UNIONE EUROPEA
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PON Ricerca e Competitività 2007-2013

Ministero dell'Istruzione, dell'Università e della Ricerca

Ministero dello Sviluppo Economico

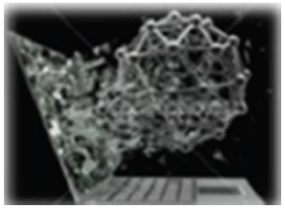
Centro Ricerca Energia e Ambiente
Dipartimento di Ingegneria dell'Innovazione
Università del Salento

CNRNANO

ordine ingegneri provincia di lecce

Collegio Provinciale Geometri e Geometri Laureati di Lecce

Fotopolimerizzazione di nanomateriali : nuova tecnologia di applicazione di coatings idrofobici per l'edilizia sostenibile



Ing. Carola Esposito Corcione
carola.corcione@unisalento.it

Nuovi sviluppi sui materiali per l'edilizia, Lecce 1/7/2105

STONE DECAY

CAUSES

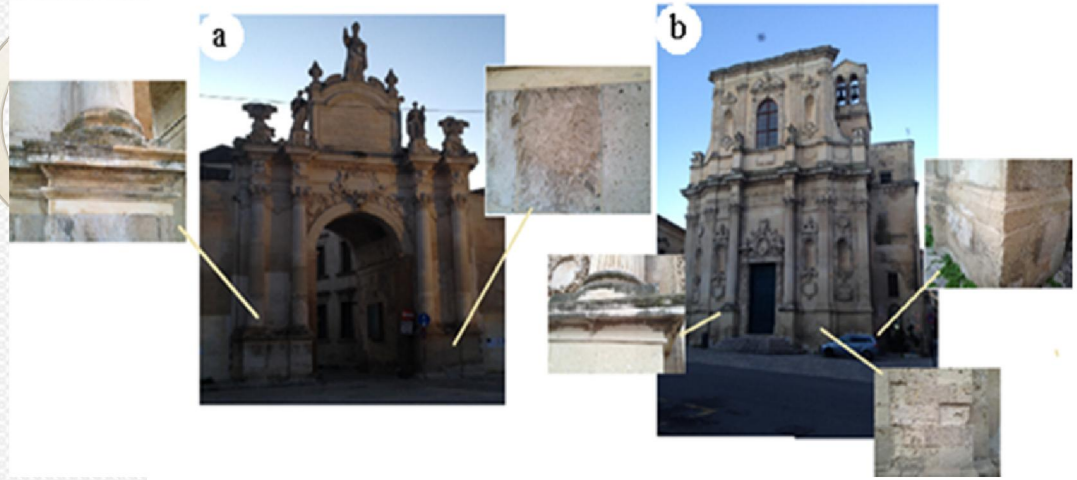
$$W = f(i,e)$$

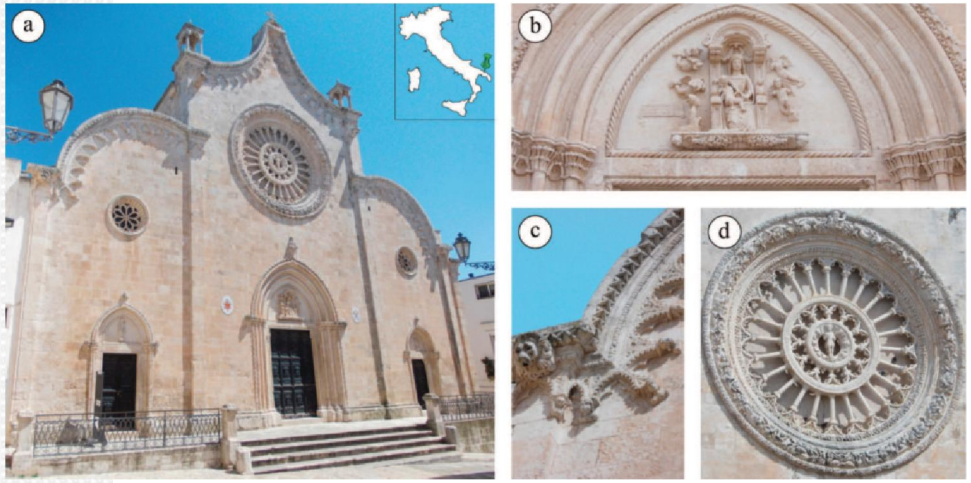
TEXTURE
COMPOSITION
POROSITY

PHYSICAL
CHEMICAL
BIOLOGICAL

WATER

STONE DECAY





ALVEOLIZATION
CRUSTS
EFFLORESCENCE
EROSION
BIOFILMS

STONE DECAY

Traditional REMEDIES

Pietra Leccese

STONE DECAY

INNOVATIVE REMEDIES

PROTECTIVE COATING

- hydro-repellence
- prevent infiltration of chemicals agents
- permeability to water vapor
- un-modify the color of the substrate
- compatibility with the substrate
- durability and reversibility

Inorganic systems

Organic systems

(Acrylic, Fluorinate, Silane and Epoxy)

COMMERCIAL ORGANIC SYSTEMS LIMITATIONS

Polymers preformed in solution → Toxic Solvents

Polymers preformed in solution → Small Penetration

Water Emulsions → Low Protection

In-Situ Polymerization → High curing time at Room Temperature

In-Situ Polymerization ↓ OUR solution

PHOTO-CURING OF NANO-STRUCTURED POLYMER BASED SOLUTIONS

NANO-STRUCTURED BASED SOLUTIONS

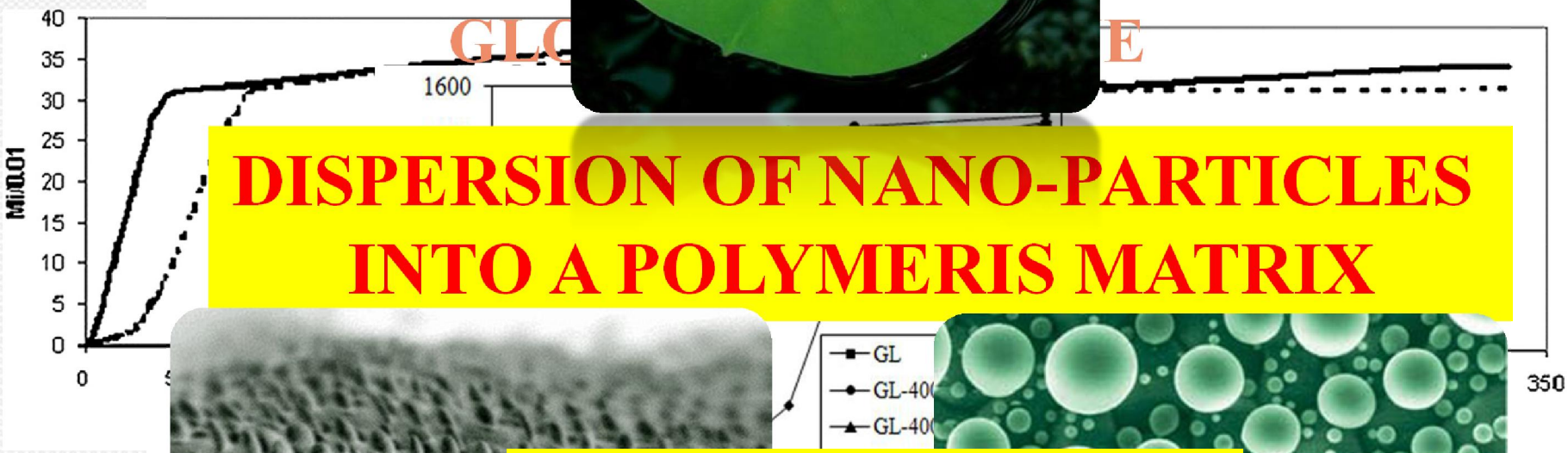
Systems typified by at least o scale (from 1 to 100nm).

CALCIUM HYDROXIDE n *(Dei et al. 2006)*

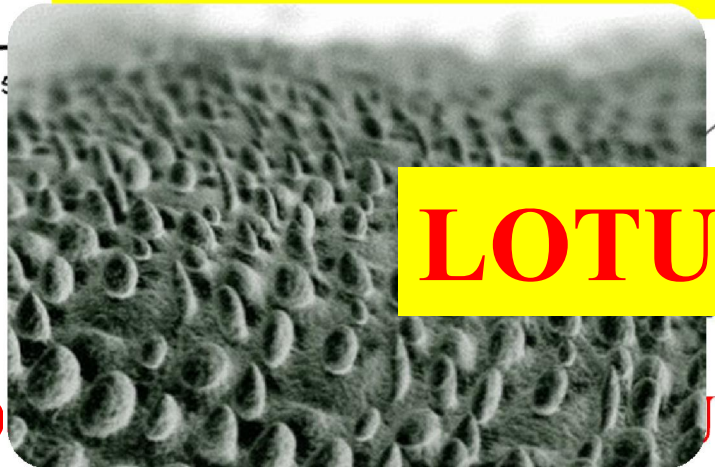
HYDROXYAPATITE in wa *i et al.-2012)*

GALLINA STONE RESE STONE

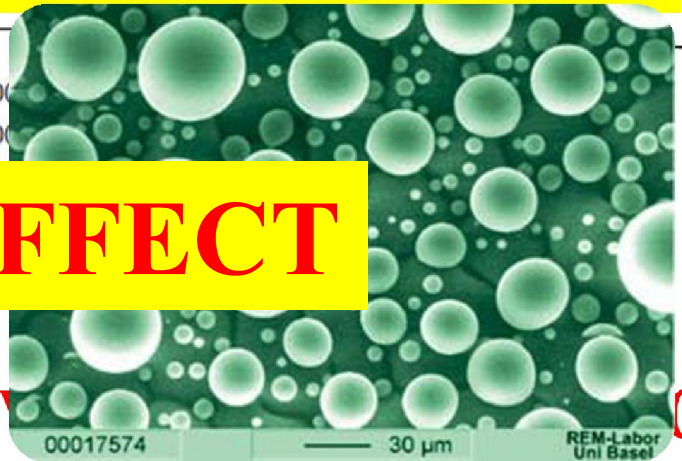
GLO E



DISPERSION OF NANO-PARTICLES INTO A POLYMERIS MATRIX



LOTUS EFFECT

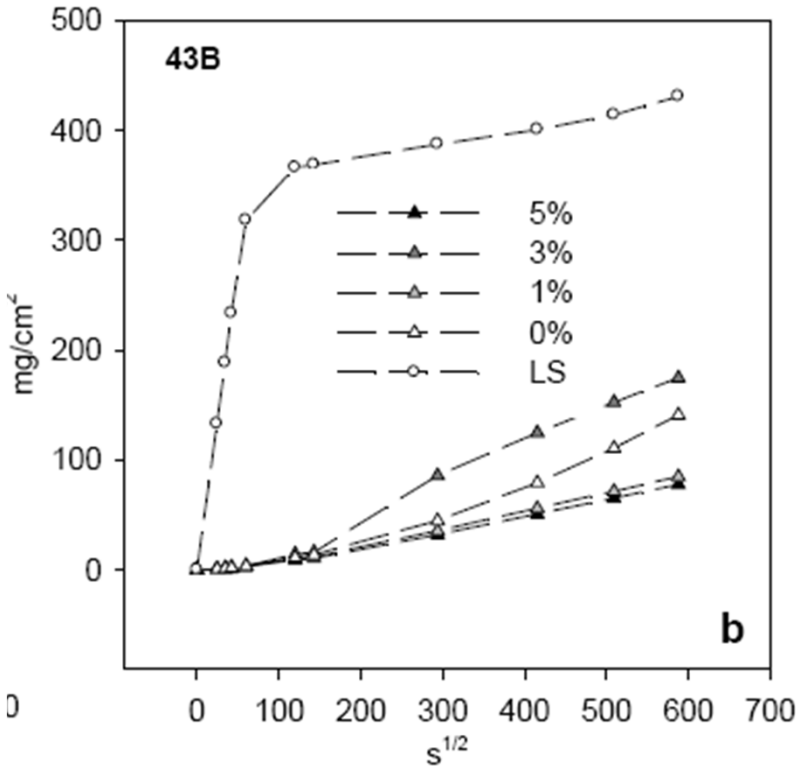


NANO UCES ON

POLYMERIC NANO-COMPOSITE (PNC)

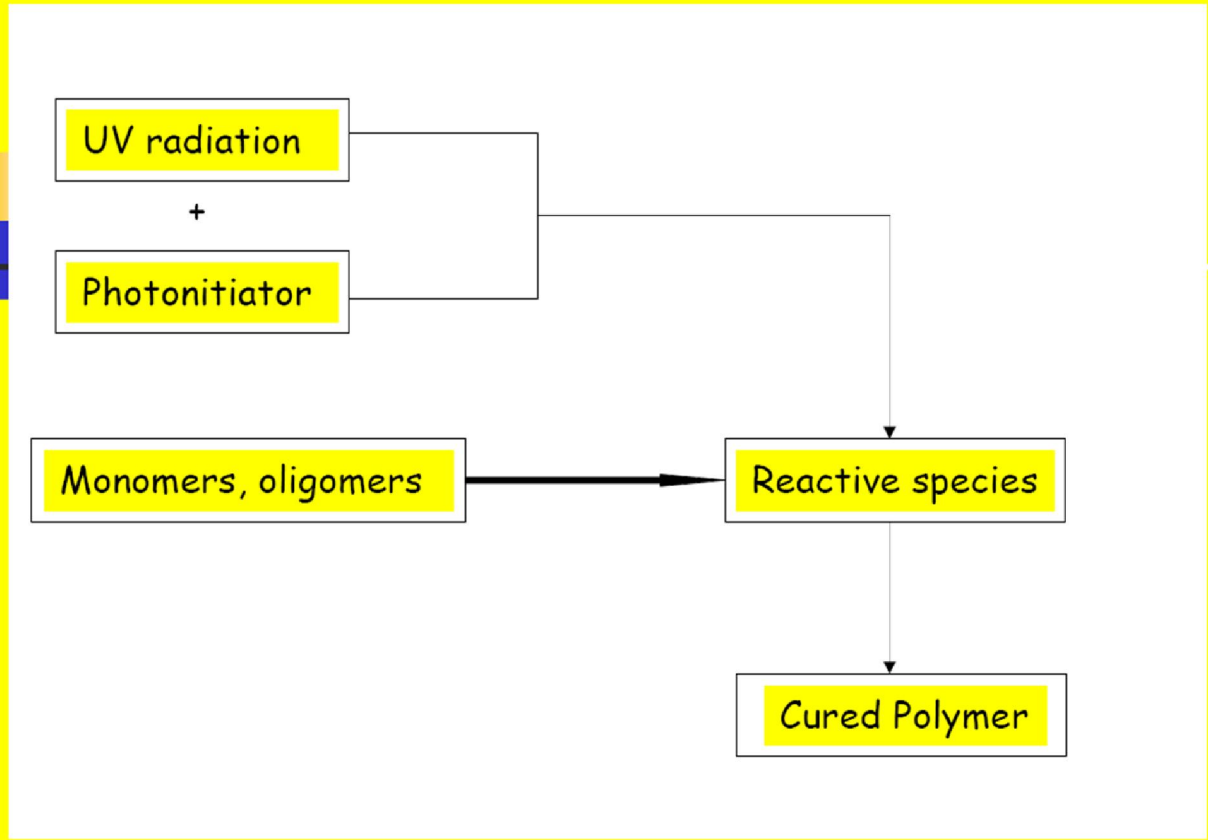
MONTMORILLONITE dispersed into commercial fluorinate polymer

(Zanchi et al.-2012)



CONSIDERABLE DECREASE OF WATER ABSORBED

PHOTO-CURING MECHANISMS



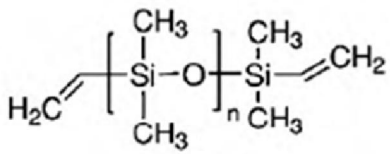
Development of photopolymerizable protective coatings for stones

$[H_2C{=}C(CH_3)CO_2CH_2]_3CC_2H_5$

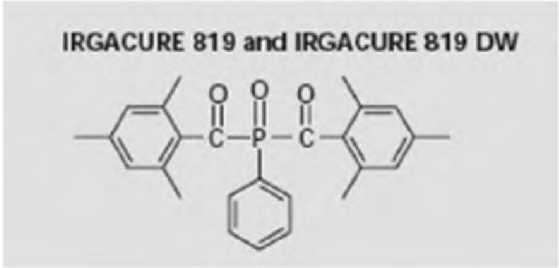
TMPTMA

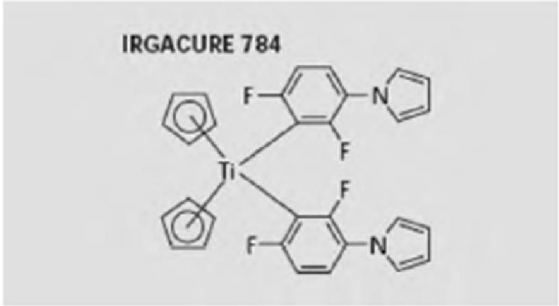
$CH_2{=}C(CH_3)\text{-}COO\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$

MEMO



VT PDMS





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Kinetics charac
siloxane-modi

C. Esposito Corcior

Dipartimento di Ingegneria dell

ARTICLE INFO

Article history:
Received 8 February 2010
Received in revised form 1 Jun
Accepted 1 June 2010
Available online 11 June 2010

Keywords:
Photopolymerizable acrylic res
Kinetics
Thermal analysis
UV radiation

e/tca

thermochimica acta

e

ent and characterization of innovative photopoly-
ossible use as protective coatings. The kinetics of
y UV and visible radiations in presence of suitable
by varying the testing conditions (temperature,

loped and rate of reaction, was generally found to
out in air, due the inhibiting action of the oxygen
of both a silane coupling agent or a high molecular
found to reduce the heat of reaction.
quantify the effects of light intensity and tempera-
greement between the experimental data and the

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C.E. Corcione et al. / Thermochimica Acta 509 (2010) 56–61

Development of photopolymerizable protective coatings for stones

Progress in Organic Coatings 72 (2011) 522–527

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

UV-cured siloxane-modified acrylic coatings containing birifrangent calcarenitic stone particles. Photo-calorimetric analysis and surface properties

C. Esposito Corcione*, M. Frigione

Department of Engineering for Innovation, University of Salento, via per Monteroni, Lecce, Italy

ARTICLE INFO

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Coatings
Photo-polymerizable acrylic resins
UV radiation
Surface properties

ABSTRACT

An experimental study was carried out for the development and characterization of innovative photopolymerizable siloxane-modified acrylic formulations for possible use as protective coatings for stone substrates.

Two amounts of calcarenitic stone particles (25 wt.% and 35 wt.%) were added to a siloxane-modified acrylic mixture. The effect of stone particles inclusion on the reactivity and surface properties of the photopolymerizable systems was investigated. To this aim, the kinetics of the radical photo-polymerization reaction, induced by UV radiations in the presence of a suitable photoinitiator, was studied by calorimetric analysis, both in air and nitrogen atmosphere. The formulations, coated on a glass substrate, were photo-cured by using a medium pressure Hg UV lamp in air. On the coatings photo-polymerized in air were measured: gel content, transparency, scratch and surface hardness.

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Development of photopolymerizable protective coatings for stones

Influence of Stone Particles on the Rheological Behavior of a Novel Photopolymerizable Siloxane-Modified Acrylic Resin

C. Esposito Corcione, M. Frigione[a]

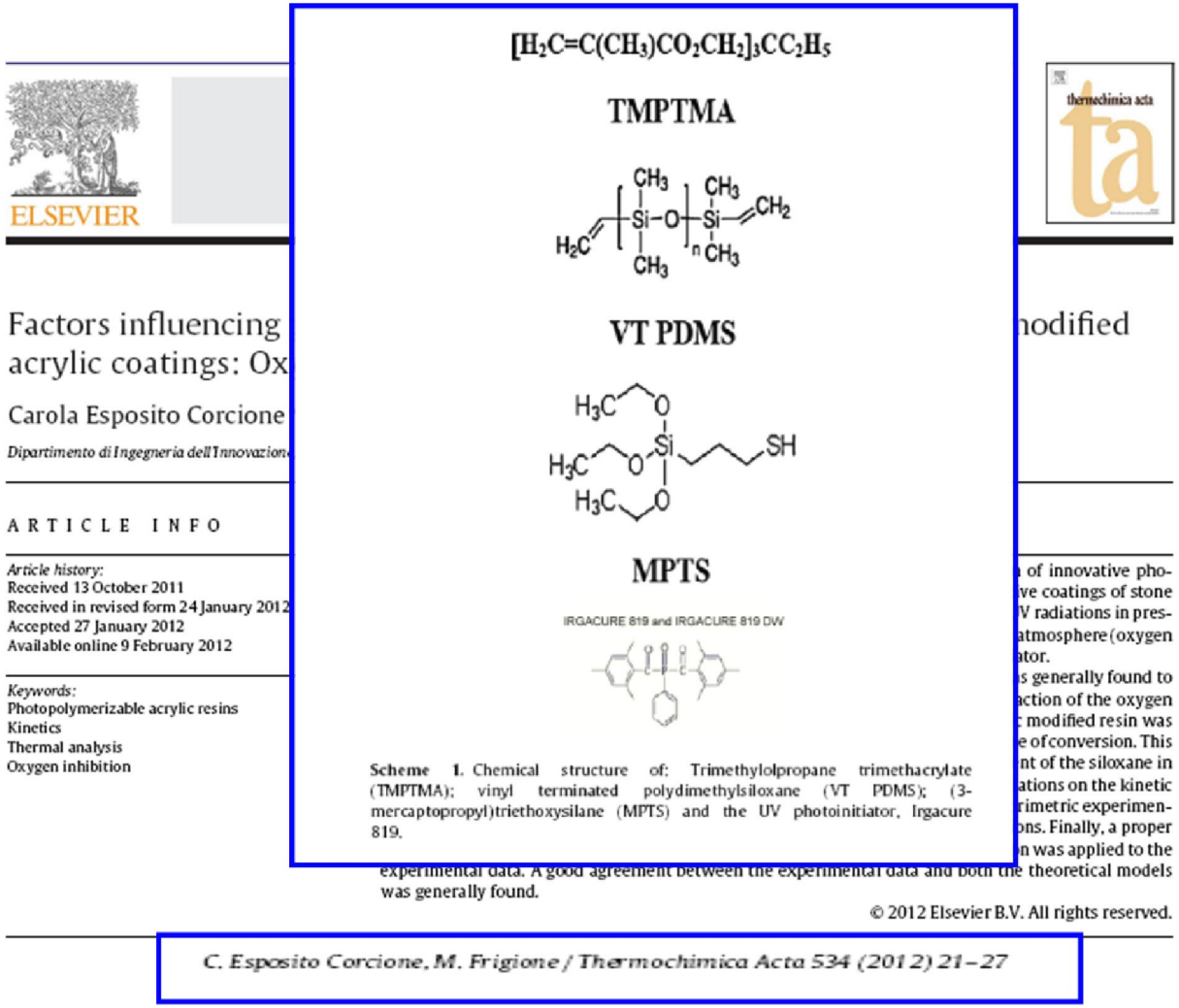
Dipartimento di Ingegneria dell'Innovazione, Università del Salento, Lecce, Italy

Received 3 November 2010; accepted 20 January 2011
DOI 10.1002/app.34201
Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A study was made of the effects of calcarenitic stone particles, known as *pietra gentile*, inclusions on the rheological behavior of photopolymerizable siloxane-modified acrylic formulations, intended as protective for the calcarenitic stone structures. Different amounts of stone particles (ranging from 15% wt to 35% wt) were added to the modified acrylic mixture to achieve a natural color matching for calcarenitic stone substrates. The presence of stone particles was expected to modify the rheological behavior of the protective formulation. Therefore, the viscosity of the mixtures was studied at ambient temperature as function of the shear rate and the solid volume fraction. A relationship was obtained to predict the modification of viscosity of each formulation as a consequence of inclusions of different amounts of stone. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2011

Key words: UV-photopolymerizable acrylic resins; rheology

Development of photopolymerizable protective coatings for stones



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thermochimica acta

Factors influencing … modified acrylic coatings: Ox…

Carola Esposito Corcione

Dipartimento di Ingegneria dell'Innovazion…

ARTICLE INFO

Article history:
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Accepted 27 January 2012
Available online 9 February 2012

Keywords:
Photopolymerizable acrylic resins
Kinetics
Thermal analysis
Oxygen inhibition

$[H_2C{=}C(CH_3)CO_2CH_2]_3CC_2H_5$

TMPTMA

VT PDMS

MPTS

IRGACURE 819 and IRGACURE 819 DW

Scheme 1. Chemical structure of: Trimethylolpropane trimethacrylate (TMPTMA); vinyl terminated polydimethylsiloxane (VT PDMS); (3-mercaptopropyl)triethoxysilane (MPTS) and the UV photoinitiator, Irgacure 819.

… of innovative pho-
…ve coatings of stone
…V radiations in pres-
…atmosphere (oxygen
…tor.
…s generally found to
…action of the oxygen
… modified resin was
…e of conversion. This
…nt of the siloxane in
…ations on the kinetic
…rimetric experimen-
…ons. Finally, a proper
…n was applied to the
experimental data. A good agreement between the experimental data and both the theoretical models was generally found.

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C. Esposito Corcione, M. Frigione / Thermochimica Acta 534 (2012) 21–27

Development of photopolymerizable protective coatings for stones

Progress in Organic Coatings 74 (2012) 781–787

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ate/porgcoat

UV-cured polymer-boeh elements

otective coating for wood

C. Esposito Corcione*, M. Frigic

Dipartimento di Ingegneria dell'Innovazione, Univers

ARTICLE INFO

Article history:
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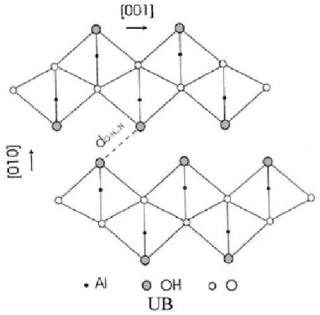
UV radiation
Cure kinetics
Wood coatings



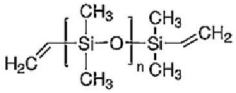
UB

$[H_2C{=}C(CH_3)CO_2CH_2]_3CC_2H_5$

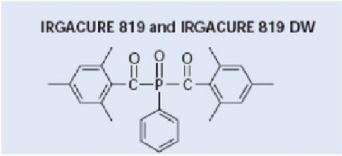
TMPTMA

$CH_2{=}C(CH_3)\text{-}COO\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$

MEMO



VT PDMS



Scheme 1. Chemical structure of: Boehmite (UM), Trimethylolpropane trimethacrylate (TMPTMA); alkoxysilane methacrylate functionalized (MEMO); vinyl terminated polydimethylsiloxane (VT PDMS); Photoinitiator (Irgacure 819).

l to prepare nanocomposite UV-cured coatings, based on
odified acrylic formulation, for possible use as protective
nto the mixture in the presence of a proper photoinitiator
oling agent were added to the mixture in order to enhance
ne siloxane-modified acrylic formulation. The kinetics of
ced by UV radiations, was studied by photo-calorimetric
nulations produced was studied as function of the shear
nulations, coated on a glass substrate, were photo-cured
ne coatings photo-polymerized in air were measured: gel
ness. The water absorption effect of the coating based on
e on walnut wood elements was evaluated.

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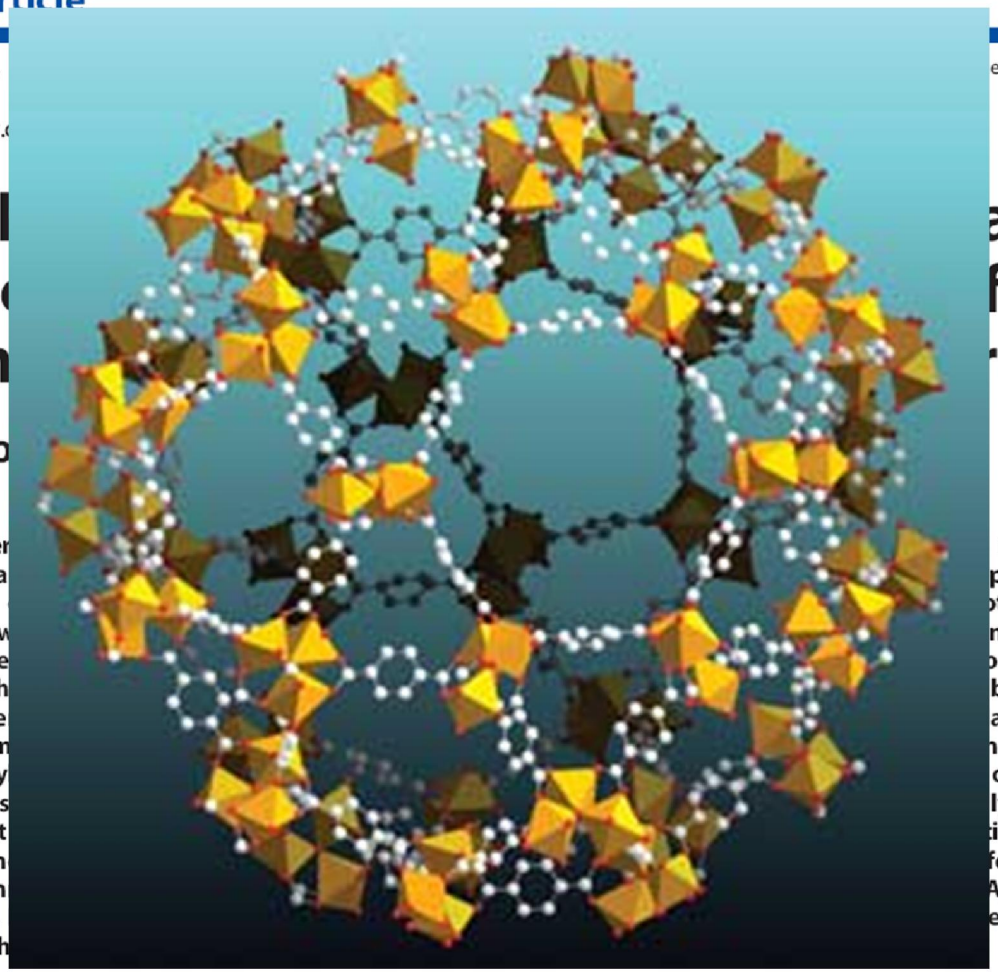
Development of photopolymerizable HYBRID protective coatings for stones

Research article

polymers advanced technologies

Received: 14 May 2014, … e Library: 18 December 2014

(wileyonlinelibrary.…



Sunligl… anic methac… f the cure m… rties

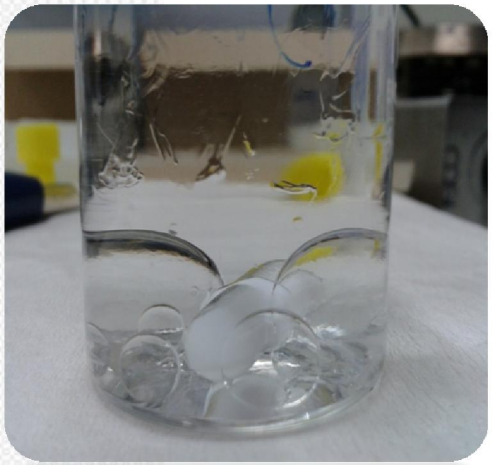
C. Esposito…

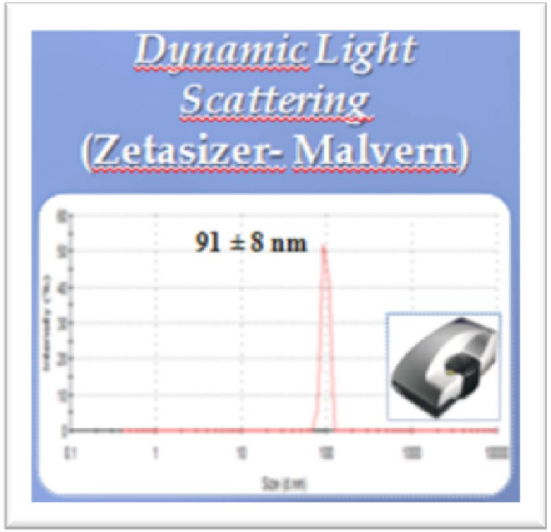
An exper… mainly intended for the surfa… patented. The hybrid product … otection of the stone against w… mance of commercial available… on of this product in-volves th… bstrate, representing this latte… amp plus 1 hr at 140° C in oven… ns of the composition of the hy… of the hybrid coating only by s… lymerize the coating, does not… ions were performed on the n… formulations. The se-lected in… Apulia Region (Pietra Leccese, … e natural stone color.

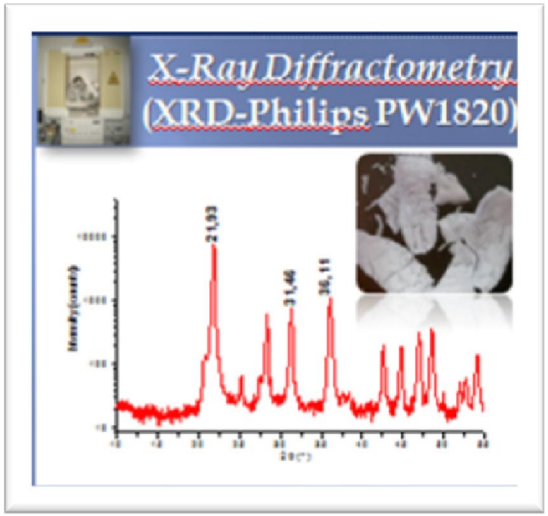
Copyrigh…

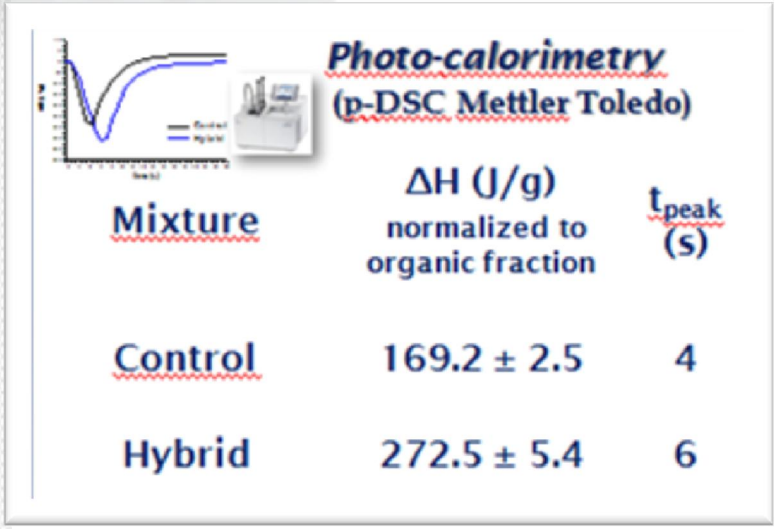
Keywords: coatings for porous stones; sunlight polymerizable methacrylic protective coating; organic–inorganic hybrids

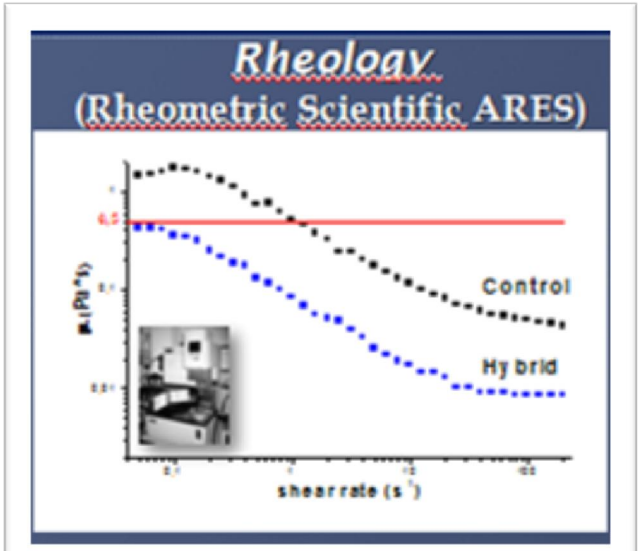
HYBRID photopolymerizable protective coatings for stones



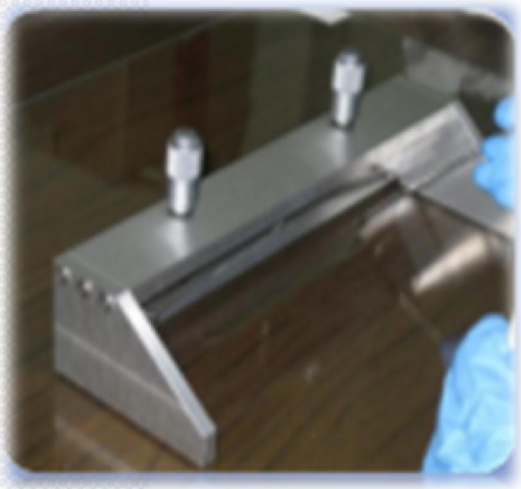


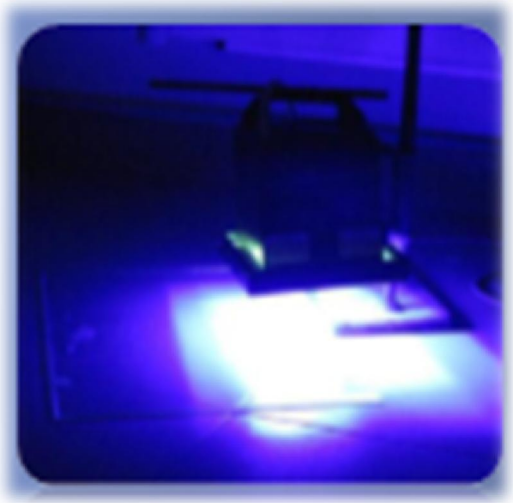


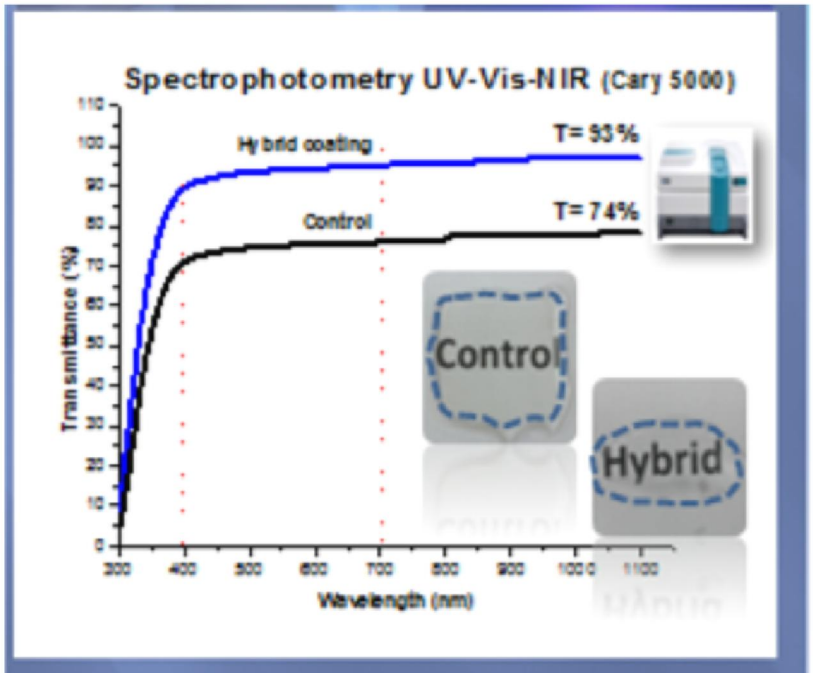




HYBRID photopolymerizable protective coatings for stones

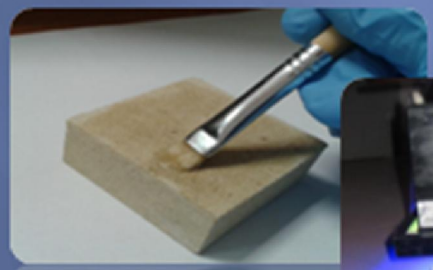


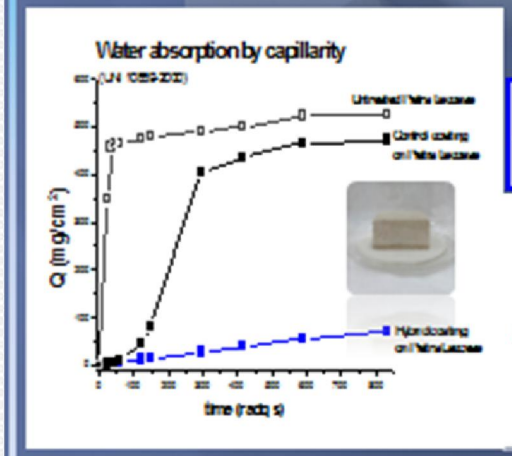




Coating	Tg (°C)	Pencil Hardness
Control	65.9 ± 3.3	5H
Hybrid	77.8 ± 3.9	9H

HYBRID photopolymerizable protective coatings for stones

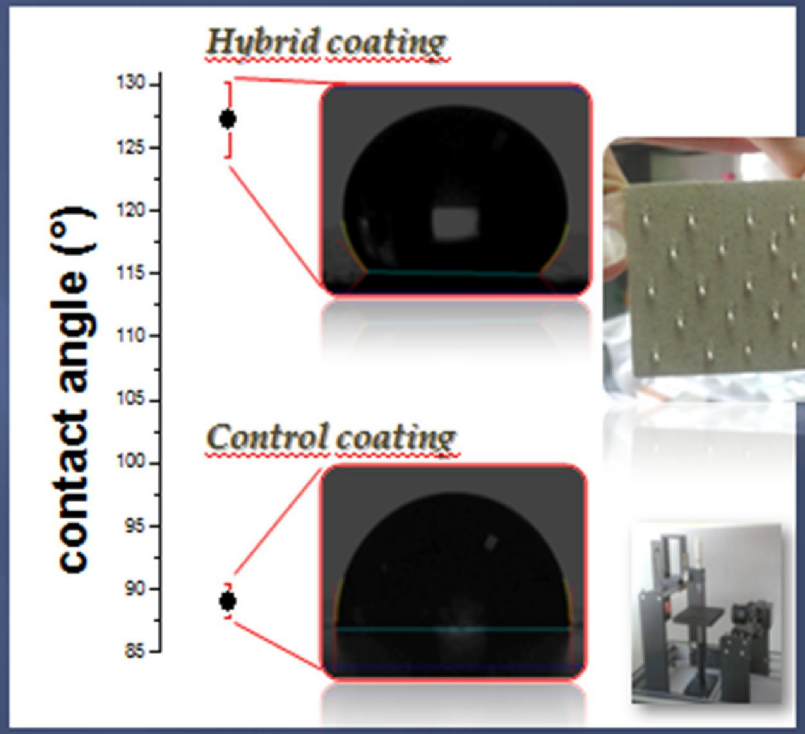


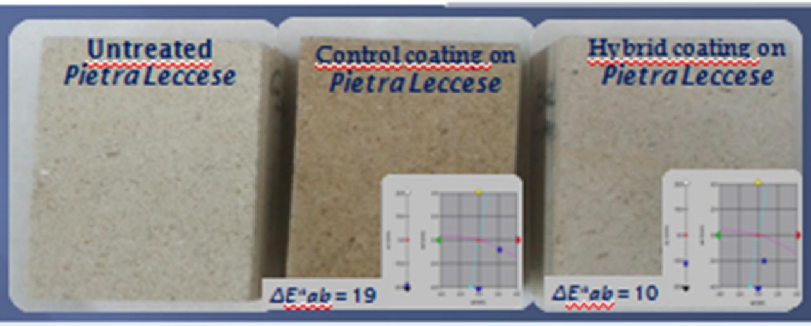


$$PE = \frac{P_{H_2O(NT)} - P_{H_2O(T)}}{P_{H_2O(NT)}} * 100$$

Protective Efficacy (%)

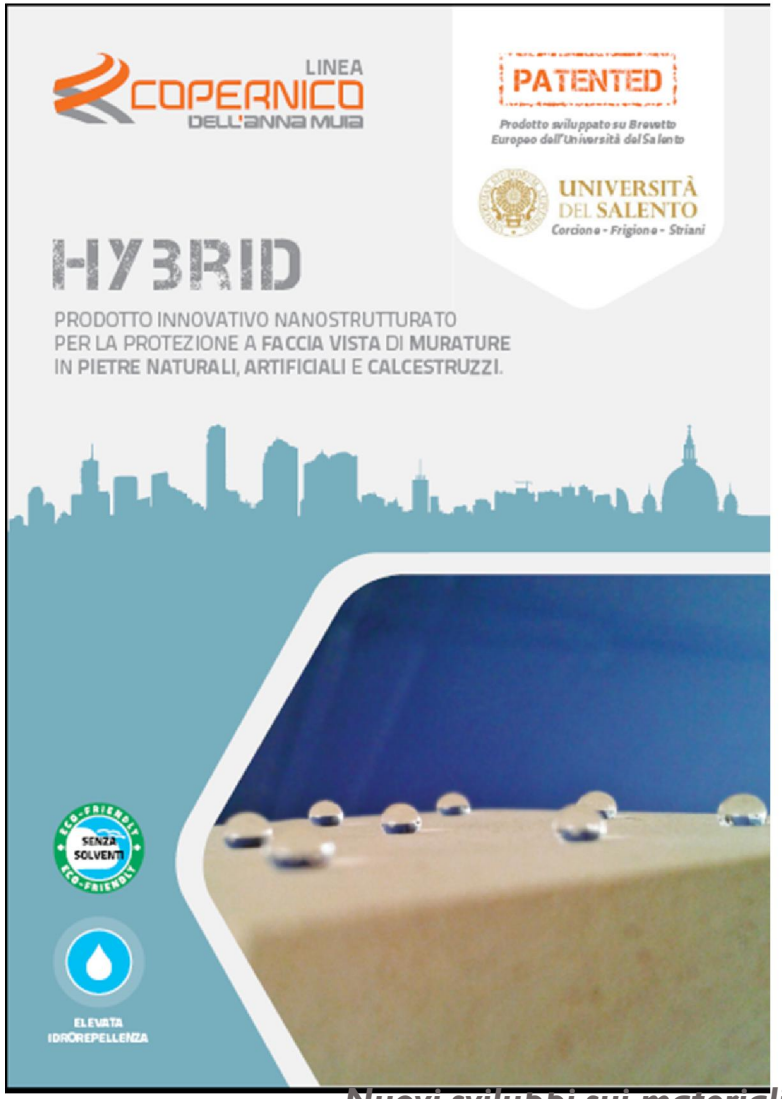
Sample	PE (%) 1 day	PE (%) 8 days
Control coating on *Pietra Leccese*	17	9
Hybrid coating on *Pietra Leccese*	94	86





Domanda di brevetto europea No. 13001868.2 del 11.04.2013
"Hybrid organic-inorganic nanostructured UV-curable formulation and Method for preparation thereof"

a nome UNIVERSITA' DEL SALENTO
Ns. rif.: FT/HG/sc 13275P12



Primo brevetto internazionale UniSalento venduto ad un’azienda pugliese

Università

Ecco "Hybrid", un brevetto tutto salentino per salvare la pietra leccese

martedì 10 marzo 2015

it/banner_click.asp?id=372&url=http%3A%2F%2Fwww%2Eotticamariano%...

“Hybrid”: un brevetto Unisalento per salvare la pietra leccese

Un brevetto targato Unisalento salverà la pietra leccese. Si chiama "Hybrid" ed è stato inventato da tre donne. La licenza è già stata acquistata da un'azienda di Copertino.

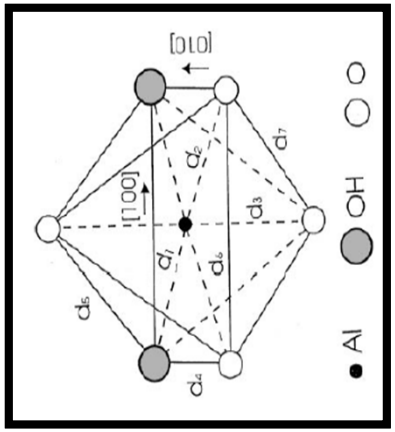
10 marzo 2015 | Eventi

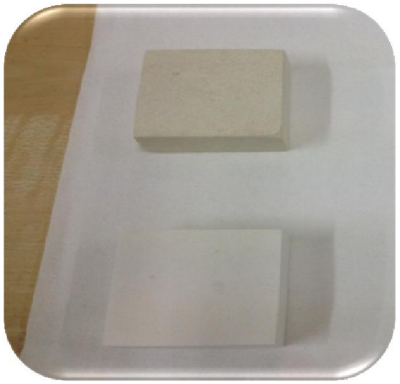
LECCE- Questa è la storia di un successo che parte dall'Università del Salento e finisce dritto nell'industria. **La storia di tre inventrici la cui scoperta sarà, da subito, al servizio del territorio.** Questo territorio. Quello in cui è nata ed è stata brevettata l'idea. **L'invenzione si chiama “Hybrid” e servirà a proteggere la pietra leccese. le inventrici sono Mariaenrica Frigione, professoressa associata di Scienza e Tecnologia dei Materiali, la ricercatrice in Principi di Ingegneria Chimica Carola Esposito Corcione e la dottoranda del corso in Ingegneria dei Materiali e delle Strutture Raffaella Striani.** “Hybrid” perché è un protettivo per le pietre porose -e quindi con ottime performances sulla pietra leccese- “che contiene una componente organica ed una inorganica”. **La licenza d'uso è già stata acquistata da un'azienda di Copertino.**

È con orgoglio che l'Università l'ha presentata.

What's going on…

DISPERSION OF **BOEHMITE** NANOFILLERS
in SUNLIGHT CURABLE FORMULATIONS





LECCESE AND GENTILE STONES

PHYSICAL-MECHANICAL PROPERTIES

NC SYSTEM

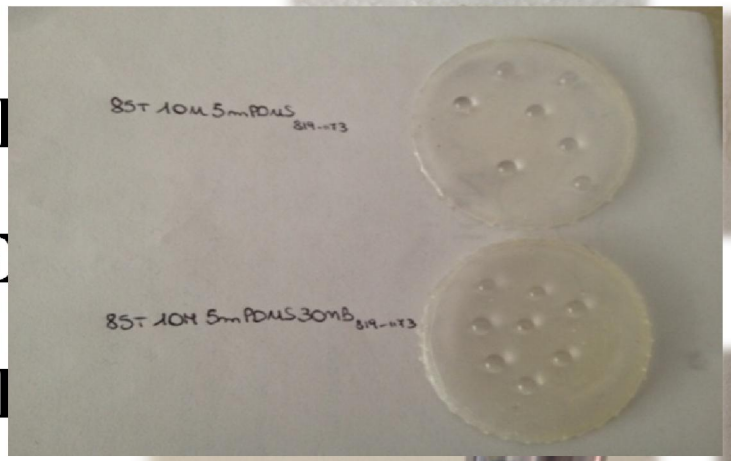
-INSULATI

- SURFACE

- TRANSMI

- CONTACT AN

-UV R



+30%

+45%

+25%

→ HYDROPHOBIC (≈90°)

	85T-10M-5mPDMS$_{819-1173}$	85T-10M-5mPDMS-3OMB$_{819-1173}$
Conductivity (W/m·K)	0,200±0,05	0,140±0,010

ADVANTAGES OF SUN LIGHT NANOFILLED FORMULATION

- LOW CURING TIME BY SUN LIGHT EXPOSURE

- INCREASE OF MECHANICAL, OPTICAL, INSULATING AND THERMAL PROPERTIES

-EXTRAORDINARY HYDROREPELLENCE OF COATING

- EXCELLENT DURABILITY RESISTANCE

What's going on…

to be continued…

Grazie per la cortese attenzione

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