an inherent weakness of positive lists, because these lists authorize the use of a substance mostly without restricting the application and without asking about transformation products. Hence the ESBO transformation products should also be studied as an example to assess whether or not present legislation is adequate.

Analytical approach

Most experiments described below were performed with ESBO. The analysis of the transformation products as triglycerides is difficult because there are exceedingly many combinations of fatty acids on the glycerol moiety. It becomes more easy after formation of fatty acid methyl esters (FAME). Transesterification is delicate, however, because of the presence of reactive epoxy and chlorohydrin functions as well as possible other structures of which the identity has not been elucidated. Epoxy groups are sensitive to acids (including boron trifluoride), while chlorohydrins are readily turned into epoxides by alkali.

Transmethylation with sodium methoxide turned out to avoid artifact formation provided the conditions minimize the stress. Such conditions have been determined in the context of a method for the determination of the fat content or the fatty acid composition in foodstuffs without isolation of the fat from the aqueous matrix: 1 min at 25°C provided complete transesterification without noticeable saponification (11, 12). Further, the hydroxyl groups must be derivatized in order to reduce the chemical reactivity of chlorohydrin functions at the temperatures necessary for GC analysis (about 240°C), particularly their conversion to epoxides. Acetylation was preferred to silylation because the latter easily causes the epoxy groups to react.

Materials and methods

Virtually fully epoxidized soybean oil, Edenol D82, was a gift from Vernicolor/Valspar, Grüningen, Switzerland, and had the following composition: 10% palmitic acid, 4% stearic acid, 21% epoxidized oleic acid, 56% diepoxidized linoleic acid, and 8% triepoxidized linolenic acid. ELO was prepared from commercially available linseed oil.

Preparation of reference materials

Fatty acid methyl esters of ESBO (ESBO-FAMES) were produced by treating 1 g of ESBO with 5 ml of 5% sodium methoxide in methanol during 1 min. Then 5 ml pentane and 10 ml of 15% disodium hydrogencitrate were added and the ESBO-FAME extracted into the pentane.

Epoxidization of FAME standards and vegetable oils was performed as described by *Gilbert and Startin* (5). For instance, 280 mg of ELO-FAME was dissolved in 5 ml of chloroform containing 10% 3-chloroperbenzoic acid and allowed to stand over night. The largely solidified product was suspended in 5 ml of water

and 5 ml of chloroform, to which 5 ml of 5 % sodium bisulfite and 5 ml of 5 % sodium bicarbonate were added. The chloroform solution was evaporated to dryness. GC showed no residual unreacted unsaturated fatty acids.

ESBO-FAME fully reacted with hydrogenchloride (HCl) (ESBO-FAME.per-HCl) was obtained by addition of 1 ml tetrahydrofurane (THF) containing 3 % concentrated hydrochloric acid to 10 mg ESBO-FAME. After 5 min at ambient temperature, water and methyl tert. butyl ether (MTBE) were added. The MTBE phase was washed with water. Partial reaction with HCl (ESBO-FAME.E.HCl) was achieved by addition of the same amount of hydrochloric acid to 40 mg ESBO-FAME.

Derivatization

For transesterification, 1–10 mg of a reference material or extract from a packing was dissolved in 0.5 ml dioxane. 0.5 ml of 2.5 % sodium methoxide in methanol, kept at ambient temperature, was added. After 40 s, the reaction was stopped by admixture of 3 ml of a 5 % disodium hydrogencitrate solution. The ESBO-FAMEs were extracted into 0.5 ml MTBE.

For acetylation, some solution to be analyzed was evaporated to dryness in a stream of nitrogen. Then 50 μ l each of pyridine and acetanhydride were added and kept at 50°C for 30 min. The reagent was removed in a stream of nitrogen and the residue diluted in 200 μ l MTBE.

GC separation

GC analysis was performed on a Fisons MEGA 5160 instrument with on-column injector and flame ionization detector FID. The 20 m \times 0.25 mm i.d. column was statically coated with a 0.12 μ m film of PS-255, a polydimethylsiloxane from Fluka. 60 kPa inlet pressure (hydrogen); 1 μ l on-column injection at 65°C oven temperature (1 min); temperature program 15°/min to 170°C, then 8°/min to 270°C.

GC-MS involved a MD800 instrument with a GC 8000 with on-column injector (ThermoQuest, Milan, Italy).

Size exclusion chromatography

Size exclusion chromatography (SEC) was performed on a 30 cm \times 7.8 mm i.d. column packed with Phenogel 5 μ m, 500 Å (Phenomenex, St. Torrance CA, USA), using THF at 400 μ l/min as mobile phase and a refractive index (RI) detector (Erma ERC-7515A).

Experiments with standards

Gas chromatography

For the gaschromatographic analysis, the following columns were tested (10–20 m × 0.25 mm i.d., ca. 0.15 µm films):

- SP 2560, Rtx 2330, OV 225-OH: no peaks for the acetylated chlorohydrins, presumably because of degradation or reaction with the stationary phase, promoted by high elution temperatures.
- Carbowax: no separation between the chlorohydrins of methyl epoxyoleate (18.OHCl, table 1) and a methyl diepoxylinoleate (18.2E); no peaks for the chlorohydrins of 18.2E, probably due to the high elution temperatures causing these components to react.
- OV 61-OH (33 % phenyl silicone): no separation between 18.OHCl and 18.2E; 18.2E reacted with one HCl (18.E.OHCl) and methyl triepoxylinolenate (18.3E) coeluted.
- PS-255: good separation between 18.OHCl and 18.2E, as well as between 18.2E.OHCl and 18.3E; stationary phase chosen.

To check whether chlorohydrins or other transformation products are partially degraded during GC analysis, quantitative results obtained for ESBO-FAME.E.HCl on a 20 m and a 3 m column (both 0.25 mm i.d., 0.13 µm) were compared. As the short column resulted in reduced thermal stress, larger peaks should have been observed for the labile components. No significant differences were noted. Fast reactions, already being complete on the short column, would not have been detectable in this way.

Table 1

Abbreviation of compounds

Abbreviation	Compound(s)
16:0	methyl palmitate
18:0	methyl stearate
18:1	methyl oleate
18:2	methyl linoleate
18:3	methyl linolenate
18.E	epoxy 18:1
18.2E	di epoxy 18:2
18.3E	tri epoxy 18:3
18.OHCl	chlorohydrins of 18.E
18.E.OHCl	monochlorohydrins of 18.2E
18.2OHCl	dichlorohydrins of 18.2E
18.2OH	diol, hydrolysis product of 18:E
18.E.2OH	monohydrolysis products of 18.2E
18.2E-deriv.	unidentified products from 18.2E + HCl
ESBO-FAME	transmethylated ESBO
ESBO-FAME.E.HCl	ESBO-FAME partially reacted with HCl
ESBO-FAME.perHCl	ESBO-FAME fully reacted with HCl

An additional test was performed in the same way as previously described for triglycerides (13). Degradation products formed in the column may not be visible as signals in the chromatogram because the reaction occurs over an extended period of time and over a long section of the column, i.e. the products do not form sharp initial bands. To focus such products as a sharp band, the column outlet was dismounted from the detector and taken outside the GC oven through the closed oven door, thus cold trapping the eluted components. ESBO-FAME.E.HCl was injected and chromatographed normally. Then the column was reversed, i.e. the former outlet was connected to the on-column injector and the former inlet to the FID, and the same temperature program applied without an injection. The resulting chromatogram showed the same peaks as in a directly obtained chromatogram, without a significant additional peak in the range where C18 FAMES are expected.

Both these tests gave no hint that the disappearance of material after heating of epoxidized oils in a PVC matrix, as noted by *Shepherd and Gilbert* (7) and confirmed during this work, resulted from GC, i.e. that components had been formed which degraded during GC analysis.

Gas chromatograms of ESBO and ELO are shown in figure 1. On the polydimethylsiloxane column, the introduction of an epoxy group strongly increases the retention time (equivalent of almost two carbon atoms). Epoxidized

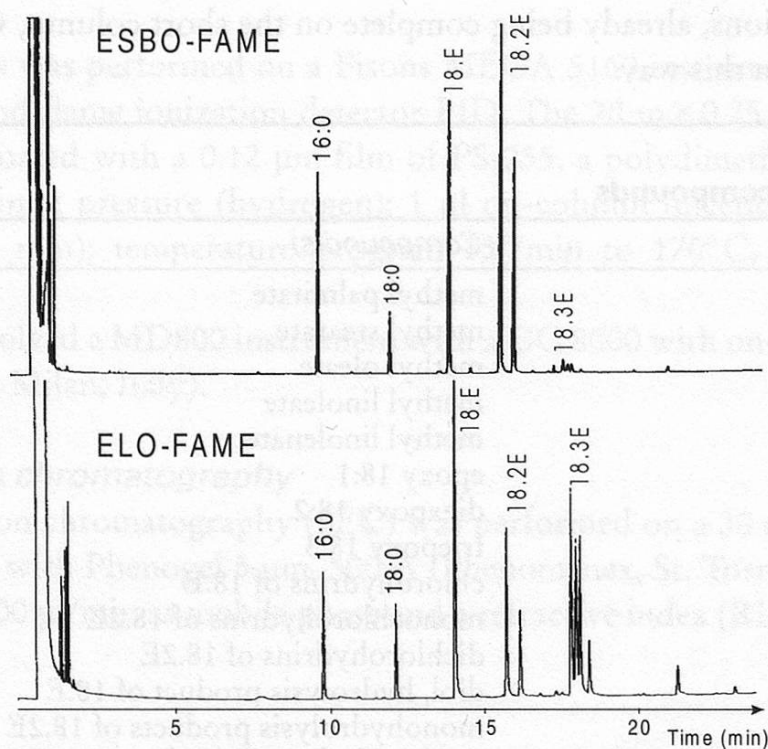


Figure 1 Gas chromatograms of transmethyated ESBO and ELO on a 100% methyl silicone column. Peak identity, see table 1

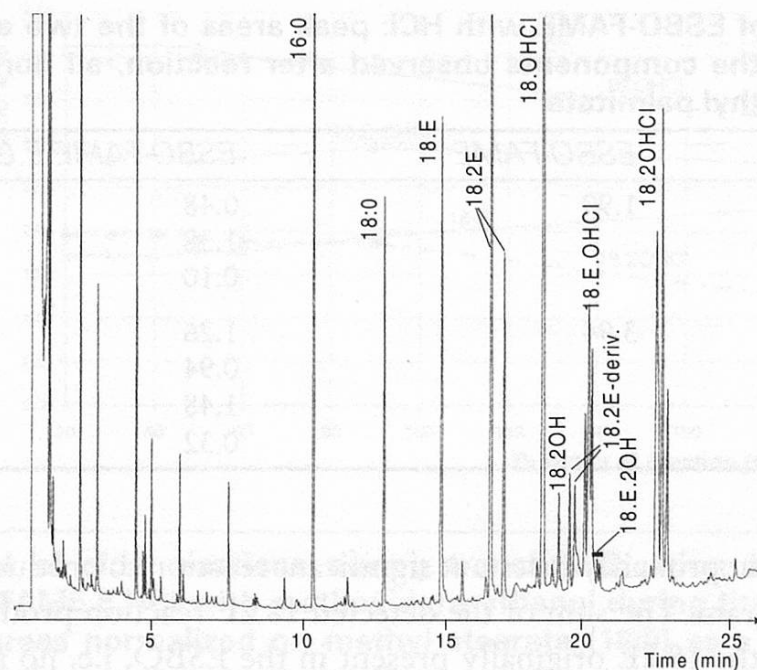


Figure 2 **Gas chromatogram of acetylated ESBO-FAME.E.HCl. Peak identities, see table 1**

linoleic acid (18.2E) forms two peaks, epoxidized linolenic acid (18.3E) four peaks, i.e. the stereoisomers are partly separated.

A GC-FID chromatogram of ESBO-FAME.E.HCl is shown in figure 2. There is a strong increase of the retention time upon conversion of an epoxy to a chlorohydrin function (see, e.g., 18.E *versus* 18.OHCl). 18.2E was converted to the products with one epoxy group reacted to the chlorohydrin (18.E.OHCl, many isomers) as well as the double chlorohydrin 18.2OHCl.

The formation of a small amount of hydrolysis product of 18.E, methyl-9,10-dihydroxyoctadecanoate (18.2OH) and of partially hydrolyzed 18.2E (18.E.2OH) is due to the small amount of water added to the reaction mixture with the concentrated hydrochloric acid. The two main peaks eluted between 18.2OH and 18.E.OHCl gave mass spectra suggesting derivatives formed from 18.E.OHCl, possibly by reaction of the hydroxy group with the epoxy function and ring formation. The structures of these and additional components eluted in the same region for ESBO extracted from organosol can coatings and PVC cling films await being elucidated.

The conversion of the epoxy fatty acids was monitored by normalizing peak areas on the methyl palmitate present in the ESBO-FAME. As shown in table 2, the peak area of 18.OHCl corresponded to 73 % of that of the 18.E originally present in the ESBO. The sum of the unreacted 18.E, 18.OHCl, and 18.2OH corresponded to 103 % of the original 18.E, which might reflect the increased FID response owing to

Table 2

Partial reaction of ESBO-FAME with HCl: peak areas of the two epoxides before reaction and of the components observed after reaction, all normalized on the non-reacting methyl palmitate

<i>Fatty acid</i>	<i>ESBO-FAME</i>	<i>ESBO-FAME.E.OHCl</i>
18.E	1.90	0.48
18.OHCl		1.38
18.2OH		0.10
18.2E	3.94	1.26
18.E.OHCl		0.94
18.2OHCl		1.48
18.2E-deriv.		0.32

the acetylation, but primarily rules out significant reaction to products not observed in the chromatogram. The sum of the detected 18.2E reaction products corresponded to 101 % of the 18.2E originally present in the ESBO, i.e. no material "disappeared" from the chromatogram.

The ratio of 18.2E, 18.E.OHCl, and 18.2OHCl is unexpected: the partially reacted 18.E.OHCl should have clearly predominated 18.2E and 18.2OHCl, but turned out to be the smallest component. If some of the 18.E.OHCl reacted further to the compounds labeled as 18.2E-deriv., the ratio becomes 1.26:1.26:1.48, which is still not that expected. Another particular observation is that 25 % of 18.E remained unreacted, whereas for the 18.2E it was 32 %, despite the two epoxy groups to react.

Transesterification, acetylation

The experiments described above were performed with an ESBO standard transformed to methyl esters prior to reaction with HCl. For the analysis of ESBO from packaging materials, however, the triglycerides must first be transesterified. Possible side effects of transmethylation on the epoxy and chlorohydrin functions as well as the unidentified transformation products were tested with the ESBO-FAME.E.HCl mixture: the mixture was treated with methoxide/methanol under conditions as used for transesterification, taking aliquots from the reaction mixture at different times up to 3 min after adding the reagent. Results are shown in figure 3. Indeed, there is a slow decrease of 18.OHCl and 18.2OHCl and an increase of the epoxy compounds. The 18.E.OHCl content remained approximately constant, indicating that as much was formed from 18.2OHCl as reacted further. However, the conversion of chlorohydrins to epoxides was noticeable only after a period of time clearly longer than the 40 s applied for transesterification. There were no significant changes regarding the other components eluted in the region of the transformation products, confirming that transesterification did not produce artifacts.

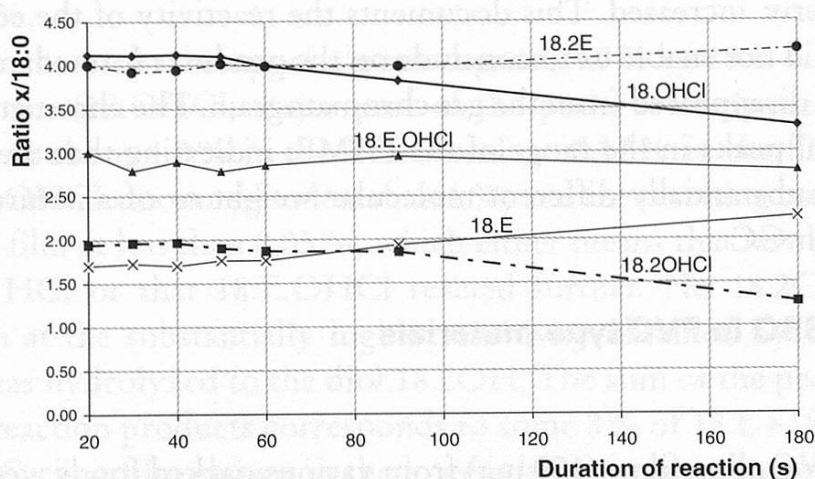


Figure 3 **Control of side reactions during transesterification by treatment of ESBO-FAME.E.HCl with methoxide/methanol during the time indicated. Peak areas normalized on methyl stearate (18:0) as a component not expected to participate at possible reactions**

Also acetylation could result in the formation of artifacts (such as opening of the epoxy function) and, thus, requires minimal stress. Completeness of the reaction was tested by monitoring the decrease of the non-acetylated 18.OHCl and the increase of the acetylated chlorohydrins related to methyl palmitate. Full acetylation was achieved after 60 min at 35°C or 30 min at 50°C. Prolonged acetylation did not result in a reduction of the peaks observed in the chromatogram.

Further transformation during heating

Reaction of epoxy groups with HCl at ambient temperature resulted in chlorohydrins almost exclusively (see above). In PVC type materials, however, HCl is formed and reacts with ESBO at temperatures near 200°C, at which additional reactions might take place. These were investigated with the non-acetylated ESBO-FAME.E.HCl mixture, of which 2 mg were flame-sealed in a small glass tube and heated to 180°C for 15 min.

As shown in table 3, the epoxy components were reduced by approximately 70%, 18.E and 18.2E being affected almost equally. The amounts of 18.OHCl and

Table 3
Peak areas relative to 16:0 for an ESBO-FAME.E.HCl mixture before and after heating to 180°C during 15 min

	18.E	18.2E	18.OHCl	18.E.OHCl	18.2OHCl	18.2E-deriv.	Sum
Before heating	0.51	1.40	1.46	0.93	1.21	0.14	5.62
After heating	0.16	0.41	1.49	0.28	1.46	0.90	4.41

18.2OHCl remained constant, while 18.E.OHCl dropped to about the same extent as the 18.2E-deriv. increased. This documents the reactivity of the components involved, but it did not enable us to conclude on the products formed: most of the lost epoxy material disappeared from the gas chromatogram. The chromatogram did not show additional peaks in the range of the FAME, indicating that the reaction products are of a substantially different molecular weight or of a nature not enabling passage through GC.

Results for ESBO in PVC type materials

PVC films

Pieces of PVC cling films (100 mg) from various packed foods were dissolved in 10 ml tetrahydrofuran (THF), transmethylated, and acetylated. The relevant parts of two resulting GC-FID chromatograms are shown in figure 4. The peaks of ESBO are well visible beside a large peak of methyl adipate (transmethylated esters of adipic acids), peaks of non-epoxidized fatty acids (e.g. fat from the food), and

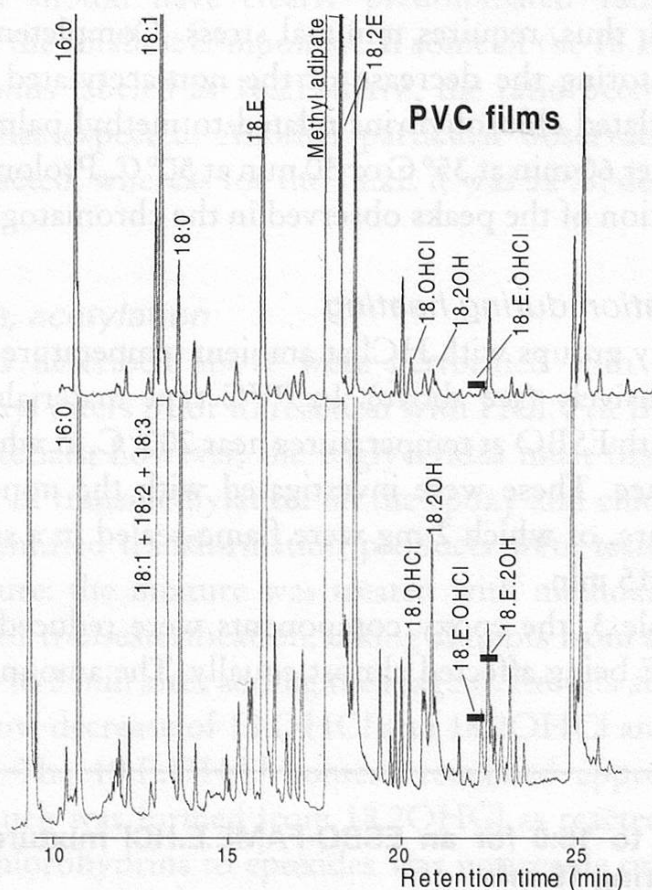


Figure 4 Relevant sections of GC-FID chromatograms of ESBO extracted from two samples of PVC cling films

some other, non-identified components. In both films, the concentration of ESBO was about 10 %.

In the film shown in the upper chromatogram, 4.3 % of 18.E was converted to its chlorohydrins (18.OHCl, major part of the peak, as confirmed by GC-MS), which relates to about 1.2 % in the ESBO and ca. 0.12 % in the film. Reaction of 18.2E to 18.E.OHCl amounted to less than 1 %, and the resulting components were present in the film at less than 0.05 %, which either means that less 18.2E than 18.E reacted with HCl or that 18.E.OHCl reacted further. No 18.2OHCl could be detected, even at the substantially higher sensitivity obtained by GC-MS. About 2 % of 18.E was hydrolyzed to the diol 18.2OH. The sum of the peaks presumably representing reaction products corresponds to some 8 % of 18.E+18.2E.

In the PVC cling film shown in the lower chromatogram (note lower attenuation), 2.1 % of the 18.E was converted to the chlorohydrins. There are larger signals for the hydrolysis products 18.2OH and 18.E.2OH. Of the three other PVC cling films tested, one contained no ESBO and in the other two the conversion of 18.E to 18.OHCl amounted to 2.6 and 2.9 %.

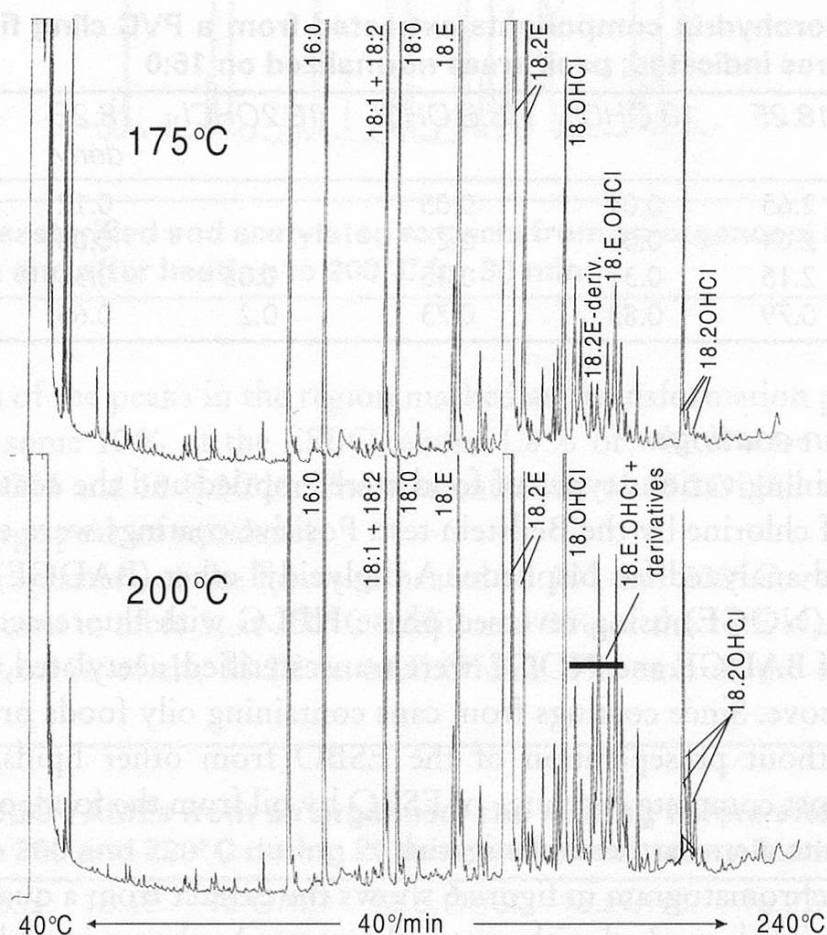


Figure 5 ESBO-containing PVC film heated to 175 and 200°C, respectively, for 15 min

100 mg portions of PVC cling film were heated to temperatures between 150 and 200°C for 15 min. The FAME composition of the extract from the film heated to 150°C was little different from that prior to heating. Those from the samples heated to 175 and 200°C are shown in figure 5. Exposure to 200°C let many peaks in the region between 18.2E and 18.2OHCl strongly grow, namely 18.OHCl from 18.E and many others presumably originating from 18.2E.

Quantitative compositions were calculated by normalization of the peak areas on methyl palmitate. Heating to 150°C caused a slight increase of 18.OHCl and 18.E.OHCl (table 4). Treatment at 175°C resulted in a 19% reduction of 18.E and 18.2E, with almost quantitative conversion to the chlorohydrins. Additional peaks in this region of the chromatogram grew, but were not identified so far. Heating to 200°C removed 70% each of 18.E and 18.2E, most of which reacted to the chlorohydrins or the non-identified products eluted nearby. The other peaks in the same region might account for another part of the lost epoxy components. In conclusion, in this case most conversion could be explained by products observed in the chromatogram.

Table 4

Epoxy and chlorohydrin components extracted from a PVC cling film heated to the temperatures indicated; peak areas normalized on 16:0

	18.E	18.2E	18.OHCl	18.E.OHCl	18.2OHCl	18.2E-deriv.	Sum 18:1	Sum 18:2
RT	1.33	2.65	0.04	0.05		0.12	1.42	2.82
150	1.37	2.64	0.09	0.2		0.08	1.46	2.92
175	1.12	2.15	0.31	0.35	0.03	0.31	1.43	2.84
200	0.39	0.79	0.83	0.73	0.2	0.65	1.22	2.37

Organosol can coatings

Cans containing various types of food were emptied and the coating tested for the presence of chlorine by the Beilstein test. Positive coatings were extracted with acetonitrile and analyzed for bisphenol A diglycidyl ether (BADGE) and novolac glycidyl ether (NOGE) using reversed phase HPLC with fluorescence detection. Extracts free of BADGE and NOGE were transesterified, acetylated, and analyzed as described above. Since coatings from cans containing oily foods proved difficult to analyze without pre separation of the ESBO from other lipids, presumably because of almost complete exchange of ESBO by oil from the food, only cans with aqueous contents were further investigated.

The upper chromatogram in figure 6 shows the extract from a quarter of the lid from a can previously packed with peas and carrots. As shown in table 5 (top line), 6% of the 18.E was converted to the chlorohydrin. The values for three other coatings varied between 5 and 11%. Maybe 4% of 18.2E has reacted to 18.E.OHCl, partly overlapped by 18.E.2OH and maybe other, unidentified components. The

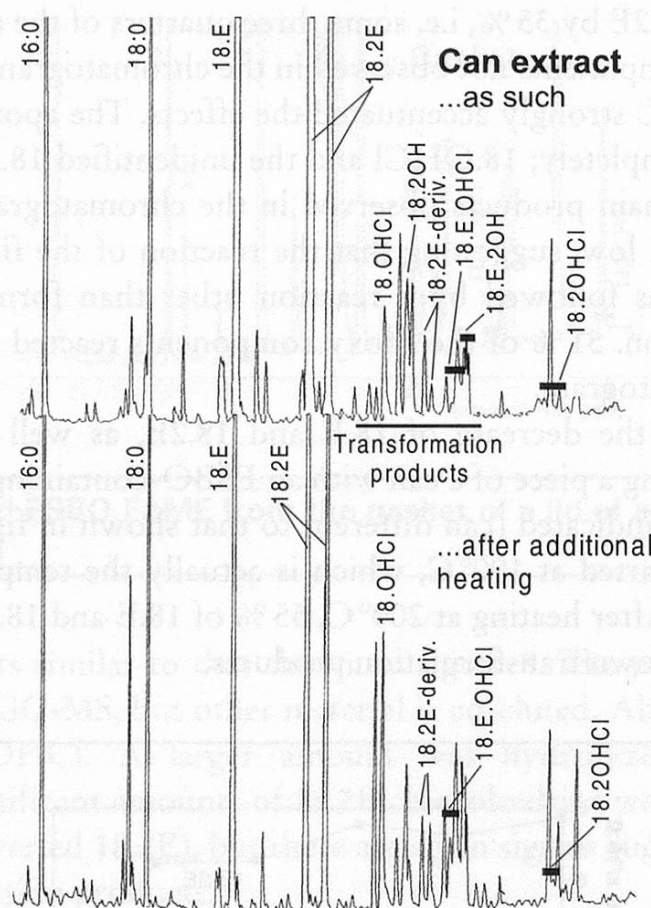


Figure 6 Transesterified and acetylated extracts from an organosol can coating as such and after heating to 200°C for 30 min

summed areas of the peaks in the region marked as “transformation products” corresponded to some 10% of the ESBO, about 1.8% of which were the hydrolysis products 18.2OH and 18.E.2OH. The concentration of 18.2OHCl was low (overlapped by a large peak of squalene).

Two other quarters of the lid were heated to 200 and 220°C, respectively, for 20 min. As shown in table 5, at 200°C additional 9% of the 18.E was converted to 18.OHCl and 6.5% of the 18.2E to 18.E.OHCl. The sum of the transformation

Table 5
Acetylated ESBO-FAMES from an organosol can coating before and after additional heating to 200 and 220°C during 20 min; peak areas normalized on 16:0

Additional heating	18.E	18.2E	18.OHCl	18.E.OHCl	18.2OHCl	18.2E-deriv.	Sum 18:1	Sum 18:2
none	1.8	3.7	0.11	0.15	0.03	0.16	1.9	4.0
200°C	1.1	2.0	0.28	0.4	0.08	0.15	1.4	2.6
220°C	0.3	0.08	1.04	0.3	0.10	1.3	1.3	1.8

products increased to 18 % of the ESBO components initially observed. 18.E was reduced by 26 %, 18.2E by 35 %, i.e. some three quarters of the reacted epoxy acids were turned into components not observed in the chromatogram.

Heating to 220°C strongly accentuated the effects. The epoxy compounds disappeared almost completely; 18.OHCl and the unidentified 18.2E derivatives (figure 2) became the main products observed in the chromatogram. The content of 18.2OHCl remained low, suggesting that the reaction of the first epoxy group of 18.2E with HCl was followed by a reaction other than formation of a second chlorohydrin function. 51 % of the epoxy components reacted to components not visible in the chromatogram.

Figure 7 shows the decrease of 18.E and 18.2E, as well as the increase of 18.OHCl after heating a piece of a can with an ESBO-containing organosol coating to the temperatures indicated (can different to that shown in figure 6 and table 5). Rapid conversion started at 190°C, which is actually the temperature needed for curing the coating. After heating at 200°C, 55 % of 18.E and 18.2E were lost, again prevailing to unknown transformation products.

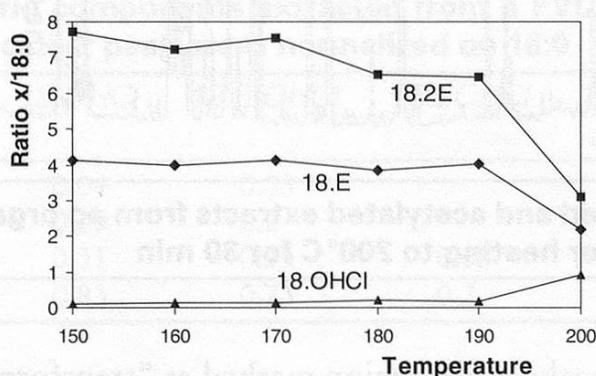


Figure 7 Decrease of 18.E and 18.2E, as well as increase of 18.OHCl after heating a piece of can to the temperatures indicated. Peak areas normalized on 18:0

These experiments were performed with ESBO already heated during curing of the organosol coating. The increase of the chlorohydrins upon additional heating to 200°C for 20 min was somewhat larger than the content before heating, which suggests that the coating was cured at a temperature between 190 and 200°C (assuming a similar duration – conditions which seem to be common). It is also extrapolated that curing converted 20–30 % of 18.E and 18.2E.

Twist-off caps

Glass jars are typically closed by metallic twist-off lids with a plasticized PVC gasket tightening against the rim. The lids from five samples of baby food in glass

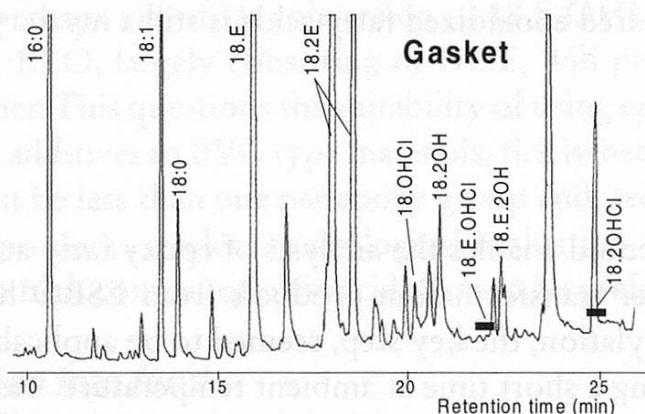


Figure 8 **Acetylated ESBO-FAME from the gasket of a lid of a glass jar containing baby food**

jars provided results similar to that shown in figure 8. The presence of 18.OHCl was confirmed by GC-MS, but other material is co-eluted. About 3 % of 18.E was converted to 18.OHCl. A larger amount was hydrolyzed to 18.2OH and 18.E.2OH. No significant amounts of 18.2E chlorohydrins were detectable (detection limit, 2 % converted 18.2E), but there are again signals suggesting the presence of other transformation products.

Polymerization?

Shepherd and Gilbert (7) checked the hypothesis that the reacted ESBO material missing in the FAME chromatograms is polymerized. In fact, at the relatively high concentration in the PVC and with the catalysis by hydrochloric acid, reaction between epoxy and hydroxy groups seems plausible. Reactions are possible also between fatty acids of the same triglyceride molecule. However, their results indicated that polymerization accounted to a small part of the loss only.

The proportion of dimerized triglycerides in the ESBO of the can coating additionally heated to 200°C was determined by SEC-refractive index detection and amounted to 20 %. This is clearly less than expected by the loss of more than 40 % of the ESBO (including the material reacted during the curing process) when quantitated through the FAME, since dimerized triglycerides include up to four unreacted acids for two reacted acids.

GC-FID of the same sample after transesterification and acetylation on a 3 m × 0.25 mm i.d. PS-255 column with on-column injection and a temperature program up to 350°C did not reveal peaks of a size anywhere near to explain the loss, particularly not in the region where the approximately 7 % of dimerized FAME were expected. The fatty acids of these dimers were joined in a way different from the dimers commonly encountered after thermal treatment and were probably

degraded because of the high temperatures required for GC. In conclusion, the nature of the disappeared epoxidized fatty acids is still a mystery.

Conclusions

Analytical method

The described method enables the analysis of epoxy fatty acids, their chlorohydrins, and some other transformation products from ESBO heated in PVC type materials. Transmethylation, the key step, seemed to be applicable when performed with methoxide during a short time at ambient temperature. Tests neither indicated significant re-conversion of chlorohydrins to epoxides, nor showed signs for loss of other, so far unidentified FAME derivatives. No final conclusions can be drawn, however, since a substantial amount of the epoxy acids are converted to material not detected in GC so far.

Transformation of ESBO

BADGE and NOGE added as HCl scavengers to organosol can coatings seemed to be quantitatively converted to their chlorohydrins (14, 15); no further reaction products were noted – a result which might need to be revisited after the present findings. ESBO as a standard partially reacted with HCl at ambient temperature contained chlorohydrins and a minor amount of two unidentified components. However, when the reaction occurs at a temperature of around 200°C, as during manufacturing of PVC articles and curing of can coatings or gaskets for lids, additional reactions take place. They result in components eluted in the same region of the chromatogram (i.e. modified fatty acids), but also in a reduction of the epoxy fatty acids stronger than the appearance of new peaks, i.e. disappearance of material. Some polymerization was observed, presumably by reaction of an epoxy group with the hydroxyl of a chlorohydrin, but the amount of dimerized triglycerides at best explained half of the missing material. This confirms the results *Gilbert et al.* (6, 7) obtained in 1980 for model compounds.

The FAME chromatograms of reacted ESBO showed numerous additional peaks. An intramolecular reaction between the chlorohydrin and the epoxy function of 18.E.OHCl seems most plausible, forming a five or six membered ring with an oxygen atom. The new components are, in fact, eluted with shortened retention time as compared to 18.E.OHCl. However, their structures remain to be elucidated.

The reaction of HCl with ESBO is more complex than that with BADGE and NOGE. For BADGE and NOGE in can coatings, up to some 80% conversion of the epoxy groups to chlorohydrins were observed (typically 20–50%), while in the materials tested the chlorohydrins of ESBO never exceeded 10% of the ESBO added to the PVC. Additional heating converted up to somewhat more than 50% of 18.E to its chlorohydrins, but the mono- and dichlorohydrins of 18.2E never reached 10% of the 18.2E originally present, even when 18.2E had disappeared

almost completely. 18.2E seems to react primarily in directions other than chlorohydrin formation (perhaps via a first conversion to 18.E.OHCl) and may be without taking up HCl. ELO, largely consisting of 18.3E, will probably react in even more complex manner. This questions the suitability of using epoxidized polyunsaturated fatty acids as additives to PVC type materials, firstly because the capacity for taking up HCl might be less than one per epoxy group and, secondly, the complexity of the reaction products renders toxicological evaluation difficult. Epoxidized vegetable oils with a high content of oleic acid seem to be preferable in this respect.

Estimated migration into food

In PVC cling films, 2.1–4.6 % of 18:E was converted to the corresponding chlorohydrins, resulting in some 0.5–1 % 18.OHCl in the ESBO. Being integrated into triglycerides, 18.OHCl can be assumed to migrate into the packed food to the same extent as the other ESBO components. This means that a foodstuff containing 10 mg/kg of ESBO from a cling film contains about 0.05–0.1 mg/kg of 18.OHCl. Other unidentified reaction products forming peaks in the same region of the chromatogram suggest a migration of the ESBO reaction products of about 0.2–0.5 mg/kg. There seemed to be little transformation material not detected in GC.

In organosol type can coatings, conversion was higher, presumably because of the longer heating during curing of the lacquer. 5–11 % of the 18:E was converted to the chlorohydrins, resulting in about 1.5–3 % 18.OHCl in the ESBO. Summing up the peaks in the area of the transformation products, some 10 % of the ESBO was converted to components visible in the FAME chromatogram. Extrapolating the data obtained by additional heat treatment backwards to the composition before curing of the coating, some 20–25 % of the ESBO was transformed, well half of which to undetected material (part of which being polymerized). The amount of the reaction products to be expected in the canned food can be estimated as follows. If a can is coated with 200 mg of an organosol containing 5 % of ESBO, it contains 10 mg ESBO with 0.15–0.3 mg 18.OHCl and totally 1–2.5 mg transformation products. Oily foods are likely to extract most of it, i.e. the consumers may ingest up to a few milligrams of ESBO transformation products with a single can. In a 200 g can the concentration might reach 10 mg/kg.

Plasticized PVC gaskets in lids for glass jars contain ESBO with roughly 1 % 18.OHCl and in total several percents of other converted material. As up to 50 mg/kg of ESBO was found in baby food (*Hammarling et al.* (4)), this means the presence of about 0.5 mg/kg of 18.OHCl and a few mg/kg for the total of the transformed material.

These rough estimations indicate the likely range of food contamination by ESBO transformation products. They should be experimentally confirmed, but the identification and the analytical determination of the relevant components in foods will probably be a demanding task. Instead of waiting for such data it might be wiser to perform a toxicological evaluation now, since the transformation products

exceed the threshold of no toxicological concern by far even if the above estimations were substantially too high.

Legislative aspects

ESBO and ELO are in the positive lists of authorized additives for plastics and coatings in food contact, because toxicity was found to be low. This evaluation did not take into account the products formed by the reaction with hydrochloric acid liberated from PVC heated near to its decomposition temperature – although this is the main application and the reaction with HCl is one purpose of adding epoxidized oils.

Present European legislations regulate starting point materials, normally giving industry the freedom of using a positive-listed substance for any application and under unrestricted conditions. The toxicological profile of these starting materials is carefully controlled, but often the reaction products are not taken into consideration. This is a principal shortcoming and, thus, the problem of the ESBO reaction products is probably also a problem of the present approach to safety of food packaging materials in general.

Summary

The transformation products of epoxidized soybean oil (ESBO) reacted with hydrochloric acid from heated PVC were analyzed by GC-FID after gentle transesterification and acetylation. Treatment of ESBO with HCl at ambient temperature results in almost quantitative conversion to chlorohydrins, but elevated temperatures, such as used to produce PVC articles or to cure can coatings, also cause further reactions, the products of which have not been identified.

In PVC cling films and PVC gaskets of lids for glass jars, probably less than 10% of the ESBO is converted, but in organosol type can coatings it might frequently be more than 20%. It is expected that with a single can or glass jar (baby food), up to a few milligrams of ESBO transformation products are ingested. When the use of ESBO was authorized, the toxicity of these reaction products has not been evaluated.

Zusammenfassung

Die Umwandlungsprodukte von epoxidiertem Sojaöl (ESBO) im Kontakt mit HCl aus erhitztem PVC wurden nach schonender Umesterung und Acetylierung mit GC-MS analysiert. Wenn ESBO bei Raumtemperatur mit HCl reagiert, entstehen fast ausschliesslich Chlorhydrine, doch bei höheren Temperaturen, wie sie bei der Herstellung von PVC-Artikeln und zum Einbrennen von Dosenlacken vom Organosoltyp angewandt werden, laufen weitere Reaktionen ab, deren Produkte noch nicht identifiziert wurden.

In PCV-Folien und Dichtungen von Schraubdeckeln für Gläser wird ESBO wohl zu weniger als 10% umgewandelt, in Dosenlacken aber oft zu mehr als 20%.

Es muss damit gerechnet werden, dass mit einem Dosen- oder Glaseinhalt (Fertigmenues für Kleinkinder) bis zu einigen Milligrammen solcher Produkte aufgenommen werden. Vor der Bewilligung von ESBO als Additiv für Kunststoffe und Lacke sind diese Umwandlungsprodukte nicht auf ihre Unbedenklichkeit überprüft worden.

Résumé

Les produits de conversion d'huile de soja époxydée (ESBO) en contact avec l'HCl de PVC chauffé ont été analysés par GC-MS après une transestérification douce et une acétylation. L'ESBO traité à l'HCl à température ambiante produit presque uniquement des chlorohydrines. Mais aux températures élevées utilisées pour la fabrication des articles en PVC ou pour cuire des vernis organosols de boîtes de conserve, d'autres réactions donnent lieu à des produits non identifiés.

Dans les films alimentaires PVC et les joints PVC des couvercles pots en verre, probablement moins de 10 % de produits de conversion sont formés, par contre, dans les vernis des boîtes de conserve, ils dépassent souvent les 20 %. La consommation d'une boîte ou d'un verre de conserve (menu cuisiné pour enfant) pourrait conduire à ingérer jusqu'à plusieurs milligrammes de ces produits. L'autorisation d'utilisation de l'ESBO comme additive pour plastiques et vernis a été établie sans que la toxicité des produits de réaction n'ait été testée.

Key words

Epoxidized vegetable oils, ESBO, Poly(vinyl chloride), Organosol can coatings, Transformation products of ESBO, Chlorohydrins of ESBO

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