



**ICCOM-COLORTEX-
ENEA - ICCOMCNR-
SERICHIM-INESCOP**

**DELIVERABLE D1
ACTION 3**

Natural Products

January 2012–May 2013

**LIFE ECOFATTING PROJECT
LIFE10 ENV/IT/000364**

**ENVIRONMENTALLY
FRIENDLY NATURAL
PRODUCTS INSTEAD OF
CLOROPARAFFINES IN THE
FATTING PHASE OF THE
TANNING CYCLE**



Prepared by SERICHIM

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1. Introduction

In accordance with the project target, SERICHIM aim is to study and to prepare products able to replace existing fatliquoring agents as chlorinated paraffins and sulphochlorinated paraffins and bearing a reduced environmental impact. Chlorinated paraffins are used as greasing agents in the finishing working step in leather manufacturing and this in order to provide an oily and soft “touch “ to the leather; in the case of chlorosulphonated paraffins these are sometimes used as direct tanning agents, but in majority of cases are submitted to a further saponification reaction in order to be used as emulsifiable greasing agents.

Environmental impact of existing products is due to two main contributions: that of the resources consumed in their preparation and that of handling the used and wasted products at the end of their useful life. Serichim contribution was focused to demonstrate that products derived from renewable raw material can offer properties as less equivalent to the existing products, offering the advantage of a reduced CO2 contribution.

According to the initial program oleochemical raw materials were under consideration, methylesters of fatty acids and fatty acid derivatives.

2. Natural products demonstration and evaluation

a. Lab-scale screening of molecules or molecule alternative to chloroparaffins or chlorosulphonated paraffins

As it was said, chlorinated and sulphochlorinated paraffines are members of a wide population of products, characterized by structural and physical properties. In order to demonstrate that they can be substituted, it was necessary to verify that it is possible to cover similar ranges of the relevant characteristics starting by renewable raw materials. As significant properties the following ones were identified:

- Total chlorine content;
- Active chlorine content;
- Viscosity as a function of temperature ;
- Density as a function of literature.

A wide number of small scale samples of chloroparaffins and of chlorinated fatty acid methyl esters were prepared and characterised for the selected properties. A mathematical model was developed, able to predict physical properties as a function of carbon chain length, both for paraffins (reference materials) and esters (new replacing materials).

The possible substitutes for chlorosulphonated paraffins were identified and were grouped into the following chemical families according to the natural substrate that was considered :

A) METHYL STEARATE

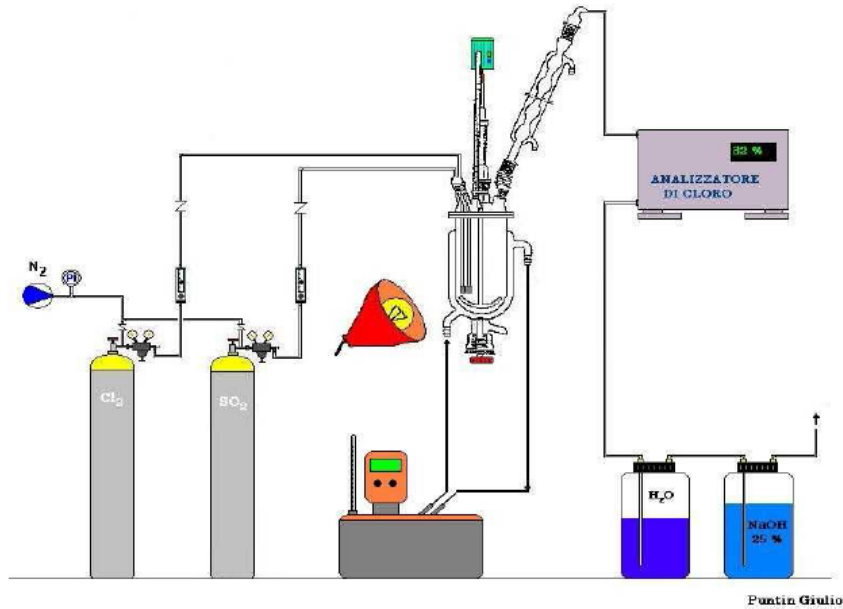
B) FATTY ACID METHYL ESTERS (SATURATED) MIXTURE

C) FATTY ACID CHLORIDES MIXTURE

D) PALMKERNEL OIL FATTY ACID METHYL ESTERS

3. Chlorination and sulphochlorination bench reactor.

In order to rely on an effective apparatus to provide – at “few kilograms scale “ – chlorinated and sulphochlorinated samples, a specific equipment for carrying out chlorination reactions was studied and assembled, and operated according to the sequence of scheme here below reported in Figure 1.



SERICHIM photochlorination lab equipment

Figure 1

Later on, the manufacturing unit was also modified in order to carry out also sulphochlorination reactions always at few kilo scale (Figure 2-5).

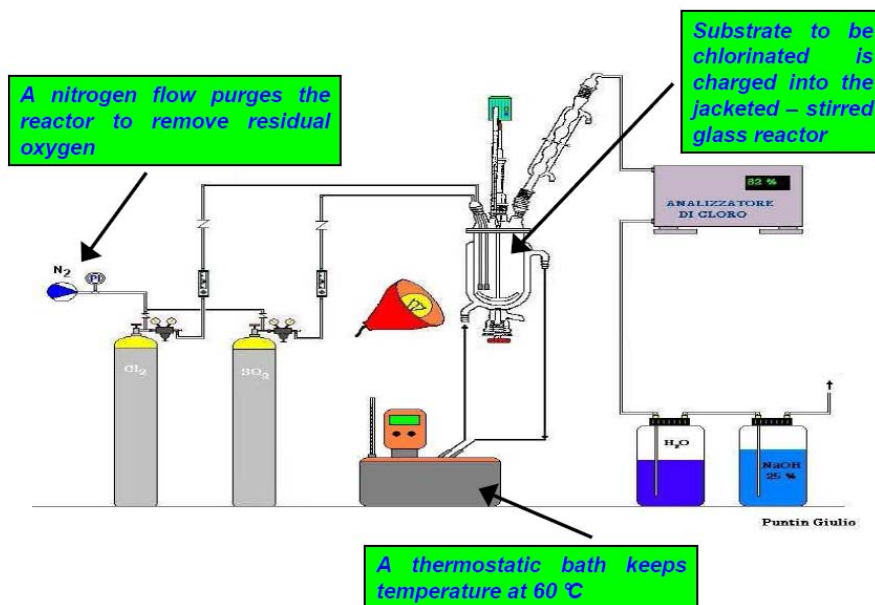


Figure 2

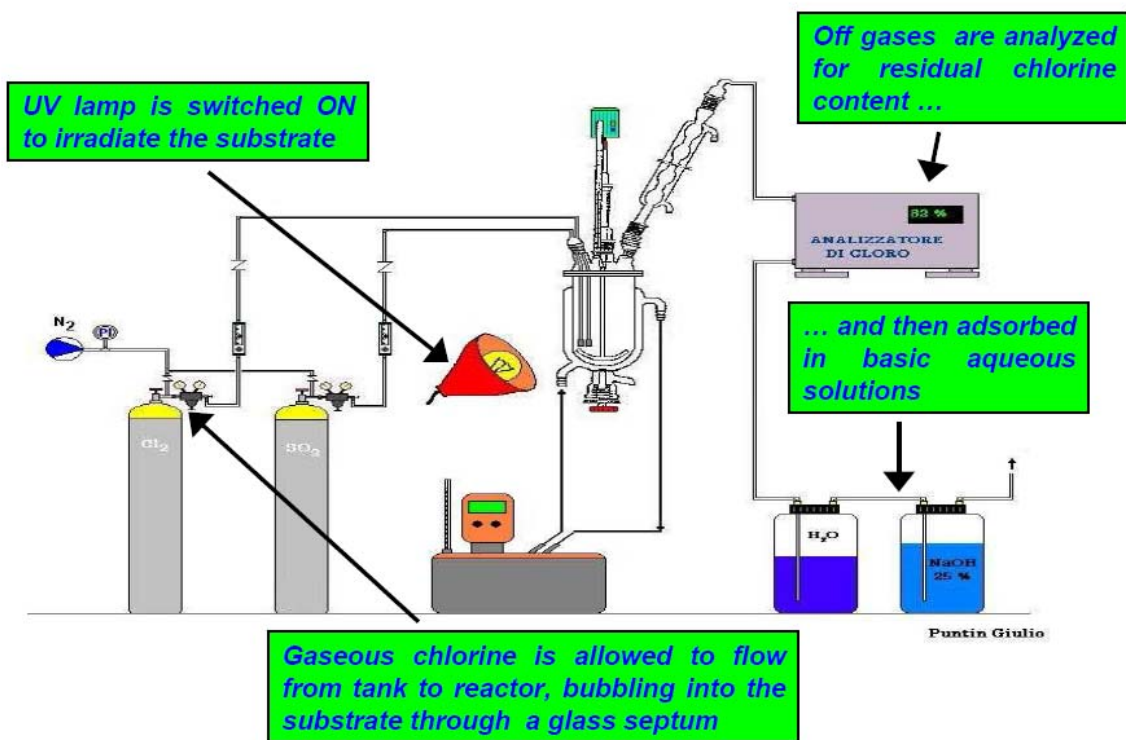


Figure 3

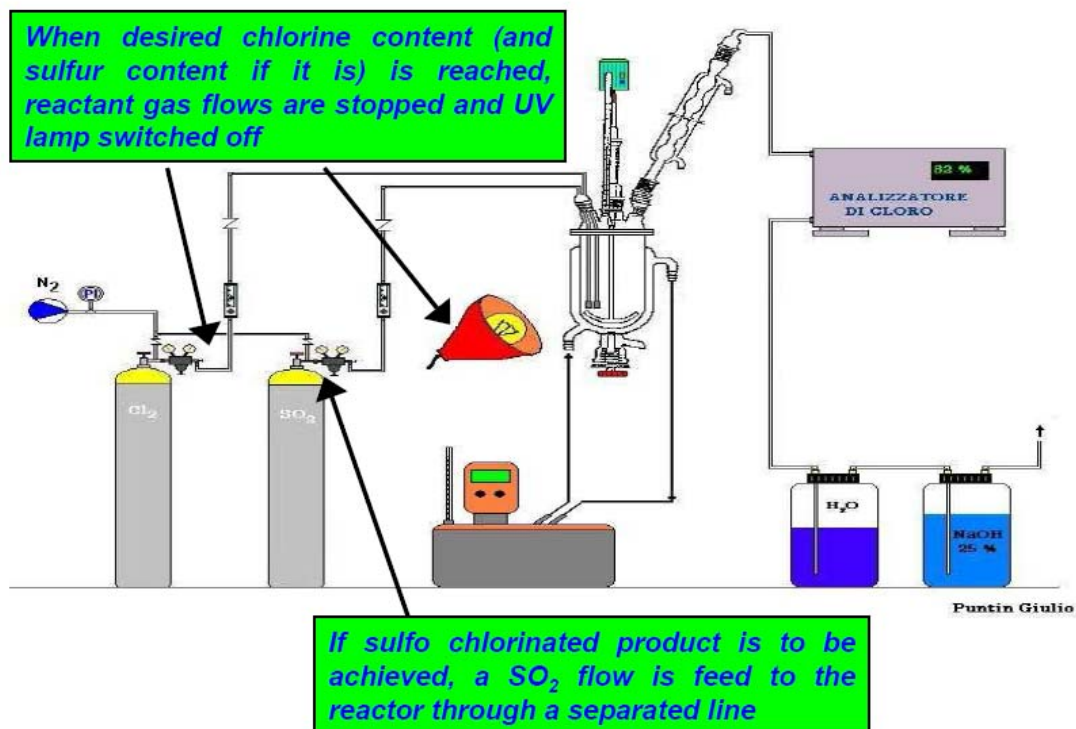


Figure 4

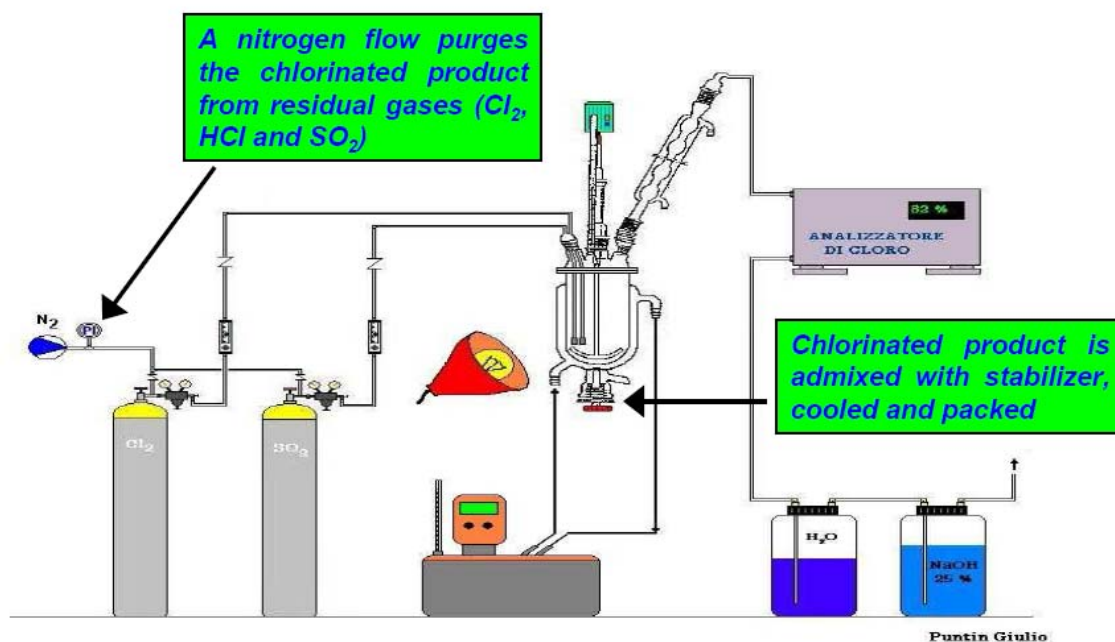


Figure 5

4. Chlorinated esters “ kilogram scale “ preparations

To put COLORTEX and ICCOM - CNR in the position to test the identified innovative products in leather treatments, Methyl Stearate and FAME Fatty Acid Methyl Esters mixture were chlorinated and also sulpho- chlorinated producing samples at the kilo scale and several hundred grams scale samples for comparison purpose.

Since July 2012 to January 2013 the following samples were prepared and delivered to project partners:

A) CHLORINATED METHYL STEARATE :

Four chlorinated methyl stearate samples at different chlorination degree were produced:

Lot 120710B (21,3 % m/m Chlorine content - 0,20 kg)

Lot 120710D (37,9 % m/m Chlorine content - 0,20 kg)

Lot 120712 (34,4% m/m Chlorine content-0,20 kg; viscosity and density as for Cloparin 44F)

Lot 120907 (45,2 % m/m Chlorine content - 0,60 kg; chlorine content as for Cloparin 44F)

B) SULFO CHLORINATED METHYL STEARATE :

Lot 120925 (8,6% m/m sulfur content - 1,50 kg)

C) CHLORINATED FAME (SATURATED) MIXTURE :

A synthetic mixture of methyl esters of fatty acids (lauric, myristic, palmitic and stearic) was prepared, simulating the acid composition of Palmkernel oil. Stearic was present as saturated substitute of oleic acid.

Lot 120903 (40,5 % m/m Chlorine content - 2,80 kg)

D) CHLORINATED PALMKERNEL OIL FAME:

Lot 130116 (47,5 % m/m Chlorine content - 2,00 kg)

E) SULFO CHLORINATED PALMKERNEL OIL FAME :

Lot 130118 (24,1 % m/m Chlorine content - 8,6% m/m sulfur content - 1,50 kg)

Action related to Activity 3 was in time for activities to be carried out by Serichim and 100 % of completion has been achieved.

5. Fattening at a semi industrial level by using natural products (Action 5)

These two action phases are jointly considered in the present report since – as far SERICHIM activity is concerned – this was constantly devoted to the production of kg samples that was targeted – on the basis of the indications coming from downstream project partners - as the most promising both in terms of industrial effectiveness and reproducibility and also in terms of “environmental friendship “.

More precisely, on the basis of the results obtained from the previous project actions and following discussion with project partners , mainly COLORTEX and ICCOMCNR it was established:

- 1) PALM KERNELOIL as the most suitable natural origin substrate to be chlorinated and sulphochlorinated as alternative to currently used chlorination and sulphochlorination of n-paraffins.

A commercially available product PALM KERNEL OIL was used being his composition the following as far as the distribution of alkyl chain lengths was concerned:

| | |
|------------|-------------------|
| <i>C10</i> | <i>0% - 3%</i> |
| <i>C12</i> | <i>54 % – 59%</i> |
| <i>C14</i> | <i>17 % – 21%</i> |
| <i>C16</i> | <i>8 % - 11%</i> |
| <i>C18</i> | <i>9 % - 17 %</i> |

- 2) to increase chlorine content in the sulpho-chlorinated product compared to previous Palm kernel Oil based samples – as per above mentioned ***Lot 130116 and Lot 130118*** - supplied to COLORTEX and ICCOMCNR

The following samples were prepared and supplied to COLORTEX and to INESCOP

D) CHLORINATED PALMKERNEL OIL FAME:

Lot 130422 (48,6 % m/m Chlorine content - 2,70 kg)

E) SULFO CHLORINATED PALMKERNEL OIL FAME :

Lot 130404 (38,0 % m/m Chlorine content - 8,6% m/m sulfur content - 1,00 kg).