BIOCOPAC project publishable report

Abstract

The goal of the project was to develop a bio-lacquer for the protection of metal food packaging to meet the demand for sustainable production and for the safeguarding of consumer health, at the same time increasing the competitiveness of the metal can industry, valorising the wastes produced by the food preserving industry and reducing refuse. The core of the research was the development of a natural lacquer obtained from industrial tomato processing by-products (skins), to be applied on the internal and external surfaces of metal cans for foodstuffs. The new type of packaging is a response to the needs of the SMEs involved in the project (lacquer producer, can makers and the food preserving industry), to increase their economic and commercial competitiveness, by improving the quality of metal cans. In fact, a highly innovative eco-friendly packaging is obtained, which is less dangerous for consumer health and able to compete with other packaging materials, such as plastic. This is a key aspect, since metal packaging is currently perceived by consumers as being out of date.

The research started with the analysis and characterization of tomato wastes, coming from different European countries, including Italy and Spain. These analyses verified that differences in composition were not significant and that dangerous substances, such as heavy metals and pesticide residues, were not present (or within the allowed limits). A relatively simple method for cutin extraction has been developed in laboratory and in a pilot plant, starting from tomato waste. Cutin is the biomolecule used as the starting substance for the development of the bioresin and of the lacquer. The yield of the extraction process, which has been patented, ranges between 8 and 10%, which is certainly good. The outcome of the extraction process of cutin from tomato peels is a monomer/oligomer product. Its principal component is the 10,16 dihydroxyhexadecanoic acid, which is suitable for bioresin preparation. The cutin composition was studied using FT-IR and GC-MS techniques. Homopolymers and copolymers resins were used for the subsequent lacquers. The lacquer has been produced utilising different crosslinkers and modifiers. On the basis of numerous tests two formulas have been selected, one specific for tinplate (TP) and another for all the metallic substrates (TP, TFS and aluminium). These formulas have been patented. A series of tests has been carried out to evaluate the properties of the lacquer applied on the substrate and to study the ideal curing conditions (time and temperature) using Differential Scanning Calorimetry (DSC) analysis. Afterwards, 3-piece tinplate cans and 2-piece aluminium cans were produced in an industrial line. The cans have been filled with four kinds of food products on an industrial line (tomato and fish foods) and with simulant solutions in the laboratory (acid and sulphurating). The pack test that followed had a limited duration, but the results obtained are very interesting and promising. The lacquer showed good properties in terms of adhesion, flexibility and corrosion resistance even at a storage temperature of 37°C and, however, comparable to those of standard lacquers.

Based on the migration tests and the risk assessment, it can be stated that the lacquer complies with the Italian and European legislations. The lacquer is compliant with the migration’s limits and it does not modify the products’ organoleptic characteristics. The environmental benefit of the "Bio-lacquer" compared with oil-based paints has to be especially noticed, as shown by the LCA evaluation. The main benefit generated by the cutin lacquer is the saving of natural resources and the recovery of part of the skins. The effects are lower consumption of fossil fuel and lower emissions of CO_2, with a decrease of 130.7 mg in the CO_2 produced for each can. The work carried out provides complete indications for the use of the new lacquers in contact with food products and evidence of their economic and environmental benefits.

The valorisation of tomato waste is now a reality. This agrees with the principles of Circular Economy Systems, as cans filled with tomato products are produced starting from tomato by-products.

Summary of the background and main objectives

In Europe, the packaging market is growing year after year and, specifically, food packaging accounts for 65% of the total packaging market, of which 1.9M tonne worth of metal packaging, for approximately €8 million, and 18M tonne worth of plastic packaging. The increasing world-wide demand for good quality and safer food products and the increasing societal concerns over food contaminants migration and health-related drawbacks are much focused on and a key item on the food industry agenda. In response to pressures from consumers and to new, widespread sensitivity and awareness, the development strategies of the packaging sector can be summed up in two words: **safety** and **sustainability**. The safety of food packaging and materials is a topic of great concern, very relevant and crucial to the entire agri-food supply chain. The issue of environmental sustainability of materials and packaging must be addressed through improved recyclability and biodegradability to reduce urban solid waste and carbon footprint.

The BIOCOPAC project faces both criticalities. The goal of the BIOCOPAC project was to develop a bio-based lacquer for food packaging. The tomato industry wastes are used as a natural raw material for the production of lacquers to be applied on food metal-cans replacing petroleum-based coatings. In short, one could say that a virtuous loop is created "from tomato to tomato" (Fig.1)

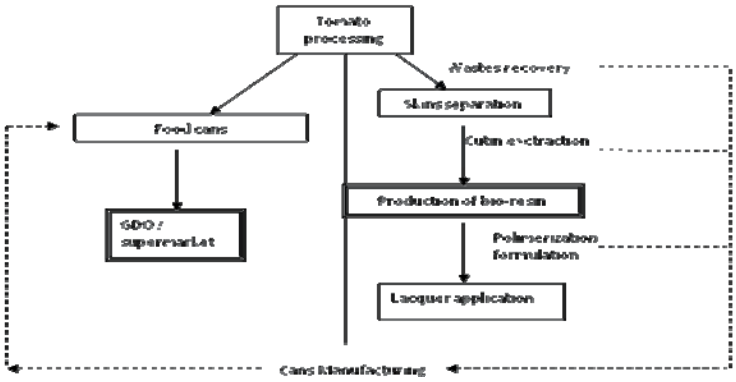


Fig.1 Virtuous loop of the BIOCOPAC project

The project was created and developed, considering social, environmental and economic factors, briefly discussed below.

Tomato industry by-products

The tomato processing industry, one of the most important in Europe, produces thousands of tons of wastes, which are only partly reused and which contribute to pollution.

The total tomato production in the EU-27 is estimated in about 15 million metric tons in 2013. Each year in the EU-27 more than 200000 tons of solid tomato residues (peels and seeds) are produced. At present, tomato waste is used partly in the zootechnical sector as a substrate for the production of fertilizers and, lately, also for the production of biogas. However, the disposal cost for the food industry is over €4.0 per tonne, due to transport.

Today, in society considerable emphasis is placed on the recovery, recycling and upgrading of by-products. By-products pose increasing disposal issues and potentially severe pollution problems, and represent a loss of valuable biomass and nutrients. The possibility of recovering and upgrading tomato wastes to higher-value and useful products is an interesting option. BIOCOPAC identifies a new and different possibility to exploit tomato waste.

Development of biobased materials in plastic packaging.

In the last years, growing demand for environmentally friendly products has led to the development of the biopolymer/bioplastics sector. Despite the fact that the cost of biopolymers is higher than that of petroleum-derived plastics, the production and the use of innovative materials from renewable resources in the flexible packaging sector are increasing, while the development of bio-based resin in the paints sector is just at the beginning.

Competitiveness of metal packaging

At world scale, among all metals packaging, steel and aluminium account for 17% of total sales (Fig.2). The global steel and aluminium packaging market is worth €100 billion, of which 25% in the EU, where the value of the food packaging industry is USD100 billion per year (+10% annual increase). The food industry uses 65% of all packaging placed on the market.

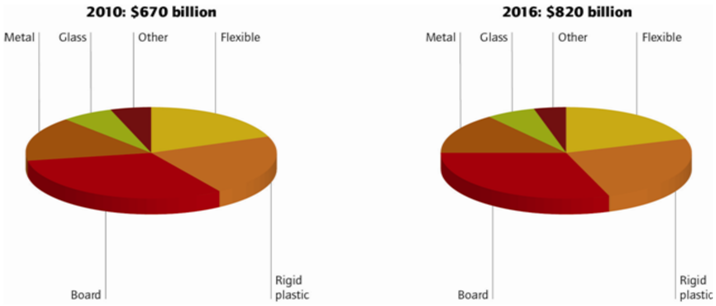


Fig. 2*: Global packaging sales by type 2010 vs. 2016*

Tinplate cans are the most widely used in the preserved food sector, while aluminium cans are the most used in the beverage sector. Production of tinplate packaging comes to 3.4 million tons, 53% of which for food and 15% for beverage. Aluminium production amounts to 600,000 tons with a production of 35 billion beverage cans. Although the metal sector has suffered little from the economic crisis and has remained broadly stable in the last ten years, the market shares of metal packaging in all preserved food sectors is likely to be eroded, mainly by plastic packaging. Moreover, metal packaging is perceived as outdated by consumers. In order to maintain the competitiveness of the metal packaging sector, metal cans must be revised. The BIOCOPAC project meets these requirements for economic sustainability and competitiveness.

Consumers concerns:

In the past 10 years, in line with greater attention paid to hygiene/health and the environment, synthetic lacquers have been the subject of several cases of alert. The problem of the migration of residues of polymerisation, monomers and oligomers (with MW < 1000 DA), as well as of additives, has given rise to press campaigns and has raised doubts and uncertainty in consumers, with consequent damage to the image of the can-making industry. In 2009-2013, the warning was raised about the presence of BPA (Bisphenol A) in food packaging and its dangerous side-effects. The BPA molecule has known endocrine disrupting effects also at low doses. In 2012, France issued a very restrictive legislation banning BPA from January 2015 onward, which generated great alarm. Many food industries and large-scale retailers, even though not yet required by law, ordered BPA n.i./BPA-free packaging to their suppliers. None of the resins that could be used as an alternative to the epoxy-based ones meets all the performance characteristics of BPA-based resins. Therefore, it is extremely important to find a different path to achieve performances at least equal to those of epoxy resin.

Recyclability of the can metals:

The coatings applied on metal food containers to prevent corrosion of the metal container and contamination of the food are one of the critical points to obtain a completely recyclable packaging (Dir. 2004/12/EC, amended by Dir. 2005/20/EC; EN13430). The use of a bio-lacquer replacing synthetic lacquers reduces the risk of environmental pollution in the steel recovery phase and thus promotes the recycling of metal containers, allowing the already high recovery percentages (70%) to increase even further.

The BIOCOPAC project fits into this background and addresses many of the above social demands.

The main objectives of the project and their positive effects on the environment, on the protection of consumers' health and for the sector competitiveness are listed below:

- To produce natural lacquers for food cans from renewable raw materials, tomato processing by-products: it can help the food industry lower the costs of waste disposal and exploit the waste by reusing it.

- To manufacture an innovative green can: this is a great challenge, which can increase the competitiveness of the whole metal packaging sector with respect to bioplastics (Fig.3).
- To improve a healthier working environment in resin and lacquer factories.
- To promote the recycling of metal cans coated with natural lacquers.
- To provide a safe metal packaging that complies with European and national legislations; it has lower risk of migration of dangerous synthesised substances and off-flavours
- To reduce the environmental impact
- To improve scientific knowledge to open the path to the use of other new molecules or to the production of new resins modified with other molecules of natural or synthetic origin.

Fig.3 BIOCOPAC cans

These general objectives have been achieved through different specific objectives, each one contributing to the success of the project in its totality. In particular, the objectives of each work phase are the following:

-Characterization and assessment of the composition of the tomato waste coming from different countries. This is a fundamental point for the standardization of the cutin extraction method.

-Development and optimization in laboratory and on a pilot plant of the cutin extraction method, which must be relatively simple and reproducible.

- Minimization of the environmental impact of the extraction process in terms of water and energy consumption

-Production of cutin with characteristics that are constant and suitable for the bioresin development.

-Development and production of a bio-resin suitable to formulate water-based and solvent-based lacquers.

-Formulation of lacquers suitable to be applied on standard industrial lines, without any alteration needed.

-The lacquers applied on different metal substrates, used in food packaging, as tinplate, tin free steel and aluminium, must fit and proper to be in contact with food products that differ in terms of composition and aggressiveness.

-Development of lacquers, which are inert from a sensorial point of view, in order to prevent any extraneous flavours or tastes in food.

-Economical evaluation of the new lacquer and implementation, in its development, of some devices so as for the final cost to remain within the range of costs of standard lacquers.

All this can contribute to the definition of a bio-based lacquer, which is safe for consumers, eco-friendly and cost-competitive.

Final Results

Abbreviations

Aluminium: Al
Tin free steel: TFS
Tinplate: TP
Infrared Spectroscopy): FT-IR
Gascromatography-mass spectroscopy: GC-MS
Gel permeation chromatography: GPC

Thermogravimetric analysis:TGA
Methylisobutyl ketone: MIBK
Methoxy propyl acetate: PMA
Methyl ethyl ketone chemical resistance: MEK
Wedge Bend Test: W.B.T.
Differential Scanning Calorimetry: DSC
Number Average Molecular Weight: M_n
Weight Average Molecular Weight: M_w
Electrochemical impedance spectroscopy:EIS
Frequency Herz: Hz
Kilo Dalton: KD
Tetrahydrofuran: THF
Draw and redrawn:DRD
Wilkens-Anderson enamel rater: WACO
Iron exposure value: IEV
Life Cycle Assessment: LCA
Equivalent Carbon dioxide: CO_2eq

The objective of the BIOCOPAC project was to develop **a natural lacquer** obtained **from industrial tomato processing by-products** (skins), **to be applied on** the internal and external surfaces of **cans for foodstuffs.**

Overall, the objective has been achieved; the lacquer from tomato peels has been obtained and applied to metal food cans.

The results of the project can be divided into five different macro-areas:

-Development of the extraction method

The process for the extraction of cutin from tomato peels has been developed and standardized both in laboratory and on pilot plant. An international patent about the extraction method of cutin has been applied for. The method allowed a monomer/oligomer product to be obtained, whose principal component is 10,16 dihydroxyhexadecanoic acid, with characteristics suitable for preparation of the bioresin and of the subsequent lacquer.

-Development and formulation of the bioresin

Starting from the cutin extracts, different batches of bioresin were been prepared, studied and analysed. From raw cutin and from preoligomerized cutin, the bioresins were prepared by means of homopolymerization and copolymerization.

-Development and formulation of the lacquer

Numerous and different samples of lacquers were prepared, compared to one another and assessed, in order to find the best final formulation. The samples of lacquers were prepared starting from the different cutin-based resin samples. Solvent- and water-based formulations were obtained.

The lacquer formulations were developed using different crosslinkers and modifiers. At the end, two solvent-borne formulations and one water-borne formulation were selected for the application on a metallic substrate. A patent on the formulation of lacquer has been applied for.

-Application of the lacquer and pack-test

The selected formulas, one for tinplate (TP) and the other for all metallic substrates TP, tin free steel (TFS) and aluminium (Al), were applied in laboratory. After a series of tests to evaluate the properties of the lacquer applied to the substrate, as well as the ideal curing conditions (time and temperature), 3-piece tinplate cans and 2-piece aluminium cans were manufactured in an industrial line. The cans were filled with four kinds of food products in an industrial line and with simulant solutions in laboratory. The pack test that followed had a limited duration, but the results obtained were interesting and promising. Based on the migration test and on the Risk Assessment, the lacquer was found to be compliant with Italian and European legislation. The bio-lacquer has performed more than well in contact with the food; it was found to be inert towards the food, even after the thermal treatments of pasteurization and sterilization.

-Life cycle assessment

The LCA study has highlighted a strong decrease in the environmental impact, in particular in the CO_2 emissions of the biolacquer in comparison with the standard oil-based one.

1. **Development of the extraction method**

In the first phase of the experimental work, some batches of tomato peels from Spain and Italy collected at three different times during the production campaign - mid-July, mid-August and mid-September - were analysed so as to obtain a sample representative of the entire processing period. Several analyses were performed to verify any possible difference in composition and the presence of organic and inorganic contaminants. The analytical evaluation about nutritional and structural parameters did not show significant differences between the different batches, as reported in table 1 below, by way of an example

	% Humidity	% Fat	% Ash	% Protein	% Carbohydrate	% Dietetic fiber	% Cellulose
Italy: July 2011	76,02	0,37	0,89	3,16	19,56	78,90	57,84
Italy: August 2011	74,63	0,69	1,00	3,82	19,87	80,21	56,62
Italy: September 2011	69,33	0,31	1,01	4,62	24,74	79,19	62,09
Spain: July 2011	76,62	0,36	0,70	2,28	20,04	75,40	55,08
Spain: August 2011	80,59	0,44	0,72	2,94	15,32	81,18	67,59
Spain: September 2011	78,48	0,35	0,47	2,39	18,30	80,99	60,63

Tab.1: Nutritional composition (mean values) of the peels

As reported in table 2, the concentrations of heavy metals analyzed were comparable.

	ppb Sn	ppb Cu	Cd	Ni	Cr	Hg	Pb
Italy: July 2011	79,26	9,28	< 10 ppb				
Italy: August 2011	78,89	9,70					
Italy: September 2011	78,93	7,60					
Spain: July 2011	81,93	3,32					
Spain: August 2011	71,96	11,85					
Spain: September 2011	88,25	4,90					

Tab. 2 Heavy metals concentration

Only tin and copper were quantified. The other heavy metals studied proved to be at values below the quantification limit of the measuring equipment. Similarly, the concentration of pesticides researched including over 14 families of different pesticides, with wide physical-chemical properties, was below the quantification limit for all the samples analyzed. .

Based on this result, which was similar in all samples, it was decided to proceed with all of them, homogenizing samples from each country. During the second part of the work, the selection and the set-up of the method for cutin extraction from tomato peels were performed. Based on the bibliography research, 4 methods were compared:

- **SSICA method based on patent B.I. no 341958 (1942),** in which the extraction process consists in a solubilisation of tomato skin in an alkaline solution.
- **Enzymatic method,** where the cuticular membrane is isolated by enzymatic treatment to degrade the polysaccharides.
- **American method based on U.S.A. patent n. US 2011/ 0319504 A1**, where the cutin is isolated by a solvent extraction and then with a system of refluxing.
- **Acid hydrolysis method,** in which cutin samples were obtained after hydrolysis of dewaxed cuticles by digestion in strong acid.

These methods included extraction with organic solvents, extraction with a basic hydrolysis and extraction with an acid hydrolysis. The results obtained with these methods were analyzed with

different analytical technique, such as FT-IR (Infrared Spectroscopy), GC-MS gascromatography-mass spectroscopy), GPC (gel permeation chromatography) and TGA (thermogravimetric analysis).
Among all the methods, the most successful one was the SSICA method, which has proved to be the best for reproducibility, yield and feasibility, while the other three methods have showed some problems related to yield and experimental procedure.
In particular, the enzymatic method isolated only dewaxed peels and peels without sugars, but not cutin.
With the U.S.A. Patent n. US 2011/0319504 A1 method, the extraction was not successful. Both these methods proved to be solvent consuming.
The acid hydrolysis method presented a low final yield and the reagent for the extraction (HCl 6 M) was dangerous and corrosive.
As regards the experimental procedure with the SSICA method, at the extraction initial stage, tomato skins and seeds were separated by flotation in water. Afterwards, the tomato peels were subjected to a thermal treatment with an alkaline solution (NaOH 3%) at high temperature. Then, the solution was filtered and the liquid filtrate was kept. To this filtered solution (brown in colour) HCl conc (37%) was added, until the solution changed colour and, from brown, it became ochre. After centrifugation the supernatant was discarded, while the solid residue was kept and washed/cleaned. In this way, **raw cutin** was obtained in a pasty mass containing around 40% of water.
After the washing, the bio-resin can be treated in an air flow oven for 30 hours at 60º C, then, dissolved in acetone and separated by centrifugation. The final bio-resin obtained, partially polimerizated, was called **pre-oligomerized cutin.**
This method was repeated several times, both in Italy and Spain, and every time cutin was extracted, showing no difference between the samples obtained in Italy and the samples obtained in Spain. This indicates strong and solid reproducibility of the method.
The analysis performed allowed a complete characterization of the cutin, as shown in figures 1-3. In the IR spectrum, **raw cutin** showed a prevalent peak around 1700 cm^{-1} (Fig.4).
The **pre-oligomerized cutin** is characterized, in the IR spectrum, by a small shoulder at 1730 cm^{-1} around the peak at 1700 cm^{-1} (Fig.5). These differences can be attributed to a partial oligomerization of cutin in the final bioresin, obtained by treating it at 60° C for 30 hours.
On the contrary, as regards the GC-MS analysis, the two kinds of samples did not have differences; in fact, the two chromatograms showed the same dominant peak, identified as 10,16 – dihydroxyhexadecanoic acid, the main component of tomato cutin, (Fig.6), as reported in the literature.

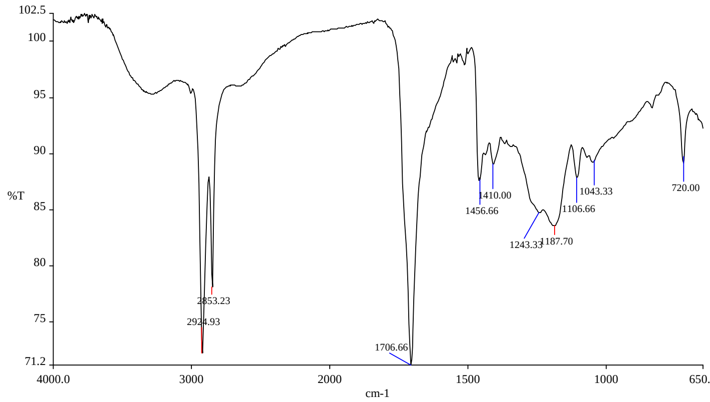


Fig. 4 : FTIR spectrum of raw cutin

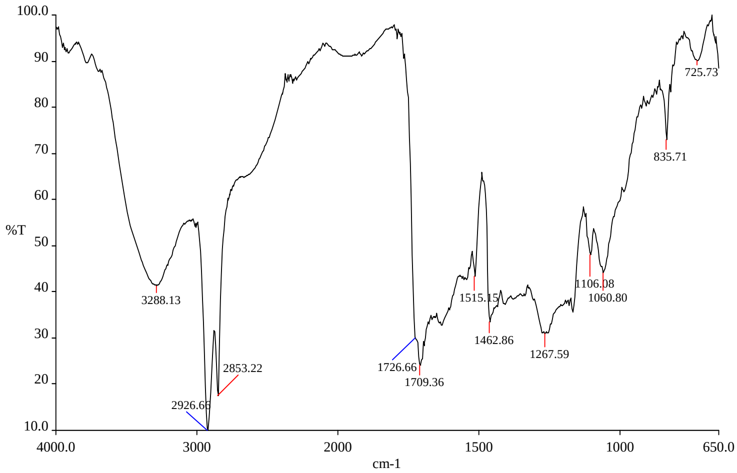


Fig. 5 : FTIR spectrum of pre-oligomerized cutin

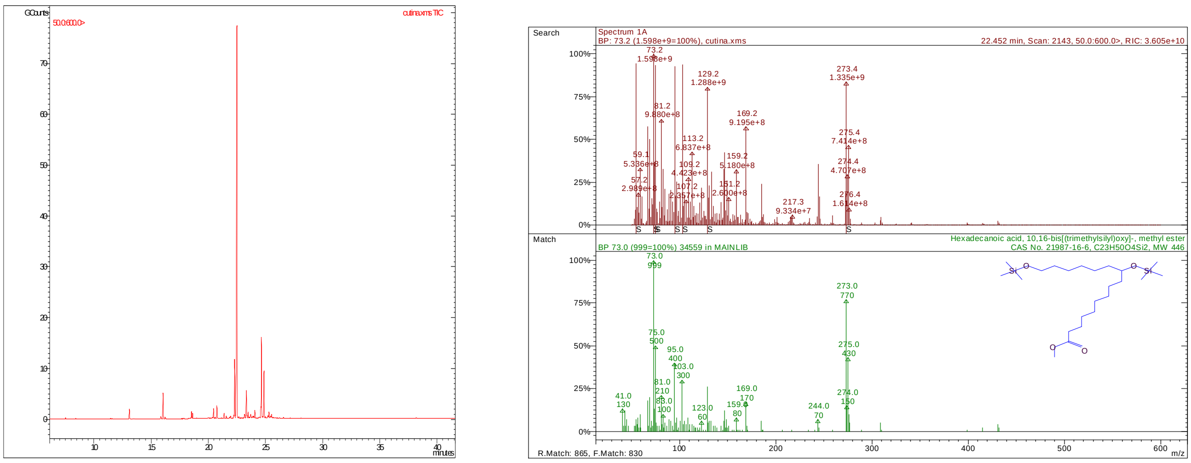


Fig. 6 : Chromatograph and MS spectrum of raw cutin

On the extracted cutin, the absence of heavy metals and pesticide residues was verified.
As regards yields, positive results were obtained: yields increased during the optimization of the experimental work and from a very low initial yield (about 1% the first time we applied the method) yields of about 20% on dried residue and of 60% on a sample extracted repeatedly were obtained. Moreover, the monomer yield for the GC-MS analysis always ranged between 70-80%, showing that the extraction procedure succeeded in isolating mainly cutin.
In order to confirm the reproducibility of the method, to increase the yield and to obtain raw cutin free from impurities and with a low degree of polymerization, some variables in the extraction procedures were studied, in particular the kind of initial sample (type of tomato skins), the ratio of the tomato peels weight to their volume NaOH (W:V), the concentration of NaOH; the cycle of thermal treatment. The best experimental conditions found were

- ✓ tomato peels: any type
- ✓ 100g tomato peels: 1 L NaOH
- ✓ NaOH 0.75 M
- ✓ Sterilization conditions : 100° C, 6 hours

All the experimental modifications applied to the standard procedure of cutin extraction did not influence the GC-MS analysis, as all the samples obtained showed the same chromatogram, with the principal peak identified as 10,16 – dihydroxyhexadecanoic acid
After the setting-up of the experimental conditions in laboratory, the method was tested even on a larger scale, in a pilot plant, with industrial equipments, like decanters or industrial retorts and high

volumes and large quantities (figures 7 and 8). Batches of 100-400kg of peels were processed. The results were good, in terms of yields and of characteristics of the cutin extract.

Fig. 7 : Extractor equipment in the Pilot Plant at CTAEX

Fig. 8: SSICA pilot plant

Two important aspects have to be highlighted:

• Any kind of tomato residue (peels and seeds) can be subjected to the pilot plant extraction procedure. This is a very important aspect for the industry players, because it means that tomato factories can collect all the tomato wastes and subject them to the same extractive treatment.

• The reproducibility of the method is an important characteristic of the extraction procedure, because it means that, even with some experimental modifications, the procedure works well. This is an important point for future industrial applications, where some experimental parameters could need to be modified to make the procedure suitable for the industrial process.

At the end of the set-up of the extraction procedure, an Italian patent was defined, applied for and it is currently being assessed, after receiving a favourable opinion (Patent n. **PR2013A000066**).
Moreover, extension at an international level has been applied for (Patent n. **PCT/EP2014/067187).**

2. Development and formulation of the bioresin

The experimental work has focused on synthesis of cutin-based polyester resin (or bio-resin) with suitable structure, molecular weight value and distribution, in order for it to be used as a binder in lacquer formulations.

First of all, the samples of cutin extract were analysed by means of GPC (Gel Permeation Chromatography) and their solubility in organic solvent was tested.

The work was developed with the two kinds of cutin, **raw cutin**, and **pre oligomerized cutin**.
The chromatograms of several raw cutin and preoligomerized cutin samples, coming from different extractions, always presented the same predominant peaks, as shown in Figures 9, 10 and 11.

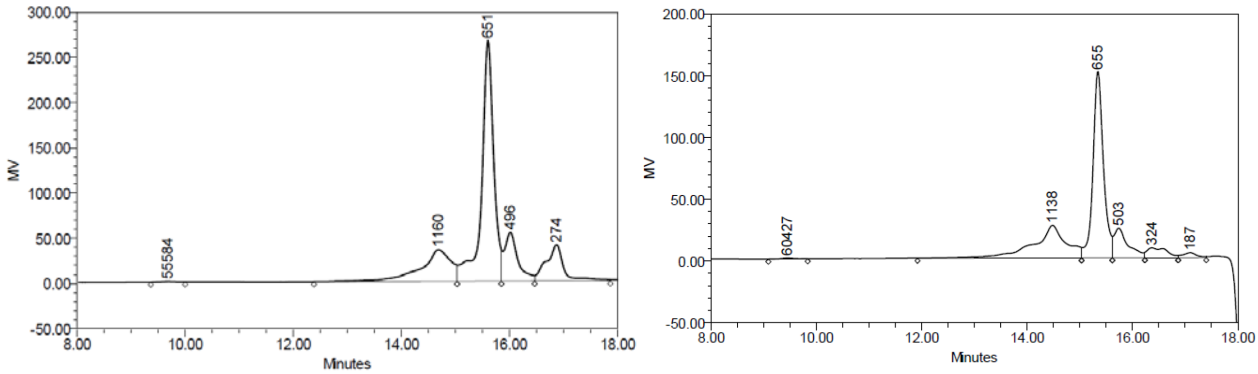


Fig. 9 and 10: GPC chromatogram of two different samples of raw cutin.

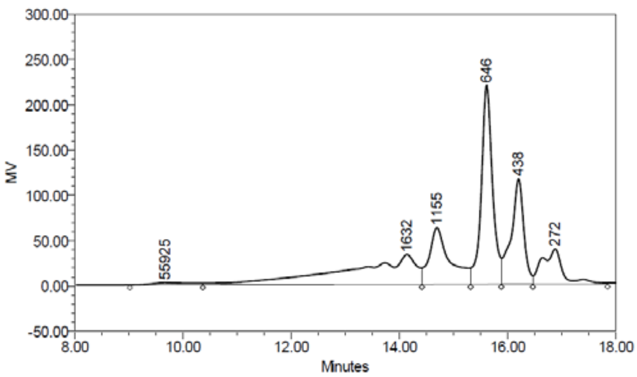


Fig. 11: GPC chromatogram of a sample of preoligomerized cutin

In all GPC chromatograms, a dominant fraction was identified with its maximum at an elution time of 15.6 minutes. This fraction with relative molecular weight 650 g/mol is likely to be a dimer or trimer, if we take into consideration that the major monomer of cutin (10,16-dihydroxyhexadecenoic acid) has molecular weight 284 g/mol.
The GPC analysis has confirmed that the raw cutin extracted from tomato skin is composed of principally lower molecular weight oligomer fractions, while higher molecular weight fractions in the elution time, ranging from 9 to 15.3 minutes, were measured in preoligomerized cutin.
In order to produce the cutin-based polyester resins, a polycondensation reaction was used for homopolymerization or copolymerization of cutin; solvent-based and water-based resins have been developed.
The starting raw and pre-oligomerized cutin was prepared within one year in several batches and assessed with GPC tests. The assessment of the bioresins produced by homo- or copolymerization was carried out by measuring some chemical properties, but above all by preparing different batches of lacquers and by assessing their properties in liquid and applied state.
During the work, a reproducibility problem was found. One potential explanation was the deviation in the quality of starting raw materials, which was different from batch to batch. Residual components based on polysaccharides, proteins, fibres, waxes and other molecules can complicate polyesterification process of cutin extract due to creation of insoluble parts in an organic solvent.
We concluded that it was necessary to include a stage for purification of raw and preoligomerized cutin to remove traces of high molecular weight and insoluble fractions, since the degree of impurities in the starting cutin resulted very variable. In this way, it was possible to obtain a resin with reproducible characteristics for the subsequent polymerization. Numerous trials were performed.

Some methods of purification were been investigated. In particular the different approaches were:
- Purification with organic solvent, acetone;
- Purification with water and acetone in a mixture of solvents, Methoxy propyl acetate (PMA) and butylglycol
- Purification with hexane

Purification using the first approaches was not successful, because such approached had problems of solubility of samples and of reproducibility. The samples of cutin that were extracted with hexane were miscible with solvent based on ketone or ether better, but even this procedure was not reproducible. Therefore, it was decided to proceed with a purification step that combined two organic solvents MIBK (methylisobutyl ketone) and PMA.

Fig. 12: Laboratory apparatus for polycondensation reaction used for synthesis of cutin based polyester**.**

The cutin-based resins obtained by means of homopolymerization consisted of 100 wt. % of cutin; the cutin extracts homopolymerize to get a targeted polymerization degree; it was subsequently diluted in selected solvents to make solvent 100 % cutin based polymeric binder for coatings. The preparation of the solvent based cutin polyester binders followed two directions (Fig.12).

The first one consisted of two steps, where the first step is the homopolymerization process and the second step is dilution of the cutin-based polyester in a suitable organic solvent. It was conducted at a temperature not exceeding 100°C, under pressure reduced to 100 mbars, sometimes in presence of polycondensation catalyst, 0.5 wt. % of organo-tin. The effective removal of about 50 wt. % of water remaining entrapped in the cutin after the extraction process was determined.

The second way consisted of a preliminary purification step in an organic solvent followed by water removal and a polycondensation process at high temperature and/or at reduced pressure.

The homopolymerization was conducted at the above mentioned conditions for between 1 and 6 hours. The preferable solvents used include, but are not limited to, distilled water, low molecular weight glycols such as glycerol, ethyleneglycol, butylglycol ethers.

After some trials, the homopolymerization process was optimized and different bioresins were produced.

Copolymerization of cutin with monomers used for conventional polyester resins was the second route to prepare a polymeric binder that could be easily manufactured using existing polycondensation reactors on an industrial scale. Another reason to use the copolymerization route was the possibility of adjusting the can coating quality by optimizing the polyester resin formulation and reaction conditions.

The copolymerisation process was performed in two ways:

A) Preparation of saturated polyester resin, in which the cutin extract represented one of several monomers together with glycols and carboxylic acids. The polymeric binders contained about 10 wt. % of cutin. The preparation of solvent-based polyester binders consisted in the copolymerization of cutin extracts in a condensation reaction, at high temperature, with conventional raw materials traditionally used in synthesis of polyester resins (dicarboxylic acids, glycols, etc), in presence of a catalyst. The reaction process was controlled by adjusting heat, stirring speed and solvent content. At the end of the synthesis process, the reaction mixture was cooled down to room temperature and diluted with a suitable solvent, such as butylglycol.

B) Preparation of saturated polyester resin, in which the cutin dissolved in an organic solvent constituted the main part of the building block in presence of glycol. The cutin extract was firstly dissolved in an organic solvent, ketone- or ethers-based, at elevated temperature, then filtration of immiscible part from solvent was performed. Then, the reaction process in presence of glycol was controlled by adjusting heat and stirring speed and applying reduced pressure in order to remove solvent and water and to reach the right viscosity/molecular weight. At the end of the reaction process, the resin was thinned using a suitable solvent or mixture of solvents such as butylglycol.

About the A) approach, several trials of copolymerization with increasing content of cutin were performed. Unfortunately, we succeeded only with the introduction of 10 wt. % of the preoligomerized cutin. Addition of 20 wt. % of cutin resulted in a rapid increase of viscosity of the reaction mixture. The obtained bulk material had a waxy appearance. Different preoligomerized cutin samples confirmed very good reproducibility of the copolymerization with 10% of extract.

Using the B) approach, the results were very interesting; in fact, the previous purification step allowed the amount of cutin in the polymer to be increased up to 80%. Some resins were produced in laboratory.

The preparation of water-born cutin-based polyester binders consisted of three steps.

The first step was polymerization (homo- or co-polymerization) processes. The polymerization process was identical to those described for the preparation of solvent-based cutin polyesters above.

The second step consisted in neutralization; the last step was dilution in water. Also in this case, some production trials were carried out in laboratory.

In the tables 3 and 4 below, some solvent-borne bio-resins produced from raw and pre-oligomerized cutin by homo or copolymerization are reported.

Cutin based resin	Process
Raw cutin 131004-2	Homo-oligomerization
Raw cutin 131004-3	Homo-oligomerization (with catalyst)
Raw cutin 131004-4	Homo-oligomerization (with catalyst)
Raw cutin 131004-6	Homo-oligomerization
Raw cutin 131004-8	Purification using Aceton, homo-oligomerization
Oligo-cutin 130801-1	Purification using Aceton, homo-polymerization
Oligo-cutin 130801-2	Purification using Aceton, homo-polymerization
Raw cutin 140129-1	Purification using water/aceton, homo-oligomerization
Raw cutin 140129-2	Purification using water/aceton, homo-oligomerization
Raw cutin 140129-3	Purification using water/aceton, homo-oligomerization
Raw cutin 140129-4	Purification using water/aceton, homo-oligomerization
Raw cutin 140129-(9+10)	Purification using MIBK, Co-polimerization with DEG
Raw cutin MIX 1407	Purification using MIBK, homo-oligomerization

Table 3 Bioresins preparation

Sample	Type of cutin	Procedure	Analysis				
			A.V. (mg KOH/g)	OHV. (mg KOH/g)	H_2O (%)	NVC (%)	Viscosity (mPa.s.)*
131004-4	Raw	Homopolymer	99	247	1.6	53	760
131004-6	Preoligomerized	Homopolymer	22	383	1.4	26	360

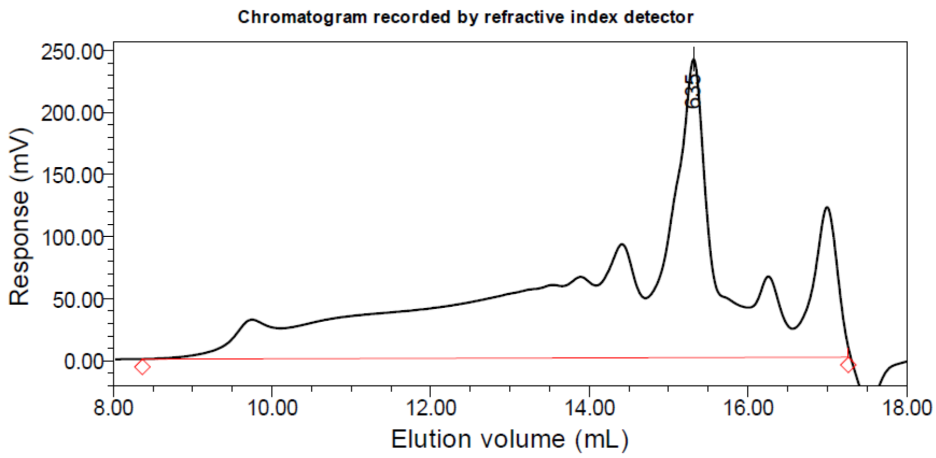
130801-2	Preoligomerized	Homopolymer	85	186	0.2	59	1300
140129-2	Raw	Homopolymer	90	199	0.6	52	1120
140129-3	Raw	Homopolymer	95	204	0.2	54	940
140129-4	Raw	Homopolymer	89	202	0.3	52	1100
140129 (9+10)	Raw	Copolymer					
1407 MIX	Raw	Homopolymer	67	263	0.8	54	1050

*(CAP, 25 °C, cone 04, 500 RPM)

Tab. 4 : Samples of bioresin prepared from raw and oligomerized cutin

Acidity (AV), hydroxyl content (OHV), solid residue (NVC) and viscosity were measured. Based on the results obtained in all the tests performed and on the assessment of the relevant lacquers, the final bioresin could be defined, from which the two final lacquer formulations were obtained and finally applied on the cans. The bioresins chosen were coded MIX 1407 and 140129 (9+10).

The homopolymerization and copolymerization reactions were selected, in order to use higher molecular weights. In particular, time and temperature of distillation in methoxy propyl acetate were increased, the latter up to 110°C. In this way, M_n, M_w of about 800, 5000 were obtained, suitable for the lacquer preparation as shown in the GPC chromatogram in Fig.13.



GPC Results

	Mn	Mw	MP	Mz	Mz+1	Polydispersity	Area (µV*sec)	End Time (min)
1	727	5133	635	26446	43983	7.06	2.62e+007	17.27

Fig.13: GPC chromatogram of the final cutin resin

The best bioresins selected for the second part of the project were obtained from purified raw cutin. In table 5, the physical properties of the selected bioresins are reported

Sample	Type of cutin	Procedure	Analysis			
			A.V. (mg KOH/g)	OH V. (mg KOH/g)	Viscosity (mPa.s.) *	Mn, Mw
140129-9	Raw	Copolymer	162	263	1078	840,5600
140129-10	Raw	Copolymer	194	254	1855	890, 7000
MIX 1407	Raw	Homopolymer	67	263	1050	727, 5133

*(CAP, 25 °C, cone 04, 500 RPM)

Table 5. Physical properties of the resins

3. Development and formulation of the lacquer

The experimental work of development of the resin was carried out in parallel with the development of the lacquer, in a continuous feedback. Starting from the developed bioresins, different formulations of lacquer were developed. Each formula was analyzed in order to study its chemical-physical properties. On the final selected formulations, hygienic characteristics were also studied.
Standard polyester resins were used as reference
In order to study the behaviour of the coating formulations before application, their viscosity, solid content and cure conditions were determined. In order to assess the properties of the applied coating the following tests were carried out.
For the assessement of the insulating and barrier properties:
- Dry adhesion
- Methyl ethyl ketone (MEK) chemical resistance;
- Water and steam sterilization resistance;
- External sterilization resistance at pH 9.5;
- Adhesion of a standard Side Stripe powder;

For the assessment of the mechanical properties:
- Sheen hardness;
- Drawing for three-piece cans;
- Drawing for aluminium lids;
- Drawing for TFS crown cork;
- W.B.T. (Wedge Bend Test);

For the assessment of the sanitary and sensorial properties:
- Colour;
- Taste and olfactory test UNI EN 10192/2000;
- Compliance with EU regulation.

In general, the developed coatings were composed as follows: cutin-based resins as main binders were crosslinked with various agents; specifically, phenolic and/or amine and/or polyisocyanate resins. The bioresin/crosslinker curing ratio was in the range from 95/5 to 65/35, calculated on solid contents.
In order to optimise the performances of the lacquers, other binders in mixture with the bio-resin were also used. To support of crosslinking, some resins were used as modifiers, such as melamine-formaldehyde. Adjuvants were used as plasticizers/thermoplastic film-forming agents or as lubricants or waxes, paraffin oils (of natural origin or from renewable sources, too). The suitable solvent phases were mixtures of different solvents or water; in fact formulations of solvent-based and water-based coatings were developed.
Starting from these formulations, several preliminary tests were performed during the assessment and selection of bioresins.
The trial using copolymerized cutin with a content of 10% of cutin in a polyester matrix did not give positive results in terms of MEK resistance, after curing with common industrial crosslinkers and, in some cases, showed also solubility problems. These data suggested poor-performance polymers, probably with insufficient molecular weights. Conversely, the trial using copolymerized cutin with a 80% cutin content (approach B) gave promising results.
The trial with the sample of homopolymerized cutin using different crosslinkers showed good MEK resistance and positive sterilization resistance in water and steam.
The application of cutin-based systems crosslinked with phenolic resin on tinplate gave films with rough appearance. This effect was not observed on the aluminium and TFS. The reason seems to be related to the presence of tin, which catalyzes the crosslinking process. The results of the preliminary trials are summarized in table 6

Properties	Formula 1	Formula 2	Formula 2	Formula 4
Appearance	Rough with presence	Rough with presence	Rough with presence	Rough with presence

	of craters and dots (---)	of craters and dots (----)	of craters and dots (-)	of craters and dots (--)
MEK resistance (double rubs)	> 100	> 100	> 100	> 100
Adhesion after drawing	100% , no breaks	100% , no breaks	adhesion loss	100% , no breaks
Ranking (1 best, 4 worst)	2	3	4	1

Tab. 6: Cutin based lacquers applied on tinplate

The best formulation was number 4, but the appearance problem on tinplate was still present. In order to overcome this problem and to optimize the lacquer different formulations with the appropriate crosslinking systems, a second series of formulations were investigated. Different types of cutin were used.

In table 7, the properties of the developed solvent-based lacquers are compared. The ratio of bio-resins with polyisocyanate to phenolic resins were optimized for each system: 70/30 by weight on solids with phenolic resin and 50/50 by weight on solids with polyisocyanate. The lacquers were applied on tinplate, TFS and aluminium sheets (Fig.14)

Properties	Formula 5	Formula 6	Formula 7	Formula 8	Formula 9
Compatibility with Polyisocyanate*	ok	ok	Negative	ok	Negative
Compatibility with phenolic resin**	ok	ok	Partially compatible	ok	Partially compatible
Appearance of the the film (cross-linked with polyisocyanate) after curing***	Bright dark gold colour, smooth to the touch	Cratering		Bright gold colour, smooth to the touch	
Appearance of the the film (cross-linked with phenolic resin) after curing***	Dark colour, Rough to the touch	Cratering	Matt appearance, dark colour	Dark colour, Rough to the touch	Matt appearance, dark colour
MEK resistance (double rubs)	>50 (for both systems)	>50 (for both systems)	>50 (for both systems)	>50 (for both systems)	>50 (for both systems)
Sterilization resistance (water/steam)	Slight Haze of film (for both systems); loss of adhesion	Blushing and haze of film (for both systems)	Blushing (system with phenolic resin)	Very Slight Haze of film (for both systems)	Blushing (system with phenolic resin)
Mechanical features (4-corner box)	Breakage on all 4 corners – suitable for 3 pieces cans (for both systems)			Breakage on all 4 corners – suitable for 3 pieces cans (for both systems)	
Comment	No confirmation of the results of the Formula 4	Negative	Negative	Promising	Negative

* Blocked IPDI-based polyisocyanate

** p.tert.butyl phenol-based phenolic resin

*** Film drying, 10 minutes at 200 ° C, applied on tinplate

Tab 7: Assessment of solvent-based bio-resin samples

Fig. 14: Solvent-based bio-resin samples

Table 8 shows the results obtained on water-based lacquer formulations

Sample	Properties	Behaviour description
Formula 10		Unusable
Formula 11	Solids content 25%, Ford 4 cup viscosity (25°C) 16 sec	No increase of viscosity; no crosslinking agent compatible; the film appearance was dark and rough; proper application starting from this viscosity is impossible
Formula 12	Solids content 30%, Ford 4 cup viscosity (25°C) 28 sec	Film appearance is dotted and rough on tinplate and no crosslinking agent was compatible with this resin. Anyway, characteristics of this bio-resin leave open the possibility of further trials and evaluations
Formula 13	Solids content 38%,	Very dense, non-homogeneous and dirty sample; unusable

Tab. 8: Evaluation of water-based bio-resins samples

Among all the formulations assessed, the solvent-based systems gave the best results using the Formula 8 samples, comparable to Formula 4 ones
On water-based resins, positive results were obtained for Formula 12.
As regards the lacquer formulation, it can be concluded that the only way to improve the appearance of the bio-lacquer on tinplate seems to be crosslinking with a high amount of polyisocyanate.
The kinetics of lacquer curing was studied by Differential Scanning Calorimetry (DSC). The analyses were performed in a sequence, on a Dynamic DSC curve (Heat Flow vs. Temperature) in order to find the minimum Temperature ($T_{100\%}$) at which a 100% degree cure was obtained, and on an Isothermal DSC curve, in order to define the time at which the cure reaction progress is almost complete, 100%.
As an example, the results obtained with Formula4 are reported below (Figg.15 and 16):

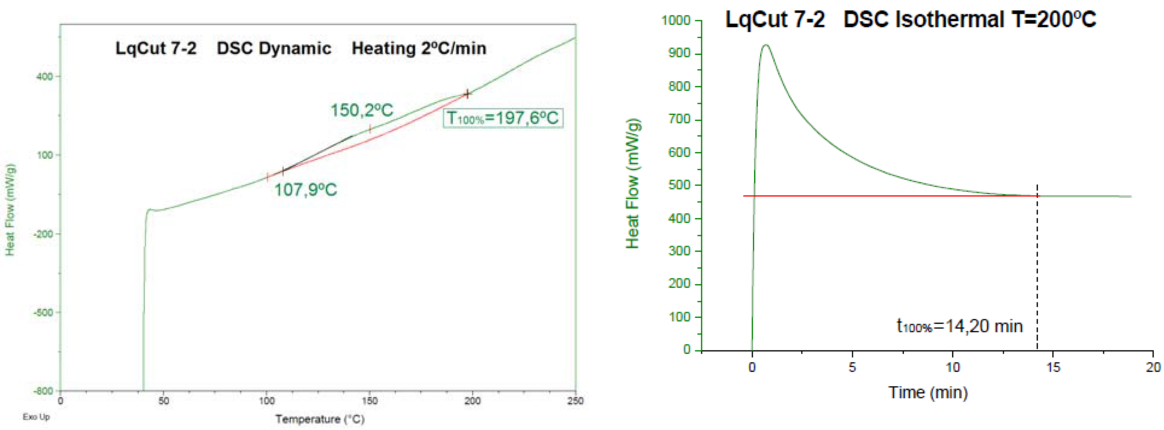


Fig 15: Dynamic and Isothermal DSC curve for LqCut 7-2

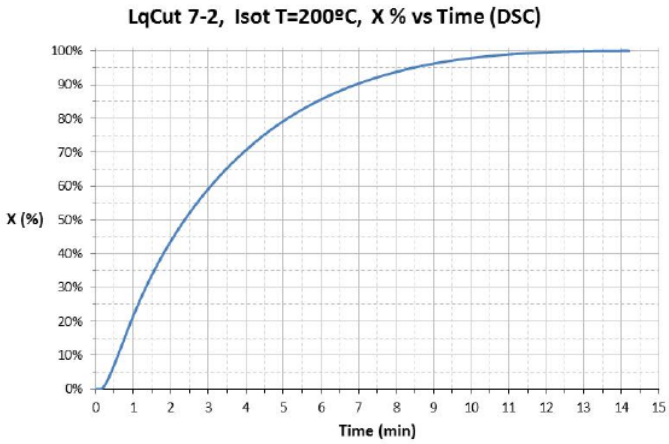


Fig 16: Reaction progress curve for Formula 4

The results obtained for some cutin based lacquers are summarized in tables 9 and 10:

Lacquer	Formula 4	Formula 5	Cutin130801-1
$T_{100\%}$	197,6ºC	199,8ºC	209,7°C

Lacquer	Formula 8	Cutin 140129 (9+10)-Isoc	Cutin 140129 (9+10)-Phen
$T_{100\%}$	195,3ºC	202,8ºC	200,9ºC

Tab. 9 and 10: Summary of results

As regards the assessment of lacquer curing parameters, it can be concluded that the curing conditions of the bio-lacquer are completely compatible with the time and temperature used to cure standard lacquers in the industrial oven. Therefore, no alterations to the standard production lines and to the related processes would be required to use the new biolacquer.

After all the preliminary trials, a second series of trials were performed on bioresins coded 130801, 140129 (9+10) and MIX 1407, produced in larger quantities. Curing conditions are shown in tables 9 and 10. The final cutin bioresin was selected and used for the final lacquer formulations, bioresins coded 14129(9+10) and Mix 1407. A formulation was developed with good performances in all tests and good sterilization resistance in the most critical conditions (Acid and basic pH, sulphuration test). It performed well also in the adherence test of a specific powder on welded side.

The final lacquer formulations were used for the application on the sheets and on the cans and were subjected to migration test to verify their compliance with the European regulations. Two different formulations were used for solvent-based lacquer, starting from homopolymerized and copolymerized cutin; for applications on all the substrates, a system with bio-resin crosslinked with polyisocyanate was defined, A1 (based on Cutin 130801-1), A2 (based on Cutin 140129/(9+10)) and A3 (based on Cutin Mix 1407). For aluminium and TFS, phenolic resin was also used (B).
One formulation was defined for water-based lacquer and applied only on Aluminium (C). The following definitive formulations were defined (extended formulations are not shown because of the pending patens):

Formulation A3 (Figg. 17 and 18) based on Cutin Mixed 1407 crosslinked with IPDI based blocked polyisocyanate
<u>Liquid lacquer</u>
Solid content (15 min at 200°C): 46 %
Ford 4 cup viscosity at 25°C: 62 sec

<u>Application on Aluminium (5-6 g/m2 of dry film, application conditions: 12 min at 200°C)</u>
Appearance of the film: dark gold colour, smooth to the touch
Adhesion on substrate: 100%
MEK resistance (double rubs): 30
Mechanical characteristics/shallow cans test: very good
Sterilization resistance (water/steam): no defect
WBT: 80 % (sufficient)

<u>Application on Tinplate (5-6 g/m2 of dry film, application conditions: 12 min at 200°C)</u>
Appearance of the film: dark gold colour, smooth to the touch
Adhesion on substrate: 100%
MEK resistance (double rubs): >50
Mechanical characteristics/4 corner-box: breakage on all 4 corners - suitable for 3 pieces can
WBT: 75 % (sufficient)
Sterilization resistance (water/steam): no defect
Sterilization resistance (acid and basic): sufficient
Sterilization resistance (sulphide staining): sufficient
Powder (ref. Mcs-0564) on welded side: very good


Figg. 17 and 18: Test using Formulation A3 applied on tinplate and on Aluminium, respectively
Formulation B (Fig.19) based on Cutin 140129/(9+10) crosslinked with Phenolic resin
<u>Liquid lacquer</u>
Theoretical solids content: 43,6 %
Ford 4 cup viscosity at 25°C: cannot be determined, but suitable for application
<u>Application on Aluminium (5-6 g/m2 of dry film, application conditions: 12 min at 200°C)</u>
Appearance of the film: dark gold colour, smooth to the touch

Adhesion on substrate: 100%
MEK resistance (double rubs): 30
Mechanical characteristics/shallow cans test: very good
Sterilization resistance (water/steam): no defect
WBT: 80 % (sufficient)

Fig. 19: Test using Formulation B applied on Aluminium

Formulation C (Fig.20) based on Cutin 140129/(9+10)
Weight (g)
<u>Liquid lacquer</u>
Solid content: 30.7 %
Ford 4 cup viscosity at 25°C: cannot be determined, but suitable for application
<u>Application on Aluminium (4-5 g/m2 of dry film, application conditions: 12 min at 200°C)</u>
Appearance of the film: dark gold colour, smooth to the touch
Adhesion on substrate: 100%
MEK resistance (double rubs): 20-30
Mechanical characteristics/shallow cans test: insufficient, to be improved
Sterilization resistance (water/steam): no defect

Fig. 20: Test using Formulation C applied on Aluminium

4. Application of the lacquer on cans

As discussed before, 5 lacquer formulations were selected for the final steps of the project, as reported in the table 11 below

Formula	Cutin type	Crosslinker	Modifier	Metal substrate
A1	Preoligomerized	IPDI based blocked polyisocyanate	Polyester resin	Tinplate/TFS/Aluminium
A2	Raw	IPDI based blocked polyisocyanate	-	Tinplate/TFS/Aluminium
A3	Raw	IPDI based blocked polyisocyanate	-	Tinplate/TFS/Aluminium/ Cans
B	Raw	Phenolic resin	-	TFS/Aluminium/Cans
C	Raw	Formaldehyde-melamin resin	Acrylic resin	TFS/Aluminium

Tab. 11: Selected formulas

Formulas A1, A2 and C were applied on metal sheets for preliminary tests, while formulas A3 and B were used for the cans manufacturing.
In any case, the lacquers were applied in laboratory and cured in an oven at 200°C for 10', as for standard lacquers in an industrial line.
Porosity, MEK resistance, appearance, dry-wet adhesion and sterilization tests showed good results for the new cutin-based lacquers. Also the mechanical properties (quarter club box) were good. The insulating properties were studied with EIS tests (electrochemical corrosion tests) The EIS measurements were done in a cell with a surface of 12.56 cm^2 exposed to the ageing solution, using a 3 electrodes setup. The EIS spectrums were recorded between 10^5 and 0.01 Hz with a logarithmic step of 7 point/decades. The measurements were performed at 70ºC (high temperature in order to perform accelerated ageing during test period) and at 37ºC (more realistic conditions). Each working day, one spectrum was recorded for each sample under investigation (up to 144h). The model solutions simulating foodstuffs utilized for the study were a salt solution at pH=5.5 in order to simulate non-acid food or food packaged with a preserving liquid such as Frankfurters or tuna in brine; a citric acid solution with salts pH=4 in order to simulate tomato-based products. The insulating properties of the new cutin-based lacquers showed by EIS tests were similar to the Standard Epoxyphenolic lacquers.
Migration tests were carried out in Acetic acid 3% (w/v), Simulant B and in Corrected olive oil, Simulant D.
The overall migration was determined in accordance with DM 21/3/73 and Reg. 10/2011 by difference of weight and subsequent treatment in chloroform in case of simulant B; for simulant D by difference of weight after extraction in hexane.
In table 12 the obtained results are reported.

	Overall migration (mg/dm2)	
Sample	Simulant B	Simulant D
A1	3.6	0.8
A2	1.9	1.1
B	0.2	5.9

Table 12. Overall Migration results

All the samples were below the overall migration limit of 10 mg/dm^2
The specific migration test has been executed on the same liquid, coming from the overall migration test. This test was performed in order to verify the cutin concentration of monomers and oligomers with a MW<1KD. The results obtained by means of mass spectroscopy analysis are reported in table 13.

The residue of the overall migration in 3% acetic solution was redissolved in THF (tetrahydrofuran) and injected in GC-MS, monitoring a mass range of 50-900 atomic mass units. The same analysis was performed even on THF as it was.
In both cases no signal was detected (therefore no component was present or was detectable in this condition).

Sample	Simulant B
A2	No migration
B	No migration

Table 13. Specific migration results

Based on the results of the sensorial test, the bio- lacquer did not cause sensorial modifications of the food product, it was inert from the sensorial point of view.
Moreover, a Risk assessment was performed; the process of cutin extraction from tomato peels was analysed in order to verify if undesired substances or degradation products could contaminate the final cutin, used as starting substance for the bioresin development. We concluded that the extraction procedure set up in the project did not cause any chemical or microbiological contamination of raw cutin, which can be thus used for the production of the bioresin after a polymerization process.
Even though it was not possible to produce the cutin-based lacquer in quantities sufficient for industrial application on tinplate sheets and for the re-protection of longitudinal weld, tinplate and aluminium cans were successfully produced in an industrial plant. Two types of cans were produced, tinplate and aluminium cans. The cans were protected with the selected lacquers. Tinplate cans were manufactured in an industrial line in Greece, while aluminium cans were made in an industrial line in Italy.
For TP cans, the process started from standard TP blanks obtained in an industrial line. Then, the blanks were lacquered in laboratory, following the curing conditions found in the industrial line. Then, from the TP lacquered blanks the cans were produced in the industrial line. The cans were produced with standard 19 beads. At the end of the process, the internal surface of the body was acceptable and completely comparable with standard cans. It did not show any macroscopic defects, pores or discontinuities of the lacquer, but only microscopic scratches on the top of the beads, that remained substantially unchanged during canmaking. For Al cans, the process started from aluminium sheets 21x29cm obtained in an industrial line. Then, the sheets were lacquered in laboratory, following the curing conditions found on industrial line. Then, from the Al lacquered sheets, the cans were produced in an industrial line. The cans were produced with two capacities, 90 and 120ml. Table 14 summarizes the characteristics of the cans (Figg. 21 and 22)

Metal substrate	Lacquer Formula	Lacquer weight (g/m^2)	Can nominal capacity (ml)	Can type	Can ends	Number of cans
Tinplate	A3	6-7	500	3 pieces	Standard	200
Aluminium-1	A3	5-6	90	DRD 2 pieces	-	10
Aluminium- 2	B	5-6	90	DRD 2 pieces	-	5
Aluminium-3	B	5-6	120	DRD 2 pieces	-	5

Tab. 14: Characteristics of the cans

Fig.21 Three-piece cans

Fig.22 DRD two-piece cans

Before filling with the food products, the cans were analyzed and some properties were checked, such as lacquer adherence, porosity, mechanical resistance and migration. The mechanical properties, hardness and resistance to axial and radial loading were acceptable and in compliance with the specific rules. Also the profile of the beads of the can body of the 0.5Kg cans was in line with the standard. The size of the aluminium cans agreed with their nominal capacity.

Dry adhesion of the lacquer was excellent in all cases, both on flat surface and in the beaded area. For 2-piece cans, dry adhesion was excellent for both types of drawing ratio. This proved that even the flexibility of the lacquer was optimal in all cases.

The values of WACO porosity, relating to the metal exposed, was very high and out-of- standard for all samples with the exception of the DRD (2-pieces) can with formula A3. This was indicative of the defects of the organic coating and probably did not depend on the lacquer's characteristics, but on the manual application system in laboratory. This application inevitably leads to defects, such as pores, discontinuity, presence of foreign particles, lacquer accumulation (not present in the industrial application), which are reflected in the porosity values of the organic coating. The porosity was limited to the lacquer and did not affect the tin coating. In fact, the value of IEV porosity, specific for the steel base, was very low.

Porosity WACO (mA/can): 169.6

Porosity IEV(mA/can): <0.001

The small scratches observed on the lacquer and oriented along the circumference of the can were well correlated with these results. The high porosity (WACO) may cause corrosion phenomena during the pack test. The thermal resistance of all the samples was good, no absorption of water was observed.

On the whole, the results were satisfying.

Overall and specific migration tests, as well as residual monomer tests based on the applicable legislations, were carried out on the cans. Moreover, specific migration tests were carried out on the food.

All the results obtained on the cans complied with the European and National Regulations, in terms of compliance with the overall and specific migration limits in the different simulants used, A, B and D and in the food products, processed tomato and crush tomato. The results obtained on the cans confirmed those obtained on the lacquered sheets. Therefore, the can manufacturing process did not modify the lacquer properties. Moreover, being in contact with the food product and the thermal treatment did not influence the lacquer migration.

Specific migration values in the foodstuff were within the standard, despite a certain contribution of standard lacquers applied on the can ends. Furthermore, the results of the analysis of the degradation product of the cutin lacquer did not show any presence in the simulants of critical molecules with MV<1KD (table 15)

	Overall migration		
Sample	Simulant A (mg/Kg)	Simulant B (mg/dm2)/(mg/kg	Simulant D mg/dm^2
A1-sheet		3.6	0.8
A2-sheet		1.9	1.1
A3-can	2.8	/4.9	0.8-1.9
B-sheet		0.2	5.9

Tab. 15: Overall migration results

The sensorial properties of the cans were within the standard range. Also in this case the can manufacturing did not modify the inertia characteristics of the lacquer. This was a very good result and not taken for granted, as one of the difficulties in the use of biopolymers is linked to anomalous flavours and tastes. The first results on the lacquered sheets were confirmed on the cans; that means that the can-making process did not modify the lacquer characteristics.
The cans produced with the bio-lacquer, together with the reference ones, were filled in an industrial line with the different products described in table 16 (Figg.23 and 24). Afterwards, the cans were stored at SSICA premises, at 2 temperatures, 20° and 37°C. Aluminium cans were filled and stored at SSICA premises.

Fig.23 Cans filled with crushed tomato

Fig.24 Cans filled with tuna in oil

At pre-set times, some BIOCOPAC cans for each batch and storage temperature were opened and analysed.

	Food product	**Number of cans**	**Storage Temperature °C**	**Time of control (days)**
Tinplate cans	Crush tomato	20	20 and 37	0; 15; 30
Tinplate cans	Elaborated tomato2	22	20 and 37	0; 15; 30
Tinplate cans	Tuna in oil	14	20 and 37	0; 15,
Tinplate cans	Tuna in brine	8	20 and 37	0; 15,
Aluminium cans	Citric model solution	3	37	4
Aluminium cans	Cystein model solution	2	37	4

Tab. 16: Number of cans and storage conditions

The results of the pack test were acceptable. The behaviour of the cans in contact with different kinds of foodstuff was good enough after 1 month/15 days of storage at 37°C and it did not show loss of adherence or solution absorption. The resistance to the thermal treatment was good.
Nevertheless, for the reasons described, the pack test was limited in time and electrochemical corrosion processes appeared limited. In fact, the iron content remained almost unchanged vs. time zero, both at 20°C and at 37°C. The tin content was below the detection limits and this confirmed that the lacquer adhesion was excellent and that the detinning corrosion was very limited. Only in the case of cans filled with more elaborated tomato products after one month, the tin concentration slightly increased. This was probably due to the presence of basil, thyme, oregano, spices rich in nitrates, which are known accelerators of tin corrosion. Even the visual examination did not show particular corrosion phenomena; ranking from 0 (no corrosion) to 5 (intense corrrosion). The decrease of the vacuum, even if in some cases was below 100 mmHg, which could be associated to the corrosion of the steel base, seemed to depend more on the conditions of packaging and on the type of product than on corrosion phenomena.
The intense sulphuration observed both in oil and in brine was correlated to the low vacuum degree and to the absence of zinc pigment in the lacquer. Both parameters were independent from the properties of the cutin-based lacquer. The lacquer did not undergo chemical changes in contact with oil or brine, as the results of the cans packaged with preserving liquids without tuna showed.
The trends discussed are illustrated in the graphs of figures 25 ÷ 27.

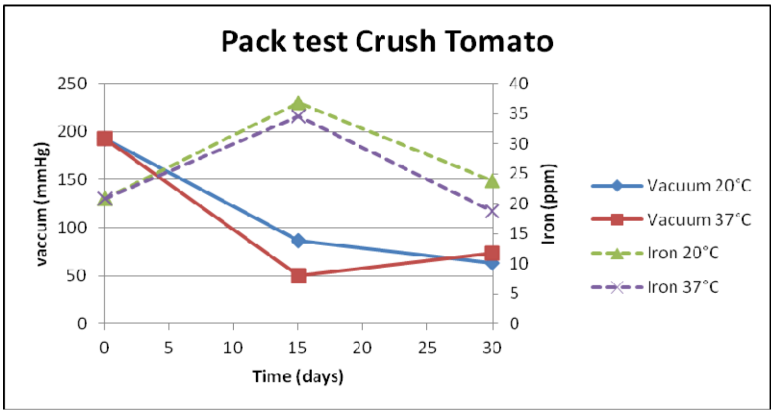


Fig.25:Vacuum degree and iron concentration over time

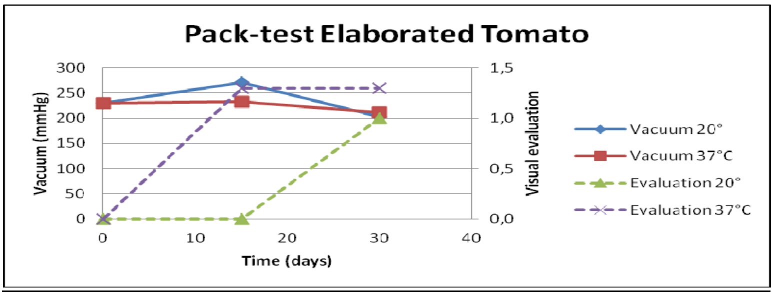


Fig. 26: Vacuum degree and visual examination over time

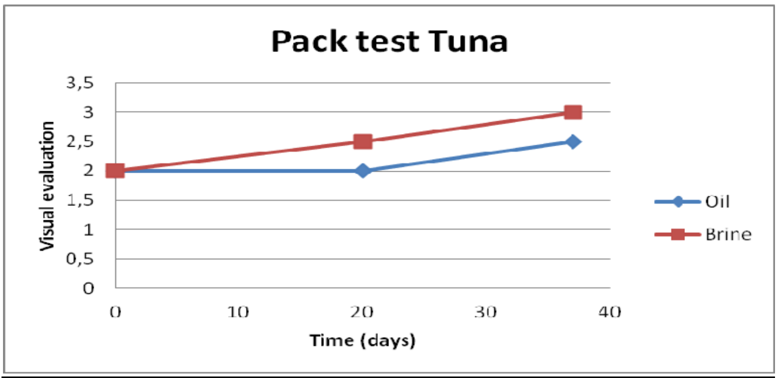


Fig. 27: Visual examination over time

The results obtained, while referring to a very short contact time, were indicative of a lacquer with good adherence and good resistance to corrosion and to thermal treatment.
As regards the aluminium cans, their behaviour in contact with the model solutions again reflected the results of porosity, which was much lower for A3 samples. In fact, after contact with both the cysteine solution and the citric solution, A3 cans showed no points of corrosion.
The aluminium cans showed loss of adherence in the flange area, while for all other cans adherence was good and no evident corrosion was developed. Loss of adherence in the flange area was due to the use of model solutions, which are more aggressive than the foodstuffs.
Overall, also the aluminium cans showed acceptable behaviours and the bio-lacquer resistance to the thermal treatment was good.

5--Life cycle assessment

Life Cycle Assessment (LCA) was carried out using the SimaPro software, version 7.1. The analyses compared the LCA of a conventional epoxy-based lacquer to a bio-lacquer, tomato cutin based, obtained from tomato processing waste. The results showed clear environmental benefits of the "Bio-lacquer". The benefit of the cutin lacquer lies mainly in the saving of natural resources and in the recovery of part of the skins. This can lead to lower consumption of fossil fuel and lower CO_2 emissions (Fig.28).

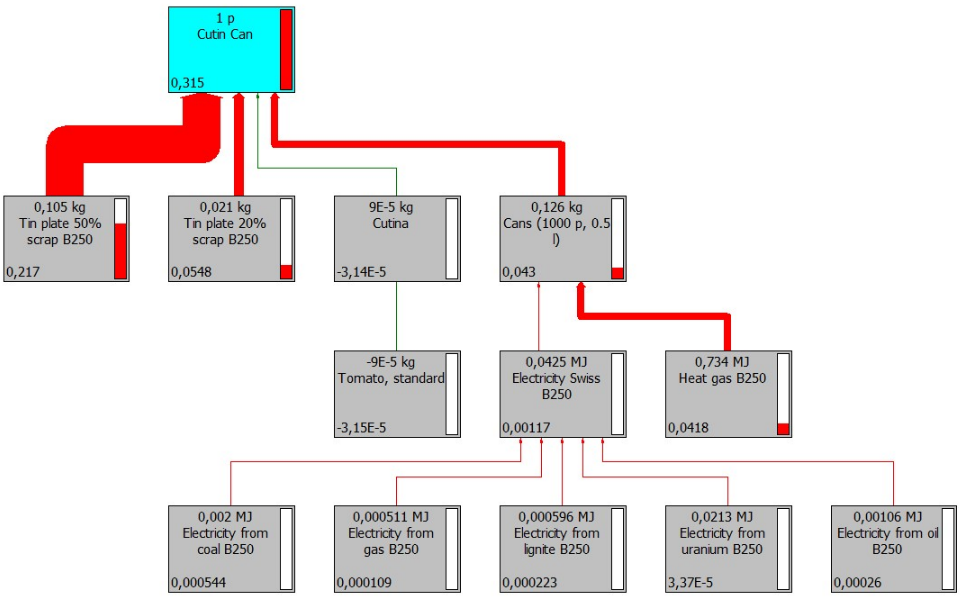


Fig. 28 Carbon dioxide emission for a Cutin can

Table 17 refers to the contributions to the formation of CO_{2eq} in the case of a bio-lacquer cross-linked with phenolic resin (90/40 mg/can).
It should be noted that the analysis was carried out considering an experimental process, partly carried out in the laboratory, which was discontinuous and with several critical points. Scaling up the production process to an industrial level will certainly reduce the consumption of solvents and energy, leading to a further improvement of the positive environmental effect of the BIOCOPAC lacquer.

Process	Conventional can	Cutin lacquered can
Tinplate 50% scrub	217 g	217 g
Tinplate 20% scrub	54.8 g	54.8 g
Epoxy resin I	99.3 mg	
Phenyl formaldehyde	20.8 mg	20.8 mg
Cutin		**- 31.4 mg**
Can process	43 g	43 g

Tab. 17: Contribution of CO_{2eq} emissions in Case 90/40 (mg/can) cutin/phenol resin

Improvements are more evident scaling up from a single can to the daily or annual output, and thus to the actual placing on the market of the containers.
For example, an average company manufacturing lacquer produces 30,000 tons/year. If in an initial phase of project development at least 4,000 tons/year are replaced with lacquer derived from tomato, the savings of CO_2 will be 2.0 tons/year.

Conclusions

The extraction process of cutin from tomato peels has allowed a monomer/oligomer product to be obtained, whose main component is 10,16 dihydroxyhexadecanoic acid, with characteristics that are suitable for the bioresin preparation and for the subsequent lacquer. The lacquer has been developed using different crosslinkers and modifiers. On the basis of several tests, two formulas have been selected, one for tinplate and the other for all metallic substrates (TP, TFS and Al). After a series of tests to assess the properties of the lacquer applied to the substrate and the ideal curing conditions (time and temperature), 3-piece tinplate cans and 2-piece aluminium cans were produced in an industrial line. The cans have been filled with four kinds of food products in an industrial line and with simulant solutions in laboratory. The pack test that followed had a limited duration, but the results obtained were interesting and promising. The lacquer showed good properties of adhesion, flexibility and corrosion resistance, even at storage temperature of 37°C and, however, comparable with those of standard lacquers. This allows a shelf-life of at least 15 months to be expected. It goes without saying that, before commercialization, a check of the results on a large scale would be required.
On the basis of the migration tests and of the risk assessment, it can be stated, that the lacquer complies with the Italian and European legislations. Finally, a very interesting result was the strong decrease in the environmental impact, in particular In CO_2 emissions, as highlighted by the LCA analysis.
It can be concluded that the possibility of obtaining a lacquer valorising tomato wastes is now a reality. This agrees with the principles of the Circular Economy Systems (Fig. 29), as shown in Fig. 30, where cans filled with tomato products are produced starting from tomato wastes.

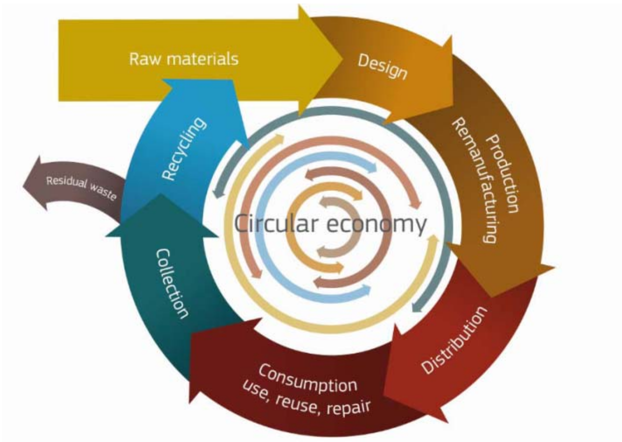


Fig.29: Towards a circular economy: A zero waste programme for Europe. Communication from the European Commission to the Parliament

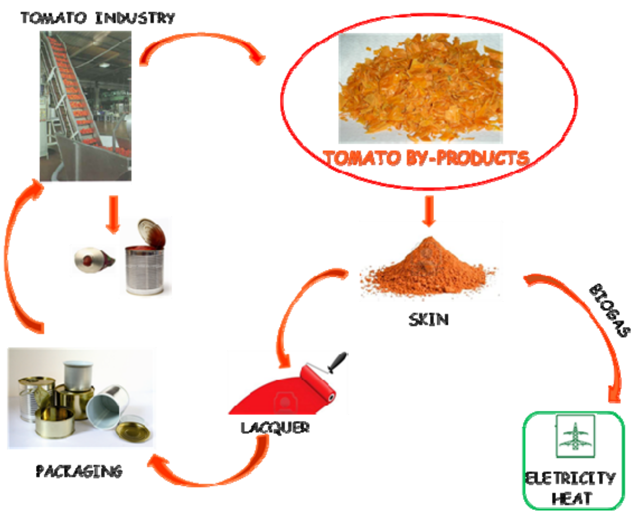


Fig.30: From tomato wastes to tomato cans

Impact

The great interest aroused by the project, both at a scientific and industrial level, is evidence of its potential.

The achievement of the BIOCOPAC objectives can certainly have a positive impact on the whole agro-industrial supply chain, from farms to large retailers, through lacquer and packaging manufacturers all the way to consumers. The acquired foreground and eco-innovation provide BIOCOPAC industrial partners with an essential time-to-market advantage over competitors in the lacquering and packaging sector. BIOCOPAC partners will be better prepared for new markets and products and, thus, will have a positioning advantage on competitors. The first industrial production line could be scheduled within the 3 years following the project completion. Furthermore, the acquired knowledge allows the scientific partners of the research to develop other studies and projects in the bio-lacquerer domain fostering cross-fertilization.

-The project can provide tomato farmers and tomato processors with advantages in terms of value given to their own processing wastes and the subsequent reduction in disposal costs. It should be considered that, in Europe, this industrial sector comprises over 3,000 processing firms and that more than 10 million tons of tomatoes are processed into tomato paste, ketchup, etc., resulting in more than 200,000 tons/year of solid tomato residues (peels and seeds).

For instance, in Italy over 6 million tons of tomatoes are processed every year (6.4M in 2011), with processing waste easily exceeding 2% of production (about 160,000 tons in 2011) and a disposal

cost of around €4.00 per ton (for transport). Every year, the disposal cost of all Italian tomato waste comes to over €600,000.
The BIOCOPAC project can reduce this cost, valorising tomato by-products. The project has proven that it is possible to separate tomato skins from tomato seeds by means of an efficient and simple method and that tomato waste can be stored during the tomato campaign and used during the rest of the year for cutin extraction. This would be an undeniable advantage for continuous exploitation of the plants. Moreover, the project has also proven that the waste remaining after cutin extraction can still be used for the production of biogas. This means that a double valorisation of tomato waste is possible, first for the extraction of a molecule with high-value added and afterwards for biogas production. Thanks to the BIOCOPAC lacquer, tomato processing industries can reduce costs, obtain benefits and increase profits. The project does not take into consideration other types of vegetables, but it can enable waste treatment companies to assess the economic feasibility of valorising other types of waste in the same way, since cutin is a component of the leaves and fruits of several plants.
Moreover, the European tomato industry would benefit from the project also at the finished product stage, for the use of more eco-friendly packaging, that is to say, metallic cans protected with cutin-based lacquers.
- With the new bio-lacquer, the chemical industry can use and exploit a raw material that is less expensive and less influenced by geopolitical conditions. Moreover, if this new procedure of bioresin preparation is used, emissions into the atmosphere would be reduced and the workplace would be safer, since the cutin extraction procedure does not require the use of organic solvents and dangerous substances. The bio-lacquer synthesis requires no specific equipment or reagents other than those generally used for traditional lacquers. This means that bio-lacquer preparation requires no additional costs and that all the equipment already used for traditional lacquers can be easily used for the new bio-lacquer.
In addition, the bio-lacquer curing conditions are fully compatible with time and temperature used to cure the standard lacquers in the industrial oven. Therefore, no alterations to the standard production lines and to the related processes would be required. The economic relevance of this is undeniable.
- Using the new bio-lacquer, packaging manufacturers would be able to supply more easily recyclable containers, since the use of natural lacquers causes fewer difficulties and fewer pollution problems at this stage. Furthermore, it must be borne in mind that the project can make this industrial sector more competitive than the chosen benchmark, i.e. plastic packaging, in that it makes it possible to produce a lacquer of natural origin and to supply green metal packaging for foodstuffs. Given that, in the mind of the public, the chemical industry is held accountable for many environmental disasters, the improvement in its image resulting from the use of natural products should not be overlooked.
-The production of a natural BPA-free lacquer would undeniably be an advantage for the whole agro-food chain, and mainly for consumers. Lacquer manufacturers would be able to make a product, which can be considered safe, eco-friendly and absolutely BPA-free, thus overcoming the problems of migration of dangerous synthesized substances from the lacquer into the food. Where used, the new BPA-free lacquer would also allow products to be exported to France, where, in 2012, a very restrictive legislation banning BPA from January 2015 onwards was approved. This Decree Law is creating an internal trade barrier and an imbalance between French food manufacturers and foreign competitors, since food manufacturers have to reformulate their products if they want to compete in the French market. The BIOCOPAC project can give a clear and precise response to this problem, providing many food industries and large-scale retailers with BPA-free packaging. The solution provided by the BIOCOPAC project to the BPA problem is concrete and feasible; the costs of the new lacquer would be equivalent to those of traditional lacquers.

- The use of this eco-friendly lacquer obtained from processing tomato waste would help reduce the carbon footprint and achieve greater resource efficiency by substituting epoxy-based lacquers and increasing the use of secondary raw materials.
The results of the LCA study, performed on the new BIOCOPAC lacquer, have shown a clear environmental benefit. The benefit of the cutin lacquer lies mainly in the saving of natural resources, in the recovery of part of the skins, as well as in the lower consumption of fossil fuel and lower emissions of CO_{2eq}. The study showed that, for a single can, it can decrease CO_2eq by 131mg. Improvements are more evident scaling up from the single can to the daily or annual output, and thus to the actual placing of the containers on the market.
The benefits of BIOCOPAC become evident if one considers that a medium-sized lacquer manufacturer produces on average 30,000 tons/year. If, in an initial phase of project development, at least 4,000 tons/year are replaced with lacquer derived from tomato, the savings of CO_2 would be 2 tons/year. On the other hand, considering availability, at a European level, of an average of 200,000 tons of waste, the savings of CO_2 cannot but improve and increase, with an industrialization of the extraction method extended to all tomato industries and biorefineries, which produce and treat this waste.
-The results of the project agree with the EU social objectives by providing substantial benefits in line with the EU policies for the environment and health protection, since, where used, they would significantly contribute to the safeguarding of both the environment and the health of workers and consumers (Fig.31).
Any change that has a positive impact on food quality is of relevance to all European Government agencies.

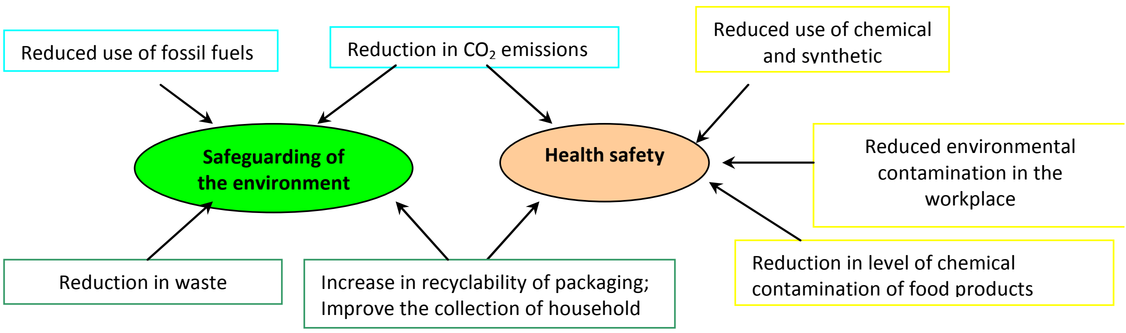


Fig. 31: Environmental and health benefits

BIOCOPAC also complies with the framework directive on waste (2008/98/EC), which has introduced the notion of sub-product – as opposed to waste - and with the principles of Circular Economy Systems (Communication from the Commission to the European Parliament, July 2014). By contributing to the strategies for sustainable development of the food industry, BIOCOPAC is fully aligned also with the scopes and ideas of the Food for Life platform and its Strategic Research Agenda. The project achievements go in the direction foreseen also by the renewed European Sustainable Development Strategy (EU SDS), which identifies Sustainable Consumption and Production (SCP) as one of the key challenges to be addressed in the context of the EU's long-standing commitment to meet the challenges of sustainable development.
The project contributes with effective solutions to reassert Europe's ability to autonomously design and manufacture products that are representative of strong cultural and environmental values and of manufacturing excellence. The possibility of producing an innovative and green can is a great opportunity for the entire industry of reference to re-launch this type of material, to make it more competitive than other materials and to gain a new market share for it. Since the production of tinplate and metal cans is growing steadily in other countries (from which Europe imports),

especially in Asia (China, India, Malaysia and Korea) and South America, the innovative impact of the project can be significant also outside Europe.
Moreover, the project has proven that not only can the new bio-lacquer be applied on metal food packaging, but also on packaging for sectors other than the food one (e.g. aerosol, general line, cosmetics, medicine). Therefore, where used, BIOCOPAC would enable SMEs to improve their competitiveness with respect to other types of packaging and to increase container recyclability.
- By using the new lacquer, he preserving industry and large-scale retailers would be provided with environmentally-friendly and safer packaging, highly appreciated by consumers and of considerable marketing appeal for large retailers.
The preserving industry would be able to promote eco-friendly products, which help reduce CO_2 emissions and help improve the environmental impact; in this way, even consumers would become more aware that buying non-petrol-based products and packaging is now actually possible.
Furthermore, it must not be forgotten that, at present, metal packaging, albeit far more ecological than other types of packaging, is perceived by consumers as having a high degree of non-freshness.
The high environmental content of BIOCOPAC packaging can and must be clearly stated and recognizable through the presence of a green label on each can and in each document. This trademark can be exploited by the food industry and by large retailers as a market penetration tool to consumers, who are always very sensitive to the environmental issues.

According to the BIOCOPAC strategy, the dissemination activities have been carried out mainly thanks to the following instruments:

- BIOCOPAC Logo
- BIOCOPAC brochure
- BIOCOPAC web site
- BIOCOPAC video clip
- Dissemination events and initiatives at European and National levels
- Specific dissemination activities at conferences, papers and posters
- Press releases and media coverage

The Key messages on the project, which have been communicated during the dissemination activities, are:

- ✓ The novel lacquer has been originated from processing by-products of the tomato industry, offering alternative strategies for waste utilization, in accordance with Directive 2008/98/EC.
- ✓ Re-utilization of processing by-products from the tomato industry. Extraction of the bio-resin from tomato peels using environmental-friendly methods only.
- ✓ Formulation of a natural lacquer to be applied to metal packaging for food products with chemical-physical properties comparable to those of conventional ones and usable in present-day industrial plants.
- ✓ Production of a natural lacquer that safeguards consumers' health and respects the environment.
- ✓ Production of an innovative metal packaging for food products, so as to increase the competitiveness of metal packaging compared to the plastic one.
- ✓ From tomato to tomato: a metal can for tomato products with a lacquer made from tomato wastes

In order for BIOCOPAC to be easily recognizable as the main Project on bio-lacquer for food packaging application, it was imperative to build a strong corporate image, brand and style. A first version of the Logo was designed at the beginning of the project, by a raw arrangement of the FP7 logo and the BIOCOPAC title, slightly stylized. Subsequently, a more suitable Logo has been designed, in order for it to be more consistent with the core strategy of the BIOCOPAC project (figure 32).

Fig. 32 BIOCOPAC logo

During the first months of the project, a brochure (Fig.33) has been developed to introduce and present the BIOCOPAC project and to publicize its main objectives. The brochure has been presented in all the events (e.g., conferences, workshops, etc.) which the BIOCOPAC Consortium or its single partners have attended and printed copies have been made available at the project stand. The brochure describes the Consortium partners and provides their main contact details, as well as the general and technical objectives of the project. The brochure is well-fashioned, user-friendly, compact and easy to understand.
During the first months of the project the website (Fig.34) was also prepared, discussed and agreed on by all the project partners (www.BIOCOPAC.eu). The website has been periodically updated thanks to the contributions (publications, meetings, documents, etc.) and suggestions from the BIOCOPAC partners. The website is characterized by two interfaces, one is public and the other is private.

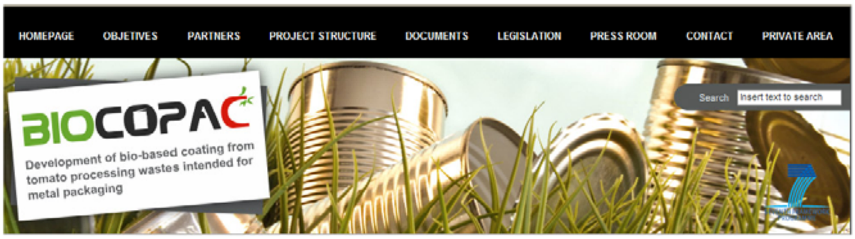


Fig 33 BIOCOPAC brochure Fig. 34 Header of the website

First, summary information about the project has been published in the public area, plus information on all the events/conferences attended by the BIOCOPAC partners. The website has been continuously used as the main dissemination tool, covering the project's goals, objectives, accomplishments, background information and partners' roles and contributions. In addition, it has run parallel with the project evolution, in order to provide timely and appropriate information, and, therefore, it has been regularly and constantly updated and maintained. In particular, the "Press Room" section of the website has always been updated and all news, events on and references to the project have been uploaded.
The BIOCOPAC website has been periodically analyzed using Google Analytics dashboard, in order to measure the number of website hits, the number of visitors, the number of pages visited, the duration of the visit and even the country and cities from where the BIOCOPAC website has been visited. The website received about 3,000 visits, with a growing trend. Visits at the BIOCOPAC website have registered a peak after the EU Open Doors and afterwards the number of visits has remained quite constant and stable. The number of new visitors is much higher than the number of returning visitors. Each visit has an average duration of more than 2 minutes, a time that indicates not a superficial and perfunctory visit, but a deeper interest towards the project. Italy and Spain are

the countries with the highest number of visits and Parma and San Sebastian are the cities from where the highest number of visits was made.
For the dissemination activity, the BIOCOPAC Project video (Fig.35) was made and it is now available on the public website and on the BIOCOPAC channel on You Tube (URL: http://www.youtube.com/user/BIOCOPAC or Click the link: http://www.youtube.com/watch?v=Vz5nCGWKqq0).

Fig. 35: the BIOCOPAC Project video

The project partners have shot other videos and interviews recorded by local televisions in the partners' Countries. For example, a video has been broadcasted by the Spanish TV, disseminating the objectives of the BIOCOPAC project. (http: // www.youtube.com/watch?v = MBz0DswUZwc&list=UU-4t4BqjCB2DaK3SXdPLrAw&index=12&feature=plcp)
A reportage about the BIOCOPAC project was made by the multilingual news television channel Euronews. The reportage was shot in different locations, in Italy at the RODOLFI plant, SSICA laboratories and SALCHI plant and in Greece at NCH plant, in order to film the main phases of the lacquer production from tomatoes to the manufacture of cans.
Finally, a BIOCOPAC green label has also been prepared, discussed and agreed on by and between all partners. The green label uses the same colours as the BIOCOPAC inscription and it contains the project key-message: a new, eco-friendly and sustainable metal can. The green label has not been registered yet, but it is ready to be submitted.
Another main tool to disseminate the BIOCOPAC results is presenting them at Conferences and Workshops of scientific/industrial or applicative interest.
BIOCOPAC participated in different congresses in Europe, such as the 10th TP Conference in Barcelona (Spain), in November 2012, the 6th Food Technology International Symposium in Cartagena (Spain), in October 2013 and the Metpack Conference 2014 in Essen (Germany), in May 2014. Not only has this dissemination activity been carried out in Europe, but also in some developing countries, such as China, which is a large-scale tomato producer. In fact, the BIOCOPAC project was successfully presented at the Green Industrial Coating Asia 2013, which took place in Shanghai on 24-25 September 2013. In all these Conferences the BIOCOPAC project results were presented and some preliminary packaging items, on which the new lacquer was applied in laboratory, were shown. Some posters were prepared reporting the project objectives and were displayed at the events, e.g. conferences, trade fairs, where the project was featured.
The public has always shown great interest in the project idea, as well as in its development and preliminary results, especially in China. In all these Congresses, the project was presented to the scientific and industrial audience and, after the presentation, many requests for further information were made by specific packaging and chemical companies.
The Festival of Europe was an interesting and significant event in which BIOCOPAC was selected to participate. To celebrate Europe Day, every year in early May, EU institutions open their doors to the public in Brussels and Strasbourg. Local EU offices in Europe and all over the world organize a variety of activities and events for all ages.
Each year, thousands of people take part in visits, debates, concerts and other events to mark the day and raise awareness about the EU. In 2013, the BIOCOPAC project was selected from among

all European projects to take part in the EU Open Doors event on 4 May 2013, as an example of successful EU-funded research project, together with other selected European projects.
Some specific tools for the dissemination activity were for this particular event: a stand for the project presentation, a poster to display the project and its first results, samples of tomato skins, cutin extracts, bioresin and bio-lacquered cans, in order to show all the chain from tomato to cans, brochures, bookmarks that were customized with the project logo and pralines that were customized with the BIOCOPAC inscription (Fig.36). This event allowed the project to be promoted to a wider audience, not limited to the scientific community, but including also the general public. The people present showed a real interest in the project, since they saw the new lacquer as a green, natural and safer packaging solution.

Fig. 36 : BIOCOPAC stand at the EU Open Doors 2013

This event allowed us to make the project known to a wider audience, both sector-insiders and not. In fact, since this event, the requests for information about the BIOCOPAC project have greatly increased in number.
Another important tool for the dissemination of the BIOCOPAC results is the publication of papers in journals, magazines and newspapers, both scientific and general interest ones. The strategy was to present the outcomes of the BIOCOPAC project to journals and reviews related to specific issues within the scope of BIOCOPAC research activities.
The BIOCOPAC partners published some papers on international journals, since they received several requests for articles from many journalists of different nationalities. Therefore, the list of all the articles about the BIOCOPAC project is very long. Many articles about the BIOCOPAC project have been published, not only in the languages of the project partners, but also in other languages. The BIOCOPAC project has obtained many references in English, Italian, Spanish, French, Czech, Slovakian, Russian, Polish, German and Bulgarian. In particular, it has received many requests for articles and interviews from French journalists, due to the problem of BPA that, in France, will be banned from January 2015. A telephone interview was released by the project coordinator to a French Press Agency. It is important to highlight that, after this interview, many articles have been published on many French newspapers (Le Parisien, La Croix), and the project has been cited in many articles and websites specific to the packaging field. This contact has proved a very interesting platform to promote BIOCOPAC all over the world.
Moreover, not only have articles about the BIOCOPAC project been published in scientific journals, but also in general-interest magazines or very important economic newspapers, such as “Il Sole 24 Ore”.
Many people contacted the partners to have information on the project and were not only journalists or scientific editors, but also some research dissemination agencies, specializing in providing strategic advice and ongoing intelligence on emerging technologies; these agencies have offered their services for the BIOCOPAC project. In particular, an agency asked us to insert the

BIOCOPAC project in its research database, while another agency proposed us a contribution to finance the industrialization of the project.
Even some trade associations, such as for example the Italian metal packaging association or the association of European metal packaging producers, have shown an interest in the project and they have followed the project development with particular attention, discussing about the BIOCOPAC project in their internal meetings. ANFIMA (the Italian association of can manufacturers) even published an article about BIOCOPAC in its internal magazine to present the project and its development.
The dissemination of the project results has been performed in a successful way, considering all the work done and all the articles published, as shown by the interest from the media and consumers, in the press and at fairs.

Next to the dissemination of the project results, exploitation of the BIOCOPAC achievements is of crucial importance. Very important results of such exploitation certainly are the two patents that have been applied for by the project partners. The two years of research work have resulted in the application for two patents, one regarding the innovative method for cutin separation and extraction from tomato processing waste and the other for the manufacturing of the cutin-based resin and the subsequent cutin-based lacquer. The cutin extraction method has been developed by two leading research centers that are project partners and expert in food technology applications and the relevant patent has been applied for by two SMEs, also project partners, which are an innovative bio-refinery and a tomato preserving industry. The preparation and formulation of cutin-based resin and lacquer have been developed by three research centers that are project partners and expert in food technologies, in polymeric materials and in industry-financing solutions and a SME, a lacquer manufacturer; the latter has also applied for the patent on the developed formulation and preparation method. The two patents have been applied for at a national level and the one on the extraction method has also been extended and applied for at an international level. Both patents are currently under evaluation; the first evaluation of the patent on the extraction method was favourable.
The SMEs have promoted, for commercial use, the new type of packaging, its environmental and health advantage and this new way to use the tomato wastes, to farmers, customers and consumers and their associations. In this way, they are obtaining commercial and marketing advantages over their competitors in the market. In particular, the SME Salchi has received many requests for information on the new lacquer, especially requests about the time-to-market expected for the new bio-lacquer.
Principally, they addressed the following groups of interest:
- the scientific community, to which the results have been presented by means of scientific papers or of specific conferences in Italy, in Spain and in German;
- metal packaging producers, can manufacturers;
- users of packaging, food preserving industry and large retailers;
- consumers and their associations

A successful outcome of the BIOCOPAC project has been the interest demonstrated by the Italian partners of the project who intend to continue the project and try to industrialize the extraction process and the lacquer production through another European project. Therefore, in June 2013 a proposal under the European call “Life+ 2007-2013” was submitted and approved. A new project, called BIOCOPACPlus (LIFE13 ENV/IT/000590 LIFE BIOCOPACPlus), started on 1 June 2014 and it will last for the next three years. Therefore, the research work about cutin extraction and cutin-based lacquer will continue and the industrialization of all the extraction process is the final goal of this new project. To achieve this objective, the Italian partners of the BIOCOPAC project have included an Italian company, a market leader in the construction and design of food processing plants, in this new project. The prototype pilot plant for cutin extraction will be assembled and constructed at a tomato wastes treatment farm, which has also a biorefinery for the treatment of vegetable wastes.

Moreover, concomitantly with the interest expressed by the Italian partners, some multinational companies have also contacted the Consortium to ask for further information on the process and to investigate the possibility to cooperate in order to industrialize the procedure. In particular, some multinational companies operating in the manufacturing of food packaging, beverage solutions and infant food products have expressed their interest in this new process.
It is to be highlighted that these leading multinational companies want to solve the BPA problem with a solution that focuses on sustainability and valorisation of industrial waste.
Finally, not only multinational companies have shown interest in the BIOCOPAC project, but also other professionals in the lacquer field, who do not belong to the industrial world, have requested information on the new lacquer and the possibility to use the new lacquer for their painting. Painters coming from Brussels and from England were interested in testing the new lacquer.
The interest and positive feedbacks generated by the successful BIOCOPAC results highlight the present pent-up demand within the packaging industry for sustainable material technology solutions.
The BIOCOPAC results acquire even greater importance considering the possibility to apply the new bio-lacquer for packaging other than the food one, such as aerosol, general line or multilayer; the impact and the results of the project can extend to a wide range of sectors of interest.

Relevant contact details :

Public website address : **http://www.biocopac.eu**

SSICA (Experimental Station for Food Preserve Industry)
Viale Tanara, 31/a 43100 Parma ITALY
Project Coordinator: Angela Montanari: angela.montanari@ssica.it
http://www.ssica.it

SALCHI METALCOAT S.r.l.
Viale dell' Industria 3A-3B**,** 20875 Burago Molgora (Monza Brianza) ITALY
http://www.salchimetalcoat.com
Sebastiano Brenni: sebastiano.brenni@salchirh.it
Paolo Brenni: paolo.brenni@salchirh.it
Luca Cioni: luca.cioni@salchirh.it
Valter Orlandi: valter.orlandi@salchirh.it
Mariarosa Biaggi: mariarosa.biaggi@salchirh.it

CTAEX (Centro Tecnologico Agroalimentario Extremadura)
Villafranco del Guadiana a Balboa, Km1,2 06195 Villafranco del Guadiana – Badajoz SPAIN
http://www.ctaex.com
Rosa de la Torre Carreras: rdelatorre@ctaex.com
Carmen Gonzalez: cgonzalez@ctaex.com

Fundacion TECNALIA
Paseo Mikeletegi, 2. Parque Científico y Tecnológico de Gipuzkoa E-20009 Donostia - San Sebastián SPAIN
http://www.tecnalia.com
Xabier Gomez: xabier.gomez@tecnalia.com

SYNPO A.s.
S. K. Neumanna 1316 532 07 Pardubice CZECH REPUBLIC
http://www.synpo.cz
Daniela Vareckova: daniela.vareckova@synpo.cz

AZIENDA AGRICOLA VIRGINIO CHIESA
Strada Canneto Asola 46, 46013 Canneto sull'Oglio (MN) ITALY
Azagr.chiesavirginio@gmail.com

RODOLFI MANSUETO S.p.A.
Strada Qualatico, 14 – 43044 Ozzano Taro, Parma ITALY
http://www.rodolfimansueto.com
Gianpaolo Ghiretti: laboratorio@rodolfimansueto.com

SAUPIQUET S.A.S.
Le Doublon, 11 avenue Dubbonet 92407 Courbevoie CedexB56 602484 Nanterre FRANCE
http://www.saupiquet.com
Daniela Villa: dvilla@boltonalimentari.it

CONSERVAS MARTINETE S.A.
CTRA. PUEBLA – LOBON S/N 06490 – PUEBLA DE LA CALZADA – BADAJOZ **SPAIN**
http://www.martinete.es
Manuel Martinete : manuel@martinete.es

NATIONAL CAN HELLAS
72nd Klm of Old National Road Thessaloniki-Athens 60066 Methoni Pieria (Thessaloniki) GREECE
http://www.natcan.gr
Kiouros Nikos: n.kiouros@natcan.gr
Athanassios Savvakis: a.savvakis@natcan.gr

BIOCOPAC

Biocopac logo

Fig. 37 Kick-off meeting in Parma (17-18/01/12)

Fig.38 Green Industrial Coating Asia 2013 - Shanghai 24/09/13

Fig. 39 EU Open Doors Day – Brussels 04/05/2013

Fig. 40 EU Open Doors Day – Brussels 04/05/2013

The Video-clip is also available on BIOCOPAC Project Channel on Youtube (URL: http://www.youtube.com/user/BIOCOPAC). Click the link: see [+] info: http://www.youtube.com/watch?v=Vz5nCGWKqq0

Dra. Rosa de la Torre speech (Spanish):
http://www.youtube.com/watch?v=uKFZ0Q7ybdw&list=PLSBa7A__l4x9_69O1DB48R5Hs9dqERDH1&index=4

Euronews reportage
http://www.euronews.com/2014/09/29/tomatoes-with-a-can-do-attitude/