

BIOCIDES – Tanning Industry

It is very important to use biocide products to avoid damage and losses in leathers by the action of micro_organisms like fungus and bacteria.

Not tanned leather must be protected during stock, soaking against the bacterial attack and also leathers pickling, tanned, dyed or Fat-liquored need addition of fungicide to avoid the fungus progress. Fungus and bacteria development depends on the presence of organic substances in the medium, as are the proteins, fats, blood, that are dissolved with water addition, initiating their degradation by microbiological enzymatic processes, and their level depends of:

- Climatic Conditions (temperature, humidity).
- Storage periods.
- Conditions of fabrication/stock.
- Leather Fat Content..
- pH

BACTERIA: Optimum growth between alkaline and slightly neutral pH
Standard Conditions, pH of 6.5-8 and temperature of 37°C.

FUNGUS: Optimum Growth in a range from neutral to slightly acid pH (3-6) at 25°C:

Fungus might be found in aqueous medium between 12-15%.

Spores survive in dry medium, developing themselves once optimum conditions are recovered.

Fungus might be found in: leather pickling acid, tanning chromo/wet-blue, vegetal tanned leather and finished leather in stock in wet atmospheres.

MICROBIOLOGICAL CONTAMINATION EFFECTS

Bacterial attack: (degradation of collagen in leather).

- Putrefaction Odour as a consequence of volatile acid formation and putrefaction process.
- Loss of hair.
- Surface stains of red, pink or purple colour, not deep, they may damage the collagen.
- Irreversible damage of the leather.

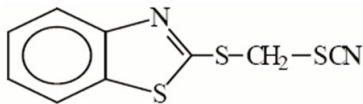
Attack by fungus (leather degradation).

- Stain, leather decolouration.
- Loss of physical properties like resistance, due to collagen degradation.

More important BIOCIDES:

TCMTB 2-(thiocyanomethylthio)-benzothiazol - CAS N.: 21564-17-0

Chemical Structure :



Synonym: TCMTB

pH Range : 3 - 8.5 (optimum: 5-7)

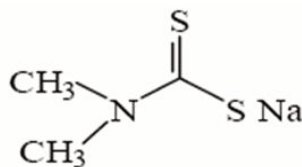
Dispersible in water once formulated

Application: pickling, wet-blue, vegetal tanning and finish leather

Fungicide activity

DMC Sodium Dimethyl-dithiocarbamate / Formula: $C_3H_6NS_2Na$ - CAS N.: 128-04-1

Chemical Structure :



Synonym: DMC

Alkaline Formulations (pH=9.5-10.5)

Aqueous Formulations

pH Range 8-13

Application: soaking, adding at the beginning of the process, directly in water.

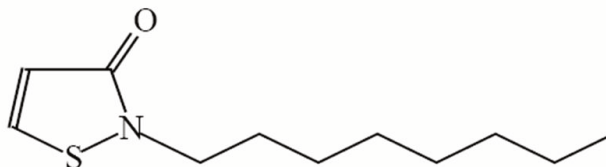
Soluble in water.

Biodegradable.

Bactericide Molecule.

NOIT 2-N-octyl-4-isothiazolin-3-one

Chemical Structure :



Synonym: NOIT

pH range 2-10

Dispersible in water once formulated.

Usual Formulations in organic solvents and glycols.

Decomposition in presence of sulphates and amines.

Fungicide activity

BIOCIDE FORMULATIONS

PRODUCT	ACTIVE MATTER	SOLVENT
K-THIO S30	TCMTB (30%)	Glycol
K-THIO N5	DMC (40-42%)	Water
K-THIO K6	CMIT / MIT (1,5 %)	Water
K-THIO VG25	TCMTB (20%) + NOIT (< 5%)	Metilester

It has been demonstrated that the TCMTB is one of the most effective fungicides for leather conservation / protection. But to optimize their use, it should be kept in mind:

- a) The oxidizers (Chlorines and Peroxides) and the reducers (Sulphides and Bisulphides) the TCMTB can break down
- b) the TCMTB loses effectiveness under alkaline conditions (pH bigger that 8). Especially in presence of Sulphides

For that reason the TCMTB should be used:

- During pickel : 15 minutes after the Salt and the acid.
- During tanning : 15 minutes after the chrome (the biggest time of rotating facilitates the penetration of the TCMTB in the skin)

c) Tanning baths with high content in fat (recycled Baths) can reduce TCMTB residual in the skin because the fat absorbs the TCMTB.

d) It is necessary a dilution 1:20 in water.



Products formulated in Glycol base present an excellent and durable emulsion in time, with easy dosage.



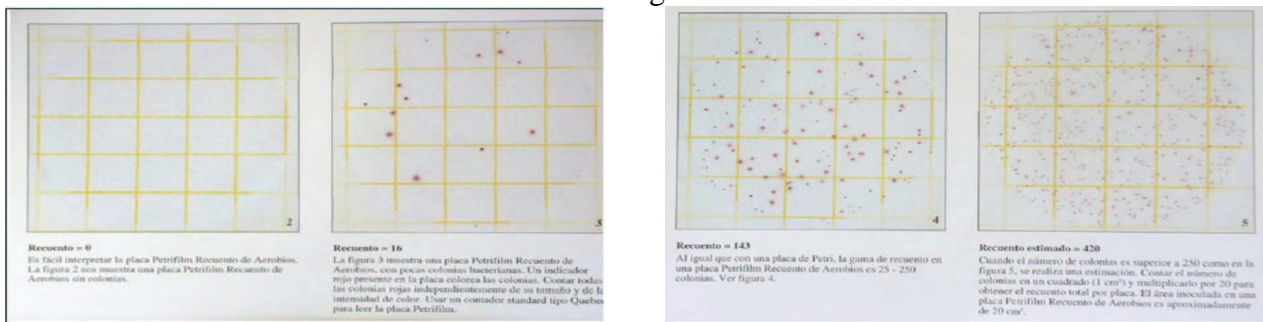
e) it is advisable the analysis / fungicidal test of the skins regularly.

ANALYTIC SUPPORT

Total bacteria determination in the bath:

- Petrifilm are used as culture medium for bacteria
- Diluted bath samples are prepared using Ringer 1/4 sterile solution
- 1 mL of the dilution in the Petrifilm (usually the 2nd, 3rd and 4th dilution)
- Incubation at 35°C during 48 hours and read-out of the number of the colonies by mL

PETRIFILM : Bacteria counting: NTB – Total Bacteria Number.



1) Initial regular analysis: establish $NTV_{average}$ (comparing values within several months)

2) Action depending results

Regular NTB measurements are to be done on a weekly basis with easy-to-handle kits that will allow the technician to have a result in 24-48 hours. When variations from the average NTB with respect to the measured NTB are detected, an adapted working programme is to be established as specified

NTB >> $NTB_{average}$:

control tanning conditions.

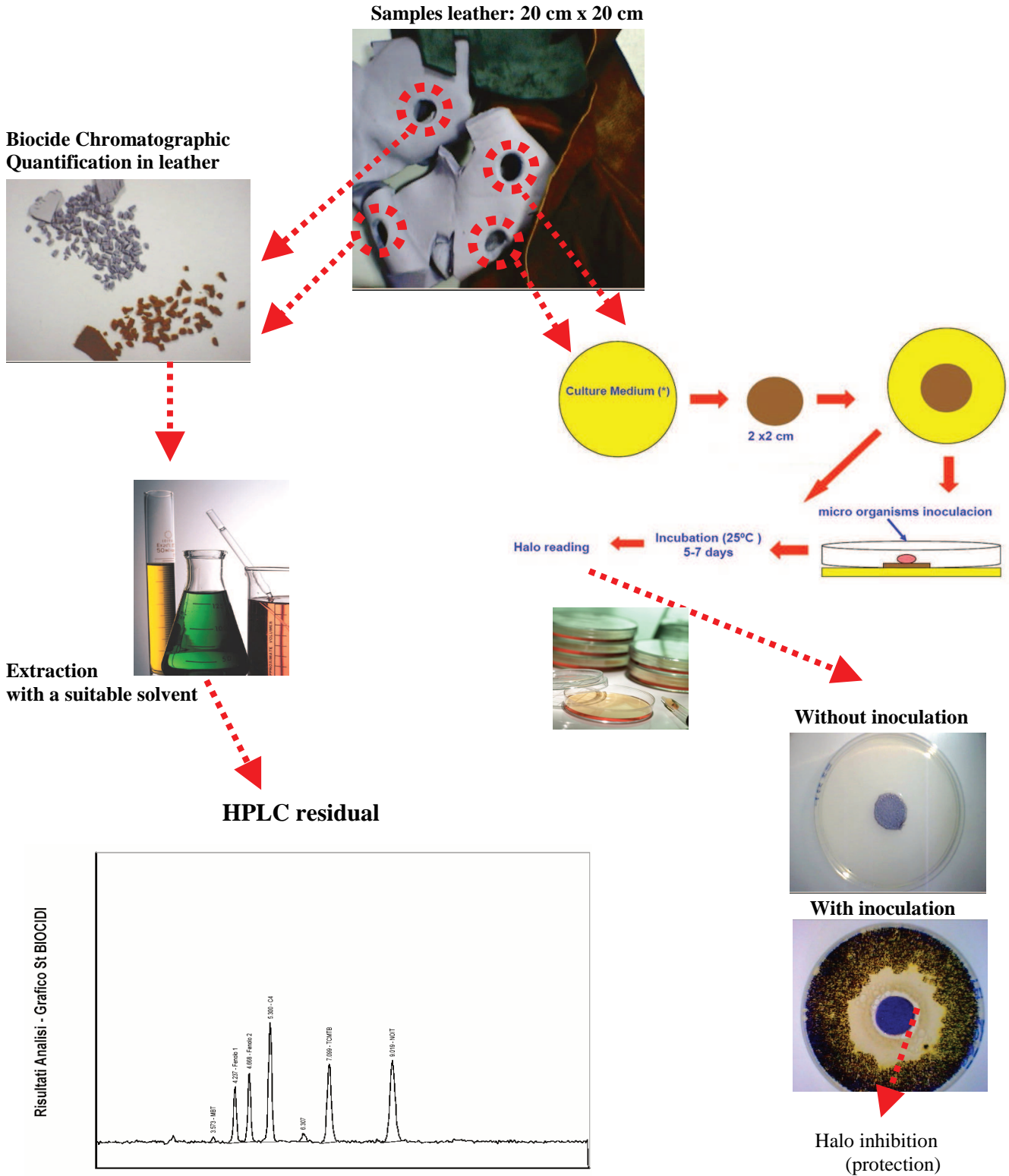
NTB << $NTB_{average}$:

Danger - 10^6

dose optimisation possible.

No danger - << $10^{4/5}$

FUNGICIDE TEST & HPLC Residual



- Values in mg/kg (ppm) or mg/gr

SOLICITUD DE ANÁLISIS
ANÁLISIS REQUEST:

Travesera de las Corts, 371 3º 1ª
08029 BARCELONA – Spain
Telf- + 34 93 4108732
Fax: +34 93 4100442

LUGAR Y FECHA / PLACE AND DATE:	REF. Num:	Año / Year
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Referencia de las muestras / Samples reference :
(Identificación del cliente / customer's identification)

Fecha recogida muestras / Pick up samples date:

Piel : Vacuno Cordero Oveja Cabra Otros
/ *Leather* *Cow* *Lamb* *Sheep* *Goat* *Others:*

Producto Utilizado **Fabricante/ Distribuidor**
Used product :..... *Maker / Agent :*.....

Principio Activo: TCMTB al % DMC BIT MBT NOIT CMI/MI
Active Matter
 OTRO/ OTHER.....

Dosis y punto de aplicación / Dose and application point:

Fecha curtición / Tanning date :

Piel lavada o no lavada / washed skin or not :

TIPO DE ANÁLISIS SOLICITADO:(Por favor indicar) / **ANÁLISIS REQUESTED** (please To mark):
 Test fungicida / Fungicide Test **Residual de fungicidas / Biocide residual**

Análisis muestra de Producto competencia - Analysis sample of Product concurrence
(indicar si es fungicida, bactericida y si se conoce posible activo o composición, el nombre comercial y el fabricante)
(To inform if it is Fungicide or bactericide / active matter – composition if it is posible, commercial name and Producer company)

Observaciones / Remarks