SIXTH FRAMEWORK PROGRAMME

PROPAINT

Mass spectra analysis of varnishes under accelerated ageing

The PROPAINT EU project for the assessment of environmental protection for paintings offered by microclimate frames and varnishes

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PROPAINT

Improved Protection of Paintings, During Exhibition, Storage and Transit

Introduction. To preserve paintings as close as possible to the artists' original expression is a central focus for museum administrators and conservators. The main aim of the project PROPAINT (EU project FP6, 044254), is to develop innovative protection treatments used as a preventive conservation measure for paintings during exhibition, storage and transit.

In this scenario, one of the important aims is to investigate the quality and protective effect of varnishes used as remediation treatment for paintings when exposed to pollutant and climatic factors generally, and in microclimate frames particularly.

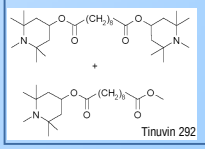
This paper presents the most significant deteriorating effects on painting varnishes (natural and synthetic) obtained by accelerated ageing experiments performed on varnish replicas under different concentrations of pollutants and climate variables.

Varnish replicas have been prepared on stainless steel

NATURAL: mastic dammar — terpenoid resins; dammar+ 2% Tinuvin 292

SYNTHETIC: MS2A — ketone resin; MS2A+ 2% Tinuvin 292

Paraloid B72 — acrylic resin



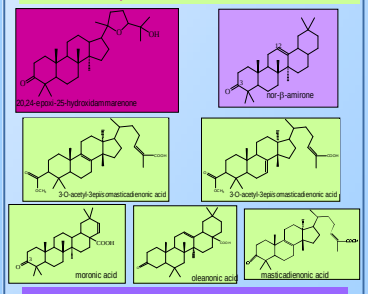
To understand the changes at molecular levels, mass spectrometric techniques have been used (Py-GC-MS; GC-MS, MALDI-MS) and some of the main results are summarised

Reference varnish replicas have been subjected to artificial ageing according to the conditions reported in the table below

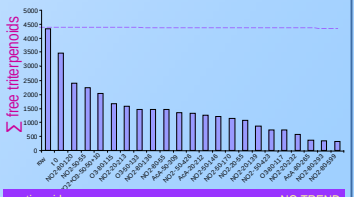
sample name	pollutant	T (°C)	exposure period (From/To)	RH (%)	C (Ch) ppm	t (days)	dose ppm day
NO2-20-55	NO_2	22	17.12.2007 / 27.12.2007	20	5.5	10	55
NO2-20-139	NO_2	22	17.12.2007 / 27.12.2007	20	13.9	10	139
NO2-20-213	NO_2	22	17.12.2007 / 27.12.2007	20	21.3	10	213
NO2-20-232	NO_2	22	14.04.2008 / 05.05.2008	20	11.0	21	232
NO2-50-55	NO_2	22	27.12.2007 / 08.01.2008	50	5.5	10	55
NO2-50-146	NO_2	22	27.12.2007 / 08.01.2008	50	14.6	10	146
NO2-50-170	NO_2	22	27.12.2007 / 08.01.2008	50	17.0	10	170
NO2-50-423	NO_2	22	29.01.2008 / 18.02.2008	50	21.2	20	423
NO2-50-146	NO_2	22	29.01.2008 / 18.02.2008	50	21.3	20	426
NO2-80-55	NO_2	22	08.01.2008 / 18.01.2008	80	5.5	10	55
NO2-80-120	NO_2	22	08.01.2008 / 18.01.2008	80	12.0	10	120
NO2-80-136	NO_2	22	08.01.2008 / 18.01.2008	80	13.6	10	136
NO2-80-293	NO_2	22	19.01.2008 / 10.03.2008	80	14.7	20	293
NO2-80-599	NO_2	22	13.03.2008 / 11.04.2008	80	20.7	29	599
O3-20-117	O_3	22	14.04.2008 / 14.05.2008	20	4.3	27	117
O3-50-133	O_3	22	16.05.2008 / 16.06.2008	50	4.3	31	133
O3-80-115	O_3	22	13.03.2008 / 11.04.2008	80	4.0	29	115
AcA-20-212	Acetic Acid	22	14.05.2008 / 02.05.2008	20	11.2	19	212
AcA-50-309	Acetic Acid	22	29.04.2008 / 13.05.2008	50	20.6	15	309
AcA-80-265	Acetic Acid	22	11.04.2008 / 28.04.2008	80	15.6	17	265
(NO2+O3)-50-(9l+13)	$NO_2 + O_3$	22	19.01.2008 / 29.02.2008	50	5.8 (1.3)	10	58 (13)

MASTIC GC-MS

the resin used for the preparation of the replicas is not "fresh"



cross-linking: DECREASE OF THE AMOUNT OF FREE TRITERPENOIDS WITH AGEING

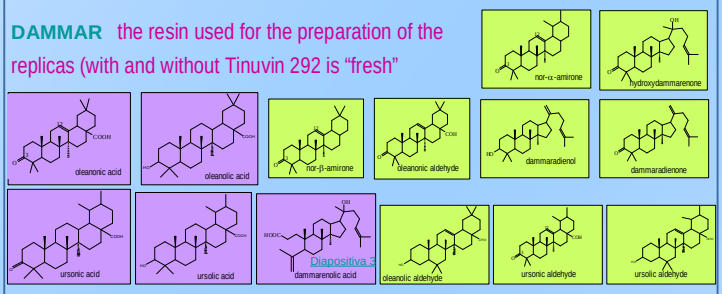


acetic acid:	NO TREND
ozone:	NO TREND
NO_2 50 ppm:	NO TREND
NO_2 150 ppm:	↓ RH => ↑ CROSS-LINKING
NO_2 250 ppm and 500 ppm	↑ RH => ↑ CROSS-LINKING
NO_2 20% RH	↑ dose => ↑ CROSS-LINKING
NO_2 50% RH	↑ dose => ↑ CROSS-LINKING
NO_2 80% RH	↑ dose => ↑ CROSS-LINKING

CROSS-LINKING SEEMS TO INCREASE WITH DOSE OF NO_2 (AT A GIVEN RH)

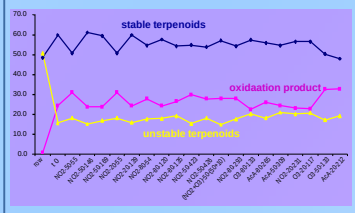
RH HAS AN EFFECT ON CROSS-LIKING THAT DEPENDS ON THE GAS, ITS CONCENTRATION AND EXPOSURE TIME

DAMMAR the resin used for the preparation of the replicas (with and without Tinuvin 292 is "fresh"



DAMMAR GC-MS

molecular composition: molecular composition of free terpenoids is almost settled since the varnish drying



acetic acid:	↓ RH => ↑ CROSS-LINKING
ozone:	↑ RH => ↑ CROSS-LINKING
NO_2 50 ppm:	↓ RH => ↑ CROSS-LINKING
NO_2 150 ppm and 250:	NO TREND
NO_2 20% RH	↑ dose => ↑ CROSS-LINKING
NO_2 50% RH	↓ dose => ↑ CROSS-LINKING
NO_2 20% RH	↑ dose => ↑ CROSS-LINKING

NO GENERAL TREND

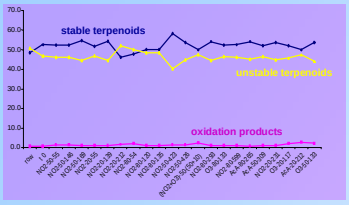
CROSS-LINKING CLEARLY DEPENDS ON A COMBINATION OF FACTORS, AND CANNOT BE PREDICTED

RH HAS AN EFFECT ON CROSS-LIKING THAT DEPENDS ON THE GAS, ITS CONCENTRATION AND EXPOSURE TIME

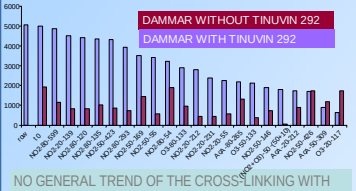
POLLUTANT DOSE AND CONCENTRATION ARE NOT THE ONLY FACTORS TO BE TAKEN INTO ACCOUNT

DAMMAR + TINUVIN 292 GC-MS

molecular composition: IN DAMMAR RESIN TINUVIN 292 HAMPERS THE DEGRADATION OF UNSTABLE COMPOUNDS AND THE FORMATION OF OXIDATION PRODUCTS

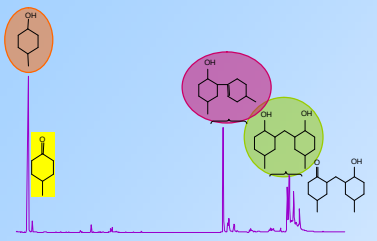


THE AMOUNT OF FREE TRETERPENOIDS IS MORE THAN RESPECT TO THE DAMMAR RESIN WITHOUT TINUVIN 292



NO GENERAL TREND OF THE CROSS-LINKING WITH RESPECT TO RH, POLLUTANT AND DOSE

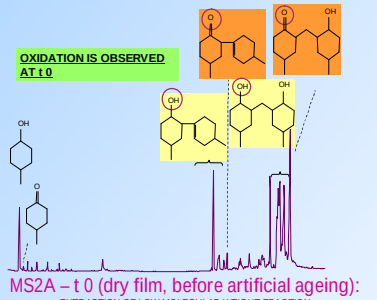
MS2A GC-MS / Py-GC-MS



MS2A ROW: *EXTRACTION OF LOW MOLECULAR WEIGHT FRACTION*

THE RESIN IS PRODUCED STARTING FROM CH_2O AND A BASE, FOLLOWED BY REDUCTION

OXIDATION IS OBSERVED AT t 0



MS2A – t 0 (dry film, before artificial ageing):
EXTRACTION OF LOW MOLECULAR WEIGHT FRACTION

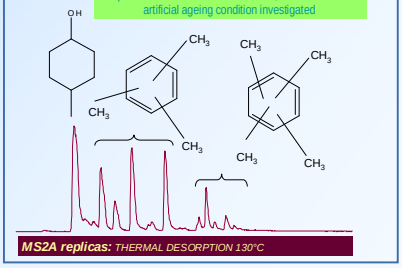
OXIDATION IS OBSERVED AT t 0 ALSO IN THE RESIN CONTAINING TINUVIN 292

THE FREE MONOMERS AND DIMERS PRESENT IN THE RESIN DO NOT DECREASE WITH TIME UNDER THE INVESTIGATED CONDITIONS, BOTH WITH AND WITHOUT TINUVIN 292

THE FREE MONOMERS AND DIMERS SHOW A QUITE CONSTANT COMPOSITION FROM THE OXYDATION DEGREE POINT OF VIEW

THE MACROMOLECULAR FRACTION SEEMS SLIGHTLY LESS OXIDISED IN THE RESIN CONTAINING TINUVIN 292 THAN IN THE RESIN WITHOUT

aromatics contained in the solvent used to prepare the replicas are retained in the resin film, even under the artificial ageing condition investigated

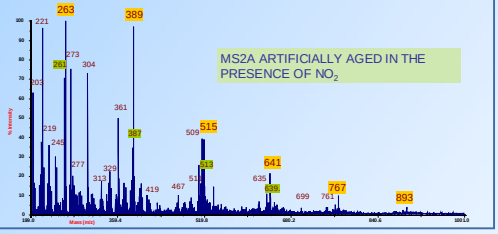


MS2A MALDI

MALDI REVEALED THE OLIGOMER DISTRIBUTION OF MS2A RESIN, SHOWING THE OCCURRENCE OF MOLECULES CONTAINING FROM TWO UP TO EIGHT UNITS.

REPLICAS ARTIFICIALLY AGED IN THE PRESENCE OF BOTH NO_2 AND O_3 CLEARLY SHOWS THE FORMATION OF LOWER MW OLIGOMERS, OBTAINED AFTER OXIDATION OF THE OH MOIETIES

Fragment	MW	sodium adduct
	240	263
	366	389
	492	515
	618	641
	744	767
	746	769
	870	893



MS2A ARTIFICIALLY AGED IN THE PRESENCE OF NO_2

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