



(86) Date de dépôt PCT/PCT Filing Date: 2006/01/20
(87) Date publication PCT/PCT Publication Date: 2006/08/24
(45) Date de délivrance/Issue Date: 2014/12/02
(85) Entrée phase nationale/National Entry: 2007/05/31
(86) N° demande PCT/PCT Application No.: AU 2006/000070
(87) N° publication PCT/PCT Publication No.: 2006/086828
(30) Priorité/Priority: 2005/01/21 (US60/646,204)

(51) Cl.Int./Int.Cl. *C09J 5/02* (2006.01),
B05D 1/38 (2006.01), *C08J 7/04* (2006.01),
C08J 7/12 (2006.01), *C09D 7/14* (2006.01)

(72) Inventeurs/Inventors:
BATEMAN, STUART ARTHUR, AU;
SIMONS, RANYA, AU;
WU, DONG YANG, AU;
MCMAHON, PATRICK JAMES, AU;
BERRY, DOUGLAS H., US;

...

(73) Propriétaires/Owners:
COMMONWEALTH SCIENTIFIC AND INDUSTRIAL
RESEARCH ORGANISATION, AU;

(54) Titre : PROCEDE D'ACTIVATION UTILISANT UN AGENT DE MODIFICATION
(54) Title: ACTIVATION METHOD USING MODIFYING AGENT

(57) Abrégé/Abstract:

The present invention relates to a method of activating an organic coating to enhance adhesion of the coating to a further coating and/or to other entities comprising applying a solvent and a surface chemistry and/or surface topography modifying agent to the organic coating. The invention also relates to a coated substrate having an activated coating, wherein the adhesion of the coating to a further coating and/or other entities has been enhanced by application of a solvent and a surface chemistry and/or surface topography modifying agent to the coating. The invention further relates to an activation treatment for an organic coating to enhance adhesion of the coating to a further coating and/or to other entities comprising a solvent and a surface chemistry and/or surface topography modifying agent and a method for the preparation of the activation treatment.



(72) **Inventeurs(suite)/Inventors(continued):** KOBAK, SEANA B., US; KIRCHNER, JAMES F., US;
STRAUS, LORI CLARICE, US; JOHNSON, MARK PAUL, US; BILYK, ALEXANDER, AU

(73) **Propriétaires(suite)/Owners(continued):** THE BOEING COMPANY, US

(74) **Agent:** BERESKIN & PARR LLP/S.E.N.C.R.L.,S.R.L.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 August 2006 (24.08.2006)

PCT

(10) International Publication Number
WO 2006/086828 A1

(51) International Patent Classification:

C09J 5/02 (2006.01) **B05D 1/38** (2006.01)
C08J 7/04 (2006.01) **C08J 7/12** (2006.01)
C09D 7/14 (2006.01)

(21) International Application Number:

PCT/AU2006/000070

(22) International Filing Date: 20 January 2006 (20.01.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/646,204 21 January 2005 (21.01.2005) US

(71) Applicants (*for all designated States except US*): **COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION** [AU/AU]; Limestone Avenue, Campbell, Australian Capital Territory 2612 (AU). **THE BOEING COMPANY** [US/US]; 7755 East Marginal Way South, Seattle, Washington 98108 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **BATEMAN, Stuart, Arthur** [AU/AU]; 3 Wortley Avenue, Mount Waverley, Victoria 3140 (AU). **SIMONS, Ranya** [AU/AU]; 15/47 Mary Street, Richmond, Victoria 3150 (AU). **WU, Dong, Yang** [AU/AU]; 6 Arnott Court, Wheelers Hill, Victoria 3150 (AU). **MCMAHON, Patrick, James** [AU/AU]; 3/3 Rupert Street, Highett, Victoria 3190 (AU). **BERRY, Douglas, H.** [US/US]; 2017 41st Avenue E, Seattle, Washington 98112 (US). **KOBAK, Seana, B.** [US/US]; 2100 216th Pl Ne, Sammamish, Washington 98074 (US). **KIRCHNER,**

James, F. [US/US]; 13819 146th Pl Se, Renton, Washington 98059 (US). **STRAUS, Lori, Clarice** [US/US]; 19602 110th Place Ne, Bothell, Washington 98011 (US). **JOHNSON, Mark, Paul** [US/US]; 620 9th Street, Snohomish, Washington 98290 (US). **BILYK, Alexander** [AU/AU]; 29 Amaroo Drive, Chelsea Heights, Victoria 3196 (AU).

(74) Agent: **GRIFFITH HACK**; 509 St Kilda Road, Melbourne, Victoria 3004 (AU).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ACTIVATION METHOD USING MODIFYING AGENT

(57) Abstract: The present invention relates to a method of activating an organic coating to enhance adhesion of the coating to a further coating and/or to other entities comprising applying a solvent and a surface chemistry and/or surface topography modifying agent to the organic coating. The invention also relates to a coated substrate having an activated coating, wherein the adhesion of the coating to a further coating and/or other entities has been enhanced by application of a solvent and a surface chemistry and/or surface topography modifying agent to the coating. The invention further relates to an activation treatment for an organic coating to enhance adhesion of the coating to a further coating and/or to other entities comprising a solvent and a surface chemistry and/or surface topography modifying agent and a method for the preparation of the activation treatment.

WO 2006/086828 A1

- 1 -

ACTIVATION METHOD USING MODIFYING AGENT**FIELD**

5 The present invention relates to a method of activating an organic coating, a coated substrate having an activated coating and an activation treatment for an organic coating. In particular, the activation method improves the adhesion of the organic coating to further coating layers and/or to other entities.

10

BACKGROUND

Organic coatings are generally used to protect the surface of materials from incidental damage, abrasion, chemical attack and from environmental or in-service degradation. Organic coatings are also used to enhance the aesthetics and/or optical properties of an object or component.

15 The surface properties of many coatings dramatically change on drying, curing and/or aging to become more inert than might be predicted based on the chemistry of their individual components alone. Whilst this phenomenon in part provides the coating with chemical resistance, impact strength, abrasion resistance and durability, it also complicates the process of applying additional coating layers, particularly when they are not applied within a predetermined reapplication window. The same problem arises with applying other entities such as sealants, pin hole fillers and surfacers such as those used on composite substrates, decals and logos applied with pressure sensitive adhesives and the like, to such coatings. In cases which require the application of additional coating layers and/or other entities, a mechanical abrasion or stripping process of the coating is generally necessary before the re-application procedure can take place.

20 25 30 35 In the specific example of aircraft coatings, it is well known that adhesion will not meet in-service performance requirements when fresh layers of coating are

- 2 -

applied over layers which have aged beyond the acceptable reapplication window. The acceptable window may be of the order of days under ambient conditions or potentially hours under certain conditions of high temperature or extreme humidity. Once the reapplication window has been exceeded, the standard practice for applying additional coating layers on aircraft involves mechanical abrasion of the aged coating.

Both chemical stripping and mechanical abrasion have limitations. Mechanical abrasion is labor intensive, the reproducibility is variable, and it is ergonomically costly due to the highly repetitive and vibratory nature of the work. As such there is a pressing need for the development of a surface treatment to improve the adhesion of aged or inert industrial organic coatings towards additional coating layers or other entities, for example, adhesives, sealants, fillers, stickers and the like.

Coating manufacturers have developed a method of improving the procedure of coating stripping through the development of barrier layers and intermediate coats which, for example, protect the primer and conversion coating of metal structures from the chemical stripping agents (US 6,217,945). Although this procedure would reduce the amount of infrastructure down time, it still relies on paint removal to provide a surface which will accept a fresh coating layer with acceptable adhesion.

Haack (*Surface and Interface Anal*, (2000), 29, p829) investigated the interaction of automotive polyurethane coatings using UV light to generate ozone. Promising results in terms of improved adhesion and reduced water contact angles were produced when paint formulations incorporating TiO_2 were subjected to H_2O_2 and UV light. However, there are obvious practical difficulties associated with this strategy, particularly in terms of its commercial viability for application in areas susceptible to corrosion and for treating larger surfaces.

- 3 -

Also the occupational health and safety issues make it less suited to commercial application.

In the biological field, Park et al. (*Biomaterials*, (1998), 19, p851) employed the surface urethane NH group to graft chemical species onto polyurethane rubber, whilst
5 Levy et al. (*Biomaterials* (2001) 22, p2683) employed a strong base to remove the surface urethane NH proton to accelerate such nucleophilic grafting reactions. Both strategies are unsuitable for activating organic coatings.
10 The chemical reaction kinetics of the first strategy would be too slow to be practical, particularly since, considering the low surface energy and inertness to bonding of such coatings, the urethane NH groups may not be oriented towards the air-coating interface. The use of
15 very strong bases, as per the second strategy, may degrade existing paint layers, resulting in a mechanically weak foundation for fresh coatings to adhere to. Furthermore, the latter strategy is also unacceptable for activating large areas due to corrosion and health and safety
20 considerations.

Other strategies in the biological field have employed free radical techniques to graft molecules onto the surface of biomedical polyurethane surfaces (Matuda et al, *J. Biomed. Res.*, (2002), 59, p386; Eaton et al,
25 *Biomaterials*, (1996), 17, p1977). Although commercially viable, the main difficulty with this strategy lies in promoting actual grafting of the substrate.

Controlled glycolysis or aminolysis as described in *Polymer Engineering & Science* (1978), 18, p844, and *J. Applied Polymer Science* (1994), 51, p675) has very slow
30 kinetics at room temperature and as such is not a practical solution. The use of reagents such as dimethyl phosphonate (*Polymer Degradation and Stability*, (2000), 67, p159) is also not appropriate since they are highly
35 toxic and act too slowly at room temperature.

The strategies disclosed above do not adequately address the need for the development of a surface

treatment to improve the adhesion of aged or inert organic coatings to additional coating layers and/or other entities. The problems of commercial viability, health and safety considerations, viable kinetics, applicability to small and large surface areas still remain and need to be resolved.

It is to be understood that, if any prior art publication in the biological field is referred to herein, such reference does not constitute an admission of a known application to the field of industrial and architectural coatings.

SUMMARY

We have now found a method which allows the activation of organic coatings to improve their adhesive properties towards further coating layers of the same or different type, and/or other entities without compromising coating integrity, via the use of mild reagents and conditions. The process of activation on aged coatings when they have exceeded the application window where adhesion will not meet in-service performance requirements when fresh layers of coating are applied over layers is also termed reactivation. Both activation and reactivation will be used interchangeably.

The term "mild" in this context refers to chemicals which are not known to be excessively corrosive, acidic, basic or toxic and are applicable for use in highly regulated industrial environments. One example of such an environment is a commercial aircraft paint hangar. Additionally the mild reagents used in the preferred application methods do not adversely affect the bulk aircraft coatings, or underlying coatings, such as primers or selectively strippable coatings, or underlying substrates, such as aluminium and composite.

Advantageously, this method no longer requires the traditional methods of mechanical abrasion or chemical stripping of an organic coating to improve its adhesive

properties towards additional coatings and/or other entities.

In a first aspect, the present invention provides a method of activating an aged or inert organic coating to enhance adhesion of the coating to a further coating and/or to other entities selected from adhesives, sealants, pin hole fillers and pressure sensitive decals or logos comprising applying a solvent and a surface chemistry and/or surface topography modifying agent which facilitates surface reduction, surface hydrolysis, surface oxidation, surface exchange, light induced surface modification and/or adds chemical functionality to the surface of the organic coating.

In another aspect, the present invention provides a coated substrate having an activated coating, wherein the adhesion of the coating to a further coating and/or other entities selected from adhesives, sealants, pin hole fillers and pressure sensitive decals or logos has been enhanced by application of a solvent and a surface chemistry and/or surface topography modifying agent which facilitates surface reduction, surface hydrolysis, surface oxidation, surface exchange, light induced surface modification and/or adds chemical functionality to the surface of the organic coating.

The solvent and the agent may be applied either simultaneously, sequentially or separately.

Advantageously, the solvent and the agent are applied to the organic coating simultaneously in the form of an activation treatment.

The agent may act independently from the solvent or alternatively the combination of the solvent and the agent may be necessary to affect a change in coating surface chemistry and/or topography.

In a further aspect, the present invention provides an activation treatment for an organic coating to enhance adhesion of the coating to a further coating and/or to other entities selected from adhesives, sealants, pin hole

- 5a -

fillers and pressure sensitive decals or logos comprising
a solvent and a surface chemistry and/or surface
topography modifying agent which facilitates surface
reduction, surface hydrolysis, surface oxidation, surface
5 exchange, light induced surface modification and/or adds
chemical functionality to the surface of the organic
coating.

The invention also provides a method for the
preparation of the activation treatment defined above
10 comprising the step of mixing the solvent with the surface
chemistry and/or surface topography modifying agent which
facilitates surface reduction, surface hydrolysis, surface
oxidation, surface exchange, light induced surface
modification and/or adds chemical functionality to the
15 surface of the organic coating.

DETAILED DESCRIPTION

In this specification, except where the context requires
otherwise due to express language or necessary
20 implication, the word "comprise" or variations such as

- 6 -

"comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

5 As used in the specification the singular forms "a" "an" and "the" include plural references unless the context clearly dictates otherwise. Thus, for example, reference to "a solvent" includes mixtures of solvents, reference to "an agent" includes mixtures of two or more
10 such agents, and the like.

 The method of the present invention involves activating an organic coating so as to enhance the adhesive properties of at least the surface of the coating towards additional coating layers and/or other entities,
15 for example, adhesives, sealants, pin hole fillers, pressure sensitive decal or logo adhesives and the like. The term 'activating' is used in this context to mean the improvement of the adhesive properties of the organic coating relative to the adhesive properties of that
20 coating, prior to application of the solvent and the agent.

 The word "coating" is used herein its broadest sense and describes decorative topcoats; undercoats; intermediate coatings; primers; sealers; lacquers;
25 coatings which are pigmented or clear; coatings designed for specific purposes, such as, corrosion prevention, temperature resistance, or camouflage; coatings which are high gloss, matte, textured, or smooth in finish; or coatings containing specialty additives, such as metal
30 flakes.

 In general, organic coatings which are cured, dried or aged beyond a certain time period develop resistance to forming strong adhesive linkages towards other entities. Their surface properties become more inert than might be
35 predicted, based on the chemistry of their individual components alone. Without wishing to be limited by theory, it is believed that this phenomena may result from a

- 7 -

reduction in coating surface energy and amount of reactive surface functional groups in conjunction with a higher cross-link density as a function of cure time/aging which makes chemical interaction and/or the formation of strong adhesive linkages with other entities difficult.

The organic coatings which may be activated include, but are not limited to, fully or partially cross-linked organic coatings. Examples of organic coatings include, polyurethane, epoxy, polyester, polycarbonate and/or acrylic coatings, more preferably polyurethane and epoxy coatings. Due to their superior mechanical properties and resistance to abrasion, chemical attack, and environmental degradation, such organic coatings are widely used to protect infrastructure in the aerospace, marine, military, automotive, and construction industries. Many of these coatings show a marked reduction in adhesion to other entities, such as additional coating layers, adhesives, sealants, pressure sensitive decals or logos and the like, with increased time of curing and/or aging.

The activation method involves applying the solvent and the agent to a surface of the organic coating. The surface treatment is not a continuous film or added coating layer, such as a primer coating or tie-coat, but rather a chemical method of modifying the surface of the existing coating so that it is more receptive to forming adhesive interactions with further coatings and/or other entities.

Without wishing to be limited by theory it is believed that the interaction of the agent and/or solvent combination with the coating modifies the coating surface chemistry and/or surface topography to enable it to be more receptive towards other entities including but not limited to additional coating layers. Such agents and/or solvents are chosen such that the bulk integrity of the coating and underlying coating and substrate structures are maintained.

Suitable agents include those which facilitate chemical and/or topographical modification of the coating surface such as but not limited to agents which facilitate surface reduction, surface hydrolysis, surface oxidation, surface exchange, light induced surface modification and/or add chemical functionality to the surface of the coating.

(a) Examples of agents capable of affecting surface reduction include:

(i) Reductants such as sodium borohydride, potassium borohydride, lithium borohydride, zinc borohydride, calcium borohydride and alkoxy, acetoxy and/or amino derivatives thereof such as sodium methoxy borohydride or lithium dimethylaminoborohydride; sodium cyanborohydride, borane and borane complexes; aluminium hydrides such as lithium aluminium hydride and diisobutyl aluminium hydride; calcium hydride; sodium hydride; Red Al (sodium bis(2-methoxyethoxy)aluminiumhydride); selectrides such as K-selectride (potassium tri-sec-butylborohydride); sodium dihydro-bis-(2-methoxy) aluminate; sodium borohydride mixed with aluminium trichloride; lithium triethylborohydride; and lithium tri-tert-butoxy aluminium hydride.

(b) Examples of agents capable of catalysing surface hydrolysis include:

(i) Acids such as organic acids, for example, formic acid, acetic acid, benzoic acid, propanoic acid, malonic acid, oxalic acid and *kemp's* triacid; and inorganic acids, for example, phosphoric acid.

(c) Examples of agents capable of affecting surface oxidation include:

(i) Oxidants such as trichloroisocyanuric acid, sodium hypochlorite, hydrogen peroxide, potassium permanganate, potassium chromate, periodic acid and lead tetra acetate.

(d) Examples of agents capable of affecting surface exchange or transesterification include:

(i) titanates and zirconates such as those marketed under the trade name Tyzor by DuPont, i.e. tetra-isopropyltitanate, tetra-n-propyl titanate, tetra-n-butyltitanate, tetra-2-ethylhexyltitanate, tetraethyltitanate, triethanolamine titanate chelate, tetra-n-propylzirconate, tetra-n-butylzirconate and triethanolamine zirconate chelate.

(e) Examples of agents capable of affecting light induced surface modification include:

10 (i) Free radical initiators such as initiators which are activated by the presence of light, preferably visible light induced free radical initiators or combinations of free radical initiators with tertiary amines and/or mono or multi-functional unsaturated species.

15 Suitable light activated initiators include but are not limited to camphorquinone and derivatives thereof; benzophenone and derivatives thereof, such as, diethylaminobenzophenone; and phenylphosphineoxide derivatives, such as, Irgacure (CIBA).

20 Tertiary amine agents include species such as N,N-dimethyl toluidine, N,N-dimethylamino ethylmethacrylate, methyl imidazole, NNN'N'tetramethyl-1,4-butane diamine and NNN'N'tetramethylphenylenediamine.

The multi-functional unsaturated species may be selected from acrylates, for example, hydroxyl ethyl acrylate; methacrylates, for example, polyethyleneglycol monomethacrylate, hydroxyl ethyl methacrylate, glycidyl methacrylate, N,N-dimethylamino ethylmethacrylate, ethyleneglycol dimethacrylate and butane diol dimethacrylate; and acrylamides, for example, hydroxyethyl acrylamide and bis acrylamide.

It will be appreciated that the agents may also be prepared in-situ from their constituent components. For example, LiBH_4 may be prepared in-situ from NaBH_4 and LiCl and sodium methoxyborohydride from methanol and NaBH_4 .

35 The agent(s) are generally present in an amount more than about 0.001%, preferably more than about 0.01%, and

- 10 -

most preferably about 0.01% to about 20% based on the total weight of the activation treatment, or the combination of solvent(s), agent(s) and any further optional additive(s).

5 Preferably the solvent and/or agent only interact with the surface of the organic coating so that the integrity of the coating is not compromised.

The solvent may be a single solvent or a combination of two or more solvents. Preferably the solvent is an organic solvent. Suitable organic solvents or solvent combinations depend on the surface modifying agent employed (e.g. (a) to (e) above) and include but are not limited to:

(a) ester based solvents such as ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, tertiary butyl acetate and glycol ether acetates;

(b) ketones such as methyl ethyl ketone, methyl propyl ketone, methyl amyl ketone, methyl isoamyl ketone, methyl isobutyl ketone and acetone;

20 (c) alcohols such as aromatic alcohols, for example, benzyl alcohol; aliphatic alcohols, for example, tertiary butanol, n-butanol, secondary butanol, isopropyl alcohol, propanol, ethanol, methanol and cyclohexanol; and glycol ethers, for example, those marketed by Dow under the trade name Dowanol such as, ethylene glycol, polyethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol and polypropylene glycol and their monoethers such as mono-C₁₋₆ alkyl ethers including but not limited to those marketed by Dow under the trade name Downanol E-series and P-series glycol ethers.

35 (d) ethers such as glycol diethers, for example, the di-C₁₋₆ alkyl ethers of glycols such as diethers of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol polyethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol and polypropylene glycol including but not limited to

- 11 -

diethylene glycol dimethylether, dipropylene glycol dimethyl ether or methyl butylether of diethylene glycol such as those marketed by Dow under the trade name Downanol E-series and P-series glycolethers; and cyclic
5 ethers such as tetrahydrofuran;

(e) amides such as N-methyl pyrrolidinone;

(f) aromatics such as toluene and xylene;

(g) halogenated solvents such as dichloromethane and tetrachloroethylene; and

10 (h) water

In view of the toxicity and negative environmental impact of halogenated solvents (g), it will be understood that they should be used within the constraints of environmental, health and safety regulations.

15 Preferred solvents are ester based solvents such as ethyl acetate, ethoxyethyl acetate, isopropyl acetate and/or tertiary butyl acetate; ketone solvents such as methyl propyl ketone, methyl amyl ketone, methyl isoamyl ketone and/or methyl ethyl ketone; alcohols such as
20 ethanol, methanol, ethoxyethanol, propanol, isopropyl alcohol, butanol, tertiary butanol and secondary butanol; ether solvents such as C₁₋₆ alkyl ethers or combinations thereof (i.e. mixed ethers) of ethylene glycols and propylene glycols including but not limited to glyme,
25 diglyme, triglyme, tetraglyme and dipropylene glycol dimethyl ether and cyclic ethers, for example, tetrahydrofuran; amide solvents such as N-methyl pyrrolidinone; and water.

Preferred solvent combinations include glycol ether :
30 acetate combinations such as dipropylene glycol dimethyl ether : tertiary butyl acetate; ether: alcohol combinations such as dipropylene glycol dimethyl ether: isopropyl alcohol, methanol, isobutanol, secondary butanol, tertiary butanol, ethoxy ethanol and/or
35 ethylhexanol; ethylene glycol monomethyl ether: ethanol, methanol, ethoxyethanol and/or isopropanol; glycols and monoether combinations such as dipropylene glycol-

WO 2006/086828

PCT/AU2006/000070

- 12 -

monomethylether, dipropyleneglycol-monobutylether, and/or dipropyleneglycol; ether combinations such as tetrahydrofuran: triglyme and tetrahydrofuran: dipropylene glycol dimethylether; ketones and acetate combinations
5 such as methylethyl ketone: ethoxyethyl acetate and methyl amyl ketone: ethoxyethyl acetate; N-methyl pyrrolidinone: ethyl acetate; ethyl acetate: benzyl alcohol; dipropylene glycol dimethyl ether: polyethylene; and methyl propyl ketone: methyl ethyl ketone. Typical solvent combinations
10 include high and low boiling point solvent combinations.

The solvent(s) are generally present in an amount of less than about 99.999%, preferably greater than about 70%, most preferably in an amount of about 80% to about 99.99% based on the total weight of the activation
15 treatment or the combination of solvent(s), agent(s) and any further optional additive(s).

One or more additives and/or inerts known in the art of coatings may also be used in the method or activation treatment of the present invention. Examples include:

20 (a) rheology modifiers such as hydroxypropyl methyl cellulose (e.g. Dow, Methocell 311), modified urea (e.g. Byk 411, 410) and polyhydroxycarboxylic acid amides (e.g. Byk 405);

(b) film formers such as esters of dicarboxylic acid
25 (e.g. Lusolvan FBH, BASF) and glycol ethers (e.g. DowanolTM, Dow);

(c) wetting agents such as fluorochemical surfactants (e.g. 3M FluoradTM) and polyether modified poly-dimethyl-siloxane (e.g. Byk 307/333);

30 (d) surfactants such as fatty acid derivatives (e.g. Akzo, Bermadol SPS 2543) and quaternary ammonium salts;

(e) dispersants such as non-ionic surfactants based on primary alcohols (e.g. MerpolTM4481, Dupont) and alkylphenol-formaldehyde-bisulfide condensates (e.g.
35 Clariant 1494);

(f) anti foaming agents;

- 13 -

(g) anti corrosion reagents such as phosphate esters (e.g. ADD APT, Anticor C6), alkylammonium salt of (2-benzothiazolythio) succinic acid (e.g. CIBA, Irgacor 153) and triazine dithiols;

5 (h) stabilizers such as benzimidazole derivatives (e.g. Bayer, PreventolTM BCM, biocidal film protection);

(i) levelling agents such as fluorocarbon-modified polymers (e.g. EFKA 3777);

10 (j) pigments or dyes such as fluorescents (Royale Pigment and chemicals);

(k) organic and inorganic dyes such as fluoroscein; and

15 (l) Lewis acids such as lithium chloride, zinc chloride, strontium chloride, calcium chloride and aluminium chloride.

The additive(s) are usually present in an amount of less than about 10% based on the total weight of the activation treatment or the combination of solvent(s), agent(s) and additive(s).

20 Specific activation methods forming embodiments of the present invention (which may optionally be used in combination) are as follows:

1. Surface reduction

25 This method involves using a solvent and an agent such as a reductant, for example, lithium borohydride to cause surface reduction or break down of the organic coating surface. While not wishing to be bound by any theory, it is believed that this method provides reactive entities or a suitable morphology to improve inter-coat adhesion with
30 further coating layers and/or other entities. Suitable solvent or solvent combinations for use in this method are, for example, ether or alcohol based solvents and their combinations such as dipropylene glycol dimethylether and isopropanol.

35 2. Surface hydrolysis

This method involves using a solvent and an agent such as a carboxylic acid, for example, acetic acid to

- 14 -

cause surface hydrolysis or break down of the organic coating. While not wishing to be bound by any theory, it is believed that this method provides reactive entities or a suitable morphology to improve inter-coat adhesion with further coating layers and/or other entities. Suitable solvent or solvent combinations for use in this method are, for example, ester or amide based solvents such as ethyl acetate or N-methyl pyrrolidinone.

3. Surface oxidation

This method involves using a solvent and an agent such as an oxidant, for example, trichloroisocyanuric acid to cause surface oxidation or break down of the organic coating. While not wishing to be bound by any theory, it is believed that this method provides reactive entities or a suitable morphology to improve inter-coat adhesion with further coating layers and/or other entities. Suitable solvent or solvent combinations for use in this method are, for example, ester or amide based solvents such as ethyl acetate or N-methyl pyrrolidinone.

4. Surface Exchange

This method involves exposure of the coating surface with a reagent capable of interacting (via transesterification or otherwise) with suitable chemical functionality such as ester and/or urethane moieties or otherwise to modify its chemistry or topography such that it improves the intercoat adhesion with subsequent coating layers. Suitable solvent or solvent combinations for use in this method are, for example, ether or alcohol based solvents and their combinations such as dipropylene glycol dimethylether and isopropanol

5. Light induced photo-grafting

This method involves applying an agent such as a visible light activated free radical initiator, for example, camphorquinone and an unsaturated species, for example, acrylate or methacrylate to the surface of the organic coating in a solvent. The influence of visible light causes free radical reactions to occur which modify

- 15 -

the surface of the coating to improve the inter-coat
adhesion of the further coating and/or other entities.
Suitable solvents for use in this method include ketone or
amide based solvents such as methyl amyl ketone and N-
5 methyl pyrrolidinone.

The substrate for the above methods having an
activated coating may be of any type including metals such
as aluminum; composites such as carbon fibre reinforced
epoxy or glass reinforced epoxy; plastics such as
10 polyimide; elastomers such as polysulfide elastomers; or
materials containing glass, wood or fabric. There may
also be various "sub" coating layers beneath the coating
requiring reactivation such as other decorative coating
layers, primers, intermediate layers, conversion or
15 anticorrosion coating layers and the like.

Although polyurethane and epoxy based coatings,
particularly polyurethane based coatings are typical, it
will be understood that other organic coatings may be
activated by the method of the invention.

20 When the solvent and agent are combined and applied
in the form of an activation treatment this may take
different physical forms such as solution, suspension,
mixture, aerosol, emulsion, paste or combination thereof.
Treatments which take the form of a solution or emulsion
25 are preferred.

The activation treatment may be prepared by mixing
the components together with any mixing equipment known to
those skilled in the art such as but not limited to
stirrers, shakers, high speed mixers, internal mixers,
30 inline mixers such as static mixers, extruders, mills,
ultra-sound and gas dispersers. When the activation
treatment is in the form of a solution, the solution may
be prepared as a concentrate and diluted before use or
prepared ready for use.

35 The activation treatment or the application of the
individual components thereof may be applied via any
method known to those skilled in the art such as but not

- 16 -

limited to spray, brush, dip, knife, blade, hose, roller, wipe, curtain, flood, flow, mist, pipette or combinations thereof. Application by spray is typical.

The method of activation may be conducted at ambient
5 temperatures or alternatively at higher temperatures if desirable. The activation treatment or individual components thereof may be applied to small or large areas, to sections of larger parts, components or full infrastructure such as infrastructure associated with the
10 aerospace (e.g. aircraft), automotive (e.g. vehicles), marine (e.g. ships), transportation (e.g. trains), military (e.g. helicopter, missile) or construction industries (e.g. buildings, factories, floors). The surface may have simple or complex geometry or may be at
15 any orientation. Treatment may be conducted once or multiple times prior to interaction with the separate entity. The exposure time of the activation treatment on the coating is more limited by the throughput and applications requirements. As such the exposure time may
20 be short for example one minute or extended for example 24 hours with no detriment to the integrity of the organic coating or materials that may be found on the organic coating such as sealants, and underlying coating structures and substrates.

25 The organic coating may remain activated in a non-contaminated environment for extended periods of time. In some circumstances, the activation treatment can remove contaminants from the surface in addition to activating the coating.

30 It may also be preferable to remove excess agent and/or treatment solution from the surface. This process may be conveniently carried out by techniques such as solvent or water rinsing; dry, water or solvent wiping; air or gas knife; vacuum application; removal by squeegee;
35 and/or natural or forced convection evaporation.

Optionally the water or solvent used to remove excess agent and/or treatment solution from the surface of

WO 2006/086828

PCT/AU2006/000070

- 17 -

the coating undergoing reactivation can contain additives for example to enhance the removal process, modify the drying time, or reduce corrosion. Such additives include but not limited to ionic and non-ionic surfactants, detergents, anticorrosion additives and wetting agents such as but not limited to those described above. The additives may also include cleaning agents commonly used to clean aircraft such as but not limited to those marketed under the trade names Isoprep, TurcoTM, CeeBee, RidolineTM, Formula and DaracleanTM by companies such as Brulin, Elf Atochem North America, MacDermid, W.R. Grace, McGean-Rohco and Henkel.

After the coating surface is activated, separate entities such as additional coating layers or coating details, adhesives sealants, pressure sensitive decals or logos, and the like may be applied either immediately or at a later time, providing the surface remains predominantly uncontaminated during storage or that the contamination can be conveniently removed. The activation solution may need to be reapplied in some cases.

Any suitable method known to those skilled in the art may be used to assess whether the adhesive linkage between the organic coating and further coatings and/or other entities is fit for purpose. Such tests include but are not limited to ASTM, ISO, and FAA standards, in-house test methods to simulate in-service performance, in-service performance itself, and durability testing either actual or accelerated. For the case of aerospace coatings, test methods based on water impact, such as whirling arm and the Single Impact Jet Apparatus (SIJA) (MIJA Limited, Cambridge, UK), have been found to be particularly useful for assessing inter-coat adhesion. In these cases, the amount of overcoat removal is related to the level of inter-coat adhesion.

For aerospace applications the activation method of the present invention offers the advantages of improved flow time for the process of reactivation, greater

- 18 -

reproducibility and consistency over larger areas and between operators, and improved ergonomics of the process leading to reduced vibration or repetitive motion based injuries for completing the process of reactivation which
5 added together provide a net cost saving.

EXAMPLES

The invention will now be described with reference to the following non-limiting examples. Although the examples
10 concentrate on coatings derived from polyurethane chemistries it will be understood that the same activation methodology could be applied to coatings such as but not limited to those based on epoxy, acrylic, polycarbonate, or polyester coatings through the appropriate choice of
15 solvent(s), agent(s) and optional additives under appropriate activation conditions.

The specific "substrate" the polyurethane topcoat is applied to is not relevant. Hence the substrate can be metal (eg. aluminium), plastic (eg. polyimide), composite
20 (eg. carbon fibre reinforced epoxy or glass reinforced epoxy) or an elastomer (eg. polysulfide elastomer). The substrate may be finished with surfacing materials, films, elastomers or coatings.

The polyurethane topcoat layer which requires
25 reactivation may have topcoat, intermediate or priming layers beneath it and again these layers are not relevant. Typical examples of build-ups employed in the aerospace industry include:

Aluminium substrate: cleaned, surface prepared with
30 anodize or conversion coat, epoxy based primer(s), optionally selectively strippable intermediate coating layer, and polyurethane topcoat layers.

Epoxy based composite: surface prepared/cleaned,
35 epoxy based primer(s), optionally selectively strippable intermediate coating layer, and polyurethane top-coating layers.

- 19 -

The reactivation treatment solution is designed in such a way that it can be applied under industrial conditions and the integrity of the "substrate" or coating layers beneath the polyurethane coating which is undergoing reactivation are not adversely effected to a point where they are unsuitable for their intended purpose by interaction of treatment solution which may inadvertently come in contact with it for short periods.

10

Example 1 : Hydrolysis Surface Activation Method

The example demonstrates that improved SIJA inter-coat adhesion relative to untreated specimens results from activation of the coating prior to over-coating. Inter-coat adhesion provided in this case is similar to specimens reactivated by sanding.

15

Example 2 : Oxidation Surface Activation Method

The example demonstrates that improved SIJA inter-coat adhesion relative to untreated specimens results from activation of the coating prior to over-coating. Inter-coat adhesion provided in this case is similar to specimens reactivated by sanding.

20

Example 3 : Reduction Surface Activation Method

The example demonstrates that improved SIJA inter-coat adhesion relative to untreated specimens results from activation of the coating prior to over-coating. Inter-coat adhesion provided in this case is similar to specimens reactivated by sanding.

25

Example 4 : Light induced photo-grafting Surface Activation Method

The example demonstrates that improved SIJA inter-coat adhesion relative to untreated specimens results from activation of the coating prior to over-coating. Inter-

30

35

- 20 -

coat adhesion provided in this case is similar to specimens reactivated by sanding.

Example 5 : Reduction Surface Activation Method

5 The example demonstrates that improved Scribe green
adhesion (predictor of possible problems during masking
tape removal) relative to untreated specimens results from
activation of the coating prior to over-coating. Inter-
coat adhesion provided in this case is similar to
10 specimens reactivated by sanding.

Example 6 : Reduction Surface Activation Method

 Stripping study indicated that coatings reactivated
by surface reduction methods strip quicker than specimens
15 sanded prior to over-coating but slower than coatings
over-coated without treatment.

Example 7 and 8 : Evidence of Surface Chemistry Change

 Results indicate that a higher Specific contribution
20 to surface energy results (γ_s^P), particularly to surfaces
activated with the reduction strategy.

Examples 9 to 33 : Reduction Surface Activation Method

25 Example 34 : Surface Activation Method with Exchange
Agents

 It is envisaged that suitable combinations of
components of the activation treatment will differ
30 depending on the type of coating to be activated. The
appropriate choice of solvent(s), agent(s), optional
additives and inerts, and activation conditions will
differ depending on the type of coating to be activated.

General Experimental Detail**Painting Conditions and Protocol**

Spray painting of many flat panels was carried out employing a Yamaha robotic painting arm incorporating a gravity fed Binks Mach 1A automatic spray gun configured with a 94 nozzle. Spray painting was conducted using an inlet pressure of 40 PSI, a scan rate of 100 mm/s and a specimen to gun distance of 300 mm. The coating thickness was controlled by the gun's fluid needle control position and scan rates. These parameters were adjusted in line with paint thickness measurements and assessed using a Fischer Isoscope (MPOD) on aluminium substrates. When coating was completed on composite substrates, the coating layer thickness was estimated by calibration with the isoscope readings from aluminium panels. An analogous strategy was employed for the application of the primers, optional intermediary and topcoat layers. For the majority of the examples, the painted films were over-coated following taping through the middle of the coupon with 3M vinyl tape (#471) to form a paint edge on its removal. This edge was the impact target for SIJA (Single Impact Jet Apparatus) analysis.

Spray painting of curved or larger surfaces (eg: rain erosion foils) and some of the smaller flat panels was typically conducted using a Binks M1-H HVLP gun configured with a 94 nozzle. Occasionally, a similar gravity fed HVLP gun or a pressure pot fed HVLP gun was used. In these cases the aluminium or composite was prepared in the same manner as the flat plates prior to the first top-coat being applied. Following cure of the first coating layer the front of the foils were masked (Intertape Polymer Group, PG-777 tape) prior to over-coating to form a leading edge once the over-coating was applied and tape removed.

Cure protocols were undertaken in a computer controlled temperature humidity chamber, such as a

Thermoline Environmental chamber and/or a conventional curing oven.

Table 1 : Paint Material Information

5

For the majority of the examples, the coatings used are listed in Table 1. In the examples, paint companies are generally abbreviated:

PRC-DeSoto International: PRC-DeSoto

10 Akzo-Nobel Aerospace Coatings: Akzo-Nobel

Table 1 : Paint Material Information

	Primer	Intermediate Coat	Topcoat
Coating	Epoxy based primers suitable for composite or aluminium based aerospace componenets	Intermediate coat that is selectively strippable	PRC-DeSoto International: Desothane HS and Akzo-Nobel Aerospace Coatings: Eclipse
Components			Base: CA8000/ByyyyyX such as CA8000/B70846X Activator: CA8000B Thinner 1: CA8000C Thinner 3: CA8000C2 or ECL-G-yy such as ECL-G-14 (BAC70846) Curing Sol: PC-233 Thinner TR-109 Thinner TR-112

Note: the thinner designation C and C2 are used to indicate the relative rate at which the paint cures. C thinners - standard cure rate with C2 producing a correspondingly faster cure rate (from incorporation of high catalyst levels into the thinner). For Akzo-Nobel - fast cure thinner is designated TR-112 and standard thinner TR-109.

Painting Conditions and Protocol

Substrates were cleaned prior to priming and optionally where appropriate treated with an alodine type conversion coating or anodized.

Polyurethane topcoats, intermediate and primer layers were mixed and applied according to the paint manufacture instructions.

Primer:

Typical conditions:

- For Composite or aluminium: application of common aerospace epoxy based primer optionally incorporating additives to aide corrosion resistance at 0.5 mil

WO 2006/086828

PCT/AU2006/000070

- 24 -

(12.5 micron) dry film thickness (dft) per
manufacturer instructions.

Intermediate coat:

- Optionally application of intermediate coat (IC) that
5 is selectively strippable at 0.35 mils (10 microns)
according to manufacturer instructions

Polyurethane topcoat:

- Application of polyurethane topcoat (eg: Desothane HS
topcoat containing CA8000/B70846X base (white color
10 of this topcoat also designated as BAC70846. In
examples it is typically designated as DesothaneTM HS
70846X) at 1.0 to 4.0 mil (typically 1.0 mil (25
micron)). Painted panels flash off for 1 hour prior
to cure and accelerated aging.

15

Standard cure / accelerated aging conditions employed
for topcoats were: (i) Cure painted panels in oven at
120°F, 5-10% RH (Relative Humidity) for 40 hours,
followed by (ii) post cure in a humidity chamber at
20 120°F (49°C) and 50% RH for 48 hours, and then (iii)
oven cure at 160°F for 24 hours. Total cure time was
112 hours. Alternatively other "accelerated" aging
protocols were employed as specified in the examples to
render the polyurethane topcoat unreceptive to
25 additional coating layers as indicated by poor adhesion
under standard adhesion tests eg: 120°F and 2-3% RH for
5 days or 120°F and 5% RH for 16 hours.

Surface Modification

30 The solvents and agents used for surface modification
were purchased from the MERK and Sigma-Aldrich or Dow
Chemical Companies. Purity was of an Analytical or
Laboratory Reagent grade purity. Isopropyl alcohol was

- 25 -

generally of an anhydrous grade. However, alternative suppliers and grades of the reagents are known to be available.

Proglyde DMM (abbreviated to proglyde) - Dipropylene
5 glycol dimethyl ether

EtOH - ethanol

EtOAc - ethyl acetate

IPA - isopropyl alcohol

tBAC - t-butyl acetate

10 MPK - methyl propylketone

MEK - methyl ethylketone

THF - tetrahydrofuran

SS - Stainless steel

HSS - High strength steel

15 h - hour

min - minutes

SOLO - Spray on leave on

SOHO - Spray on hose off

SOWO - spray on wipe off

20 RH - relative humidity

Table 2 : General Activation Protocol

Task	Strategy
Treatment	Spray application of the reactivation treatment solution employed a Binks M1-H HVLP gun with a 92 or 94 nozzle and 20 psi inlet pressure or, on occasion, a similar HVLP gravity or pressure fed gun or by a flood application where indicated. The active agent (eg: reducing agent such as LiBH_4) was dissolved, dispersed or suspended in the solvent/s at a percentage based on weight and the hence prepared "reactivation treatment" applied to the substrate for a given period
Post-Treatment	Spray on leave on application (SOLO) Optionally the polyurethane surface may be "post" treated Washed with water (or solvent) a period following treatment – spray on-hose off (SOHO) or Wiped with an isopropanol, ketone (eg: methyl-propyl ketone) or water soaked cloth – spray on wipe off (SOWO)
Re-coating	Samples were over-coated with polyurethane topcoat either: • Same day (5 mins to 4 hours after treatment) • Some period following reactivation. Unless otherwise specified for SIJA or rain erosion adhesion testing, over coat thickness was 100 micron employing Eclipse or Desothane HS coatings cured with standard thinners. Cure conditions were 120F under 10-20% RH for at least 48 hours unless specified. Scribe test overcoat paint thickness was typically 25 to 50 microns

5 Analysis

Table 3 provides the equipment and conditions used for testing for analytical purposes.

Table 3 : Testing Equipment & Conditions

Equipment	Conditions										
SIJA	Adhesion testing was completed using a Single Impact Jet Apparatus (SIJA, Cambridge). The initial equipment was typically configured using a 0.8 mm nozzle typically and employed 0.22 calibre 5.5 mm Crosman Accupell Pointed Pellets (#11246). Testing was completed following immersion in water for 16 to 18 hours, employing a line laser to locate the impact position, and using a 45° specimen to impact droplet geometry. A single water jet was employed at each site to test adhesion with the pressure employed for the "shot" indicated below its impact. The velocity of each individual shot was recorded for future reference, but generally the pressure to velocity conversion is specified below (± 25 m/s). <table> <tr> <td>Pressure (PSI)</td><td>Velocity (m/s)</td></tr> <tr> <td>L</td><td>350</td></tr> <tr> <td>50</td><td>610</td></tr> <tr> <td>100</td><td>725</td></tr> <tr> <td>200</td><td>895</td></tr> </table> Alternatively the impact was dictated by a "dot" or via the velocity employed - eg. 600 m/s. In some cases the amount of overcoat removed, and hence the inter-coat adhesion was assessed employing image analysis techniques to quantify the area of paint removed. However regardless of the impact velocity relative to the unmodified reference more overcoat removed corresponded with inferior inter-coat adhesion.	Pressure (PSI)	Velocity (m/s)	L	350	50	610	100	725	200	895
Pressure (PSI)	Velocity (m/s)										
L	350										
50	610										
100	725										
200	895										
Scribe Adhesion	Scribe adhesion was assessed according to (BOEING Specification Standard) BSS7225, Class 5. This adhesion test is a five line cross-hatch tape (3M tape, No. 250) pull test. Briefly heat aged polyurethane coatings were reactivated and then over-coated (25 - 80 micron thickness) curing the over-coat for 16 hours at room temperature and 50% RH. The coatings were then scribed according to BSS7225 (5 scribe cross-hatch) and the adhesion test performed. The paint adhesion of specimens are rated on a scale of 10 to 1 with "10" being no paint removed and "1" being all paint removed.										

WO 2006/086828

PCT/AU2006/000070

- 28 -

Equipment	Conditions
Whirling Arm Rain Erosion Testing	Rain erosion testing was completed on a whirling arm rain erosion apparatus employing a 52 inch zero lift helicopter like propeller run at 3600 rpm. Reference and activated polyurethane topcoat foils were over-coated (60 to 120 micron paint thickness) following masking to produce a leading edge. The foils were attached to the propeller at a distance along the propeller correlating to a velocity of 380 mile per hour at the mid point of the foil. The effective rain field density of 2 mm droplets used during the experiment was 1 inch per hour. After 30 min the impact of rain erosion on the inter-coat adhesion of the foils was evaluated according to a 0.5 to 5 rating correlating the amount of paint removed or tear lengths. The impact of water droplets on the leading edge of the over-coat formed on removal of the tape during the experiment erodes the over-coating layer relative to the strength of the inter-coat adhesion.
Paint Stripping	Procedure for the complete strip test is described in SAE MA4872, Annex A, pages 51 to 53. In this Stage an abbreviated version was completed using benzyl alcohol based paint strippers without thermal cycling to compare how the activated and over-coated specimens to untreated and reference specimens. Aged specimens (Aluminium or composite substrate) were untreated, sanded, or activated, were over-coated (60-75 micron), and cured for 40 hours at 120°F. The edges were taped with Aluminium tape (such as 3M Scotch™ Brand No, 425) prior to commencing the test. Stripper was applied every 2 hours until the coating was removed. Lifting paint was removed just prior to reapplication of the stripper using a plastic squeegee.
Contact Angle	Contact angle analysis was completed using "FIRST TEN ANGSTROMS" semi-automated video equipped contact angle analyser. CH ₂ I ₂ and H ₂ O were employed as the reference solvents to calculate the dispersive (γ_s^d) and polar (γ_s^p) contributions to surface energy (γ_s) through the Young-Dupre relationship and Fowkes equation.

WO 2006/086828

PCT/AU2006/000070

- 29 -

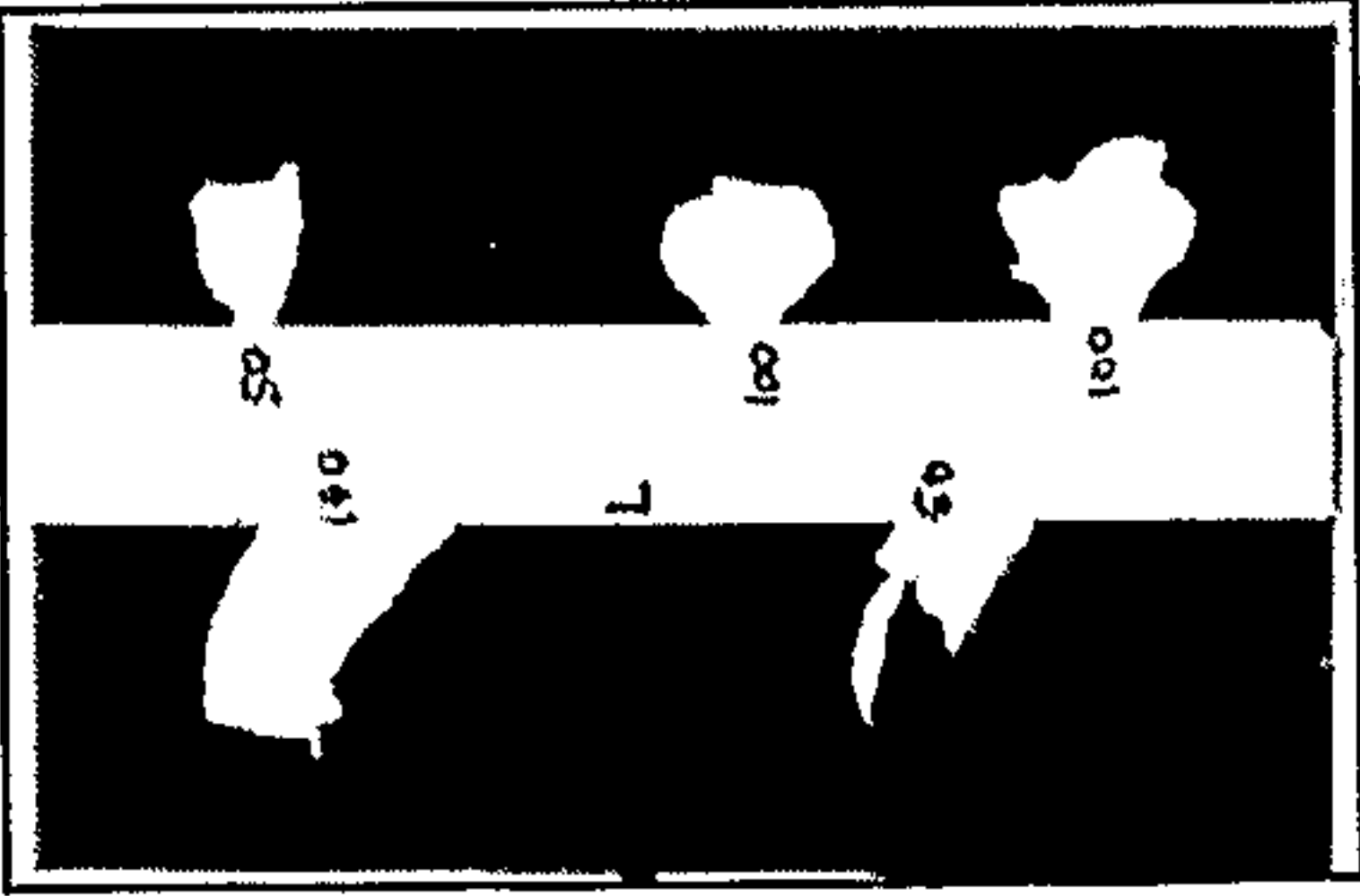
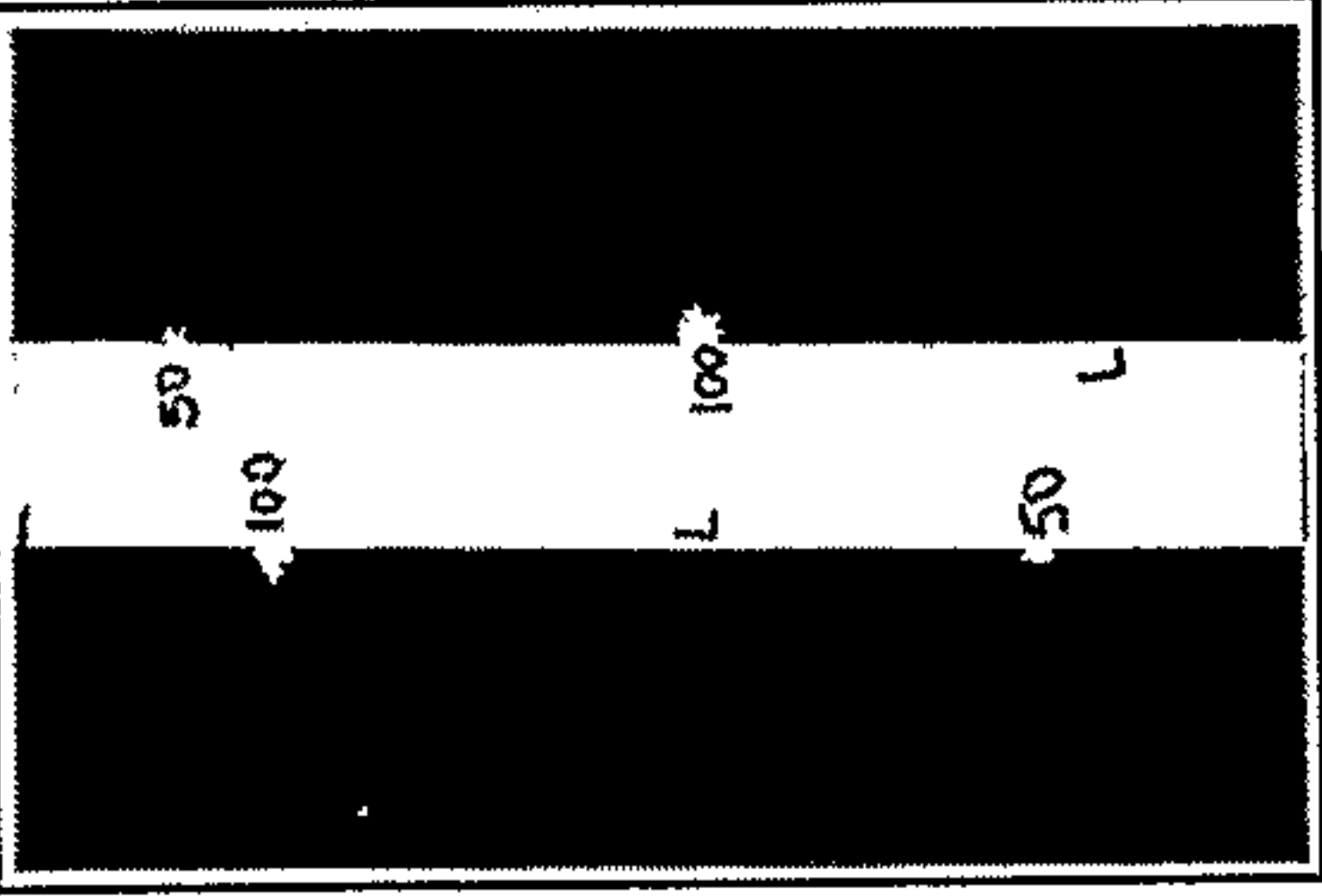
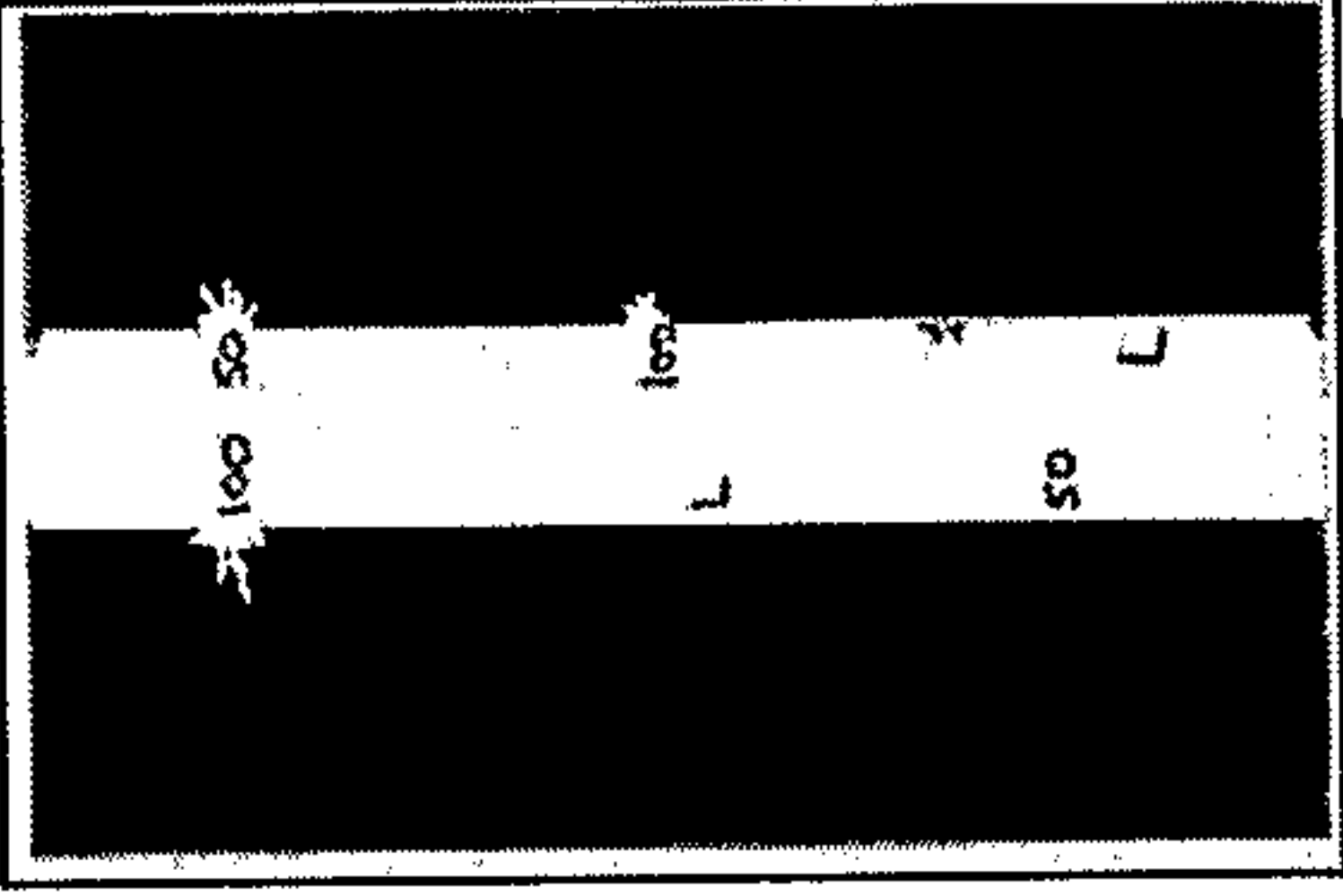
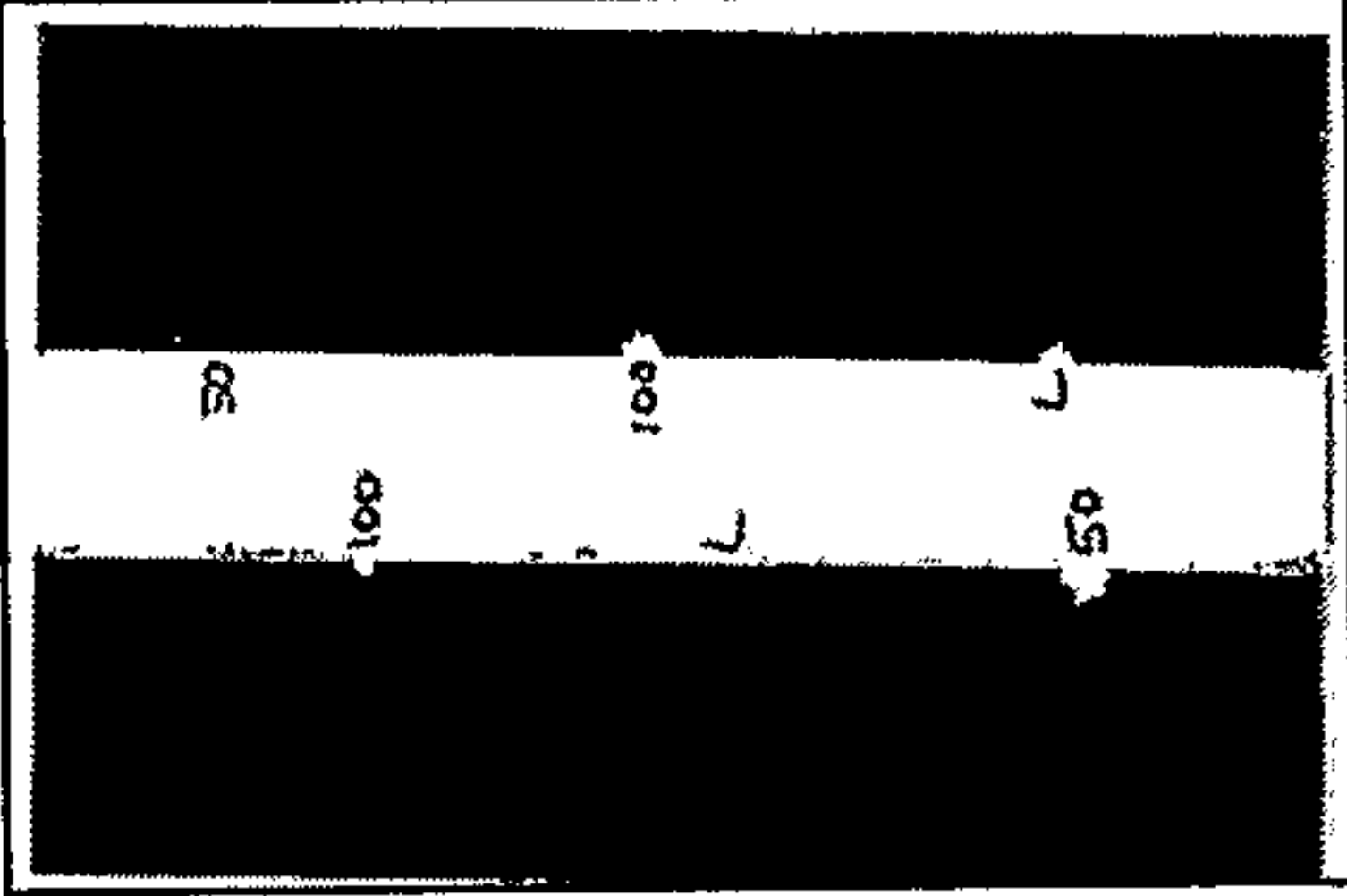
Equipment	Conditions
FTIR	FTIR analysis was carried out on a BRUKER™ FTIR/NIR spectrometer or Nicolet Instruments, employing NaCl plates or an ATR KRS-5 TiBr / TiI mixed crystal associated with the microscope. Extent of surface contamination was assessed by swabbing the surface with a "Q-tip" soaked with hexane. Following evaporation of the hexane solution onto NaCl, powder NaCl plates suitable for FTIR analysis were prepared by compression moulding.
SEM	SEM analysis of the polyurethane cross-sections were collected on a Oxford™ Pentafet detector controlled by an Oxford ISIS system. Cross-sections of the samples, prepared with a cut off saw appropriate for non-ferrous materials, were mounted in epoxy resin, ground and polished to a 1 micron finish and gold coated. Imaging and x-ray analysis was conducted using a 15 KV accelerating voltage and a 17 mm working distance. EDX analysis was specifically refined for carbon, nitrogen, oxygen, and chlorine.
Hydrogen Evolution	Activity of reducing agent was determined by employing Hydrogen Evolution techniques. The activity of the reducing agent solution (eg. LiBH_4 in Proglyde DMM) was determined by measuring the quantity of hydrogen evolved following interaction with dilute aqueous acid.
Accelerated UV exposure	- Equipment: Atlas™ (Xenon Arc) Weatherometer - Outer filter = borosilicate - Inner filter = quartz - Light intensity: $0.55 \text{ W/m}^2/\text{nm}$ @340nm - Operation Cycle (~SAE J1960): - Panels: Desothane HS 70846 White - Test for: - Colour shift of previously reactivated (but not over-coated) panels

- 30 -

	- Reactivation potential of samples conditioned through aging protocol then a UV cycle.

Example 1 : Hydrolysis Method

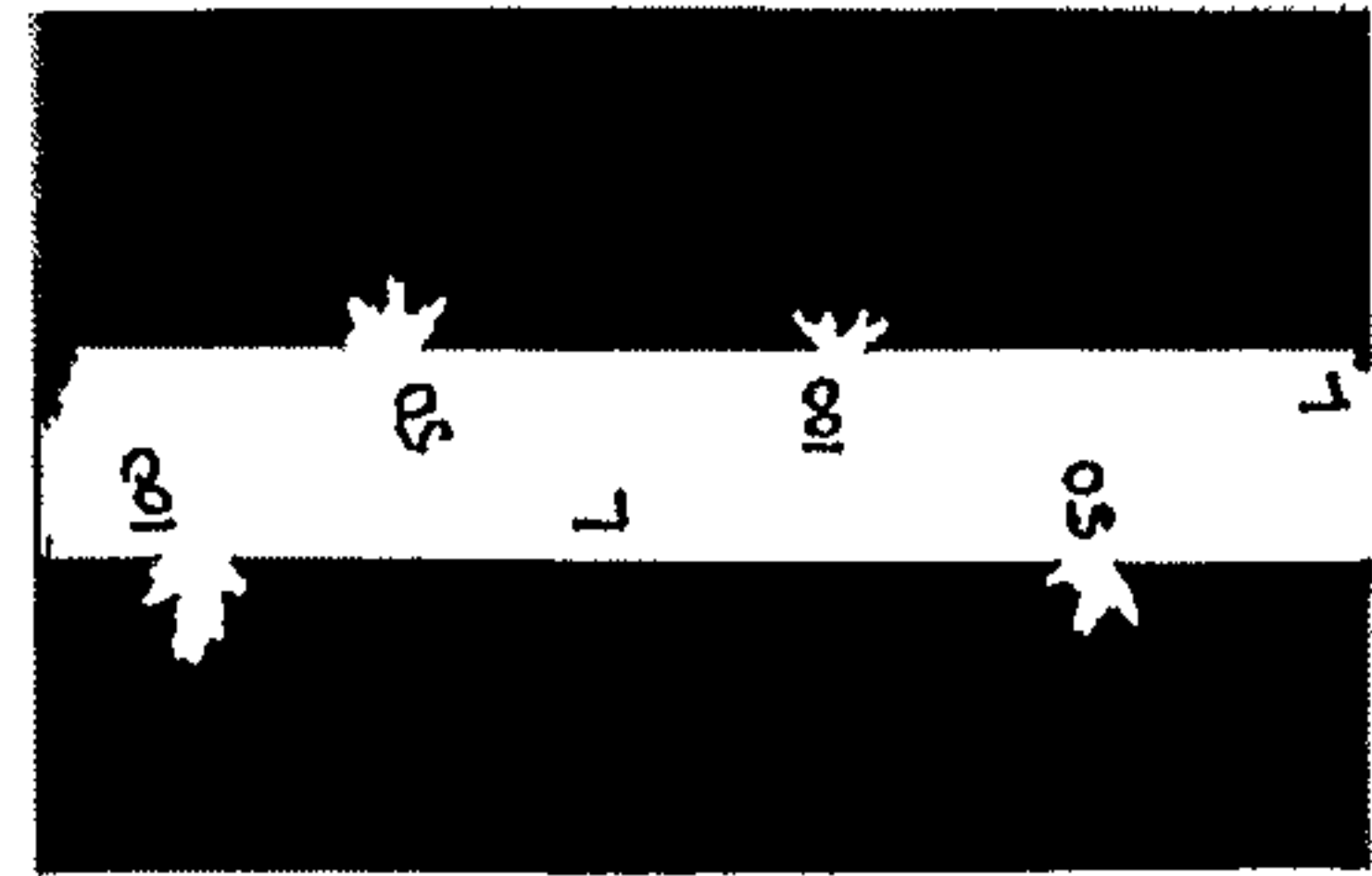
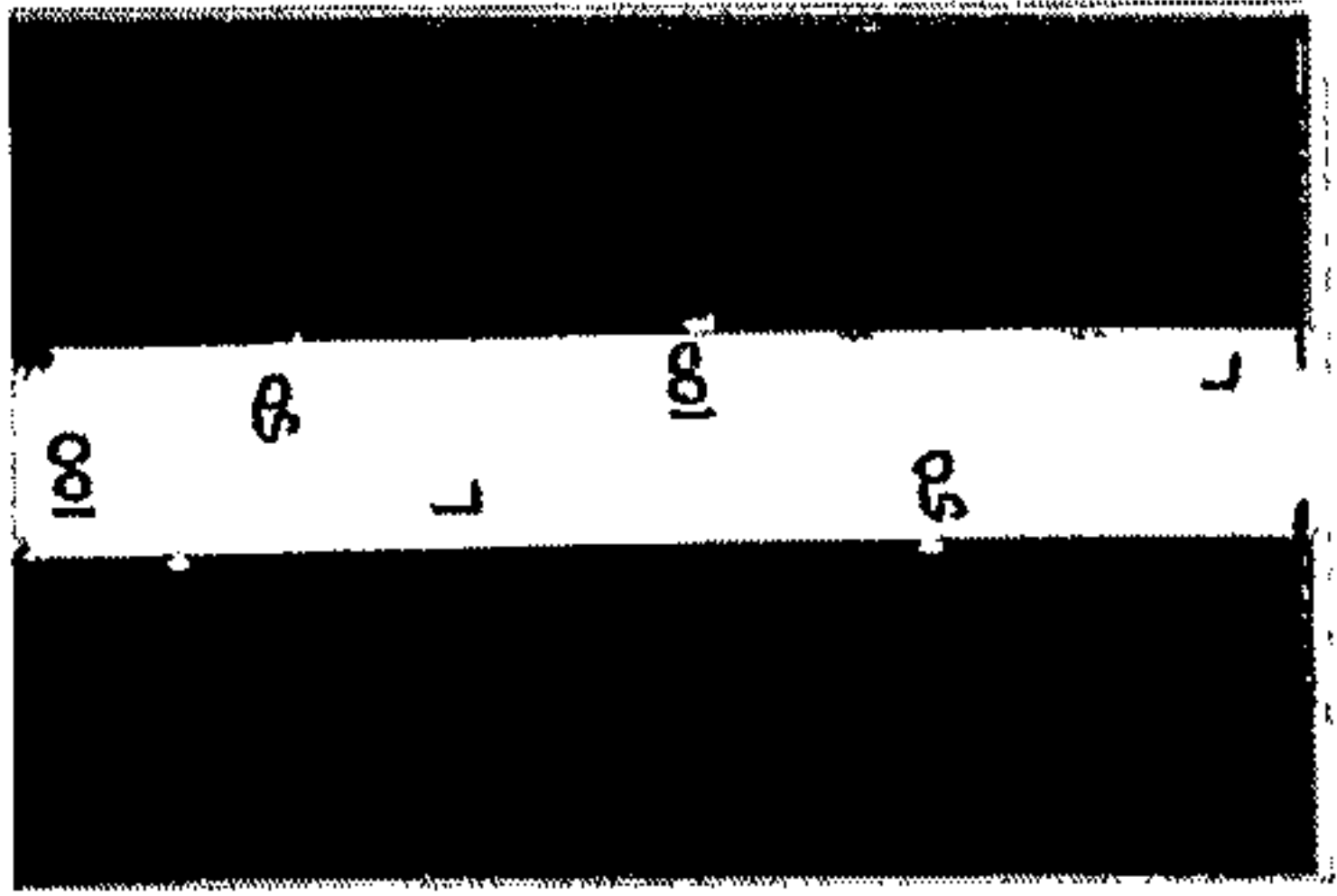
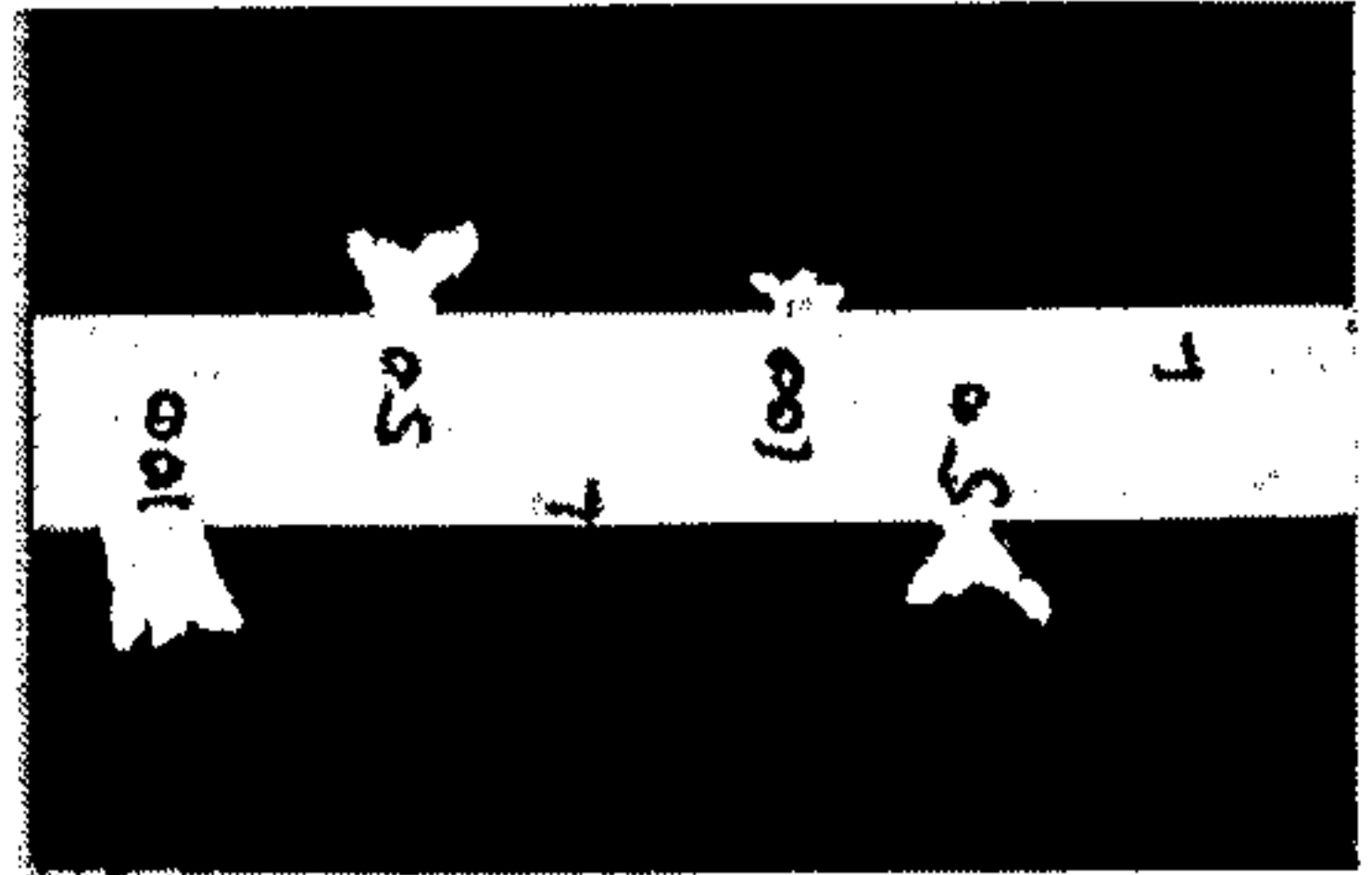
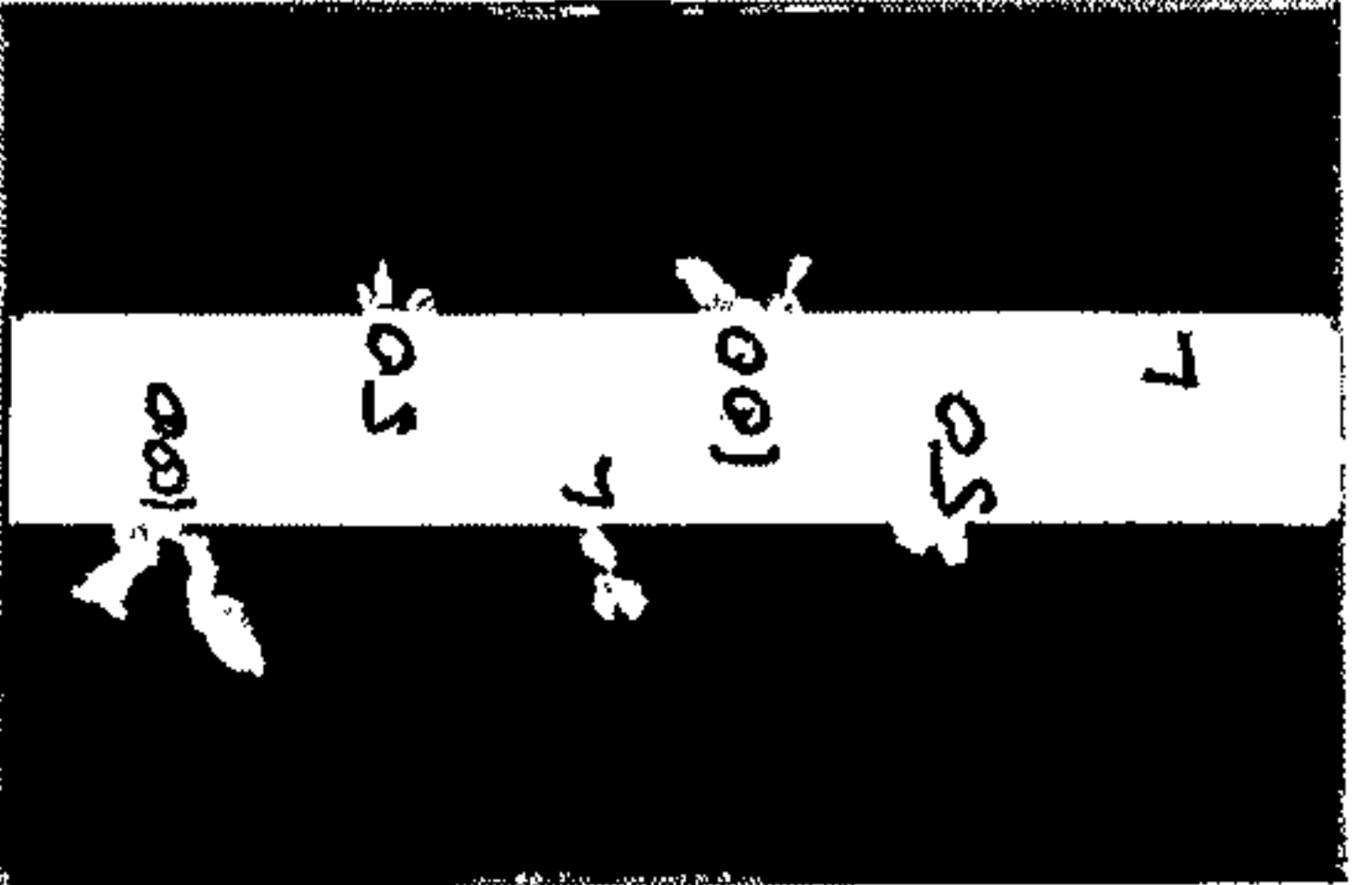
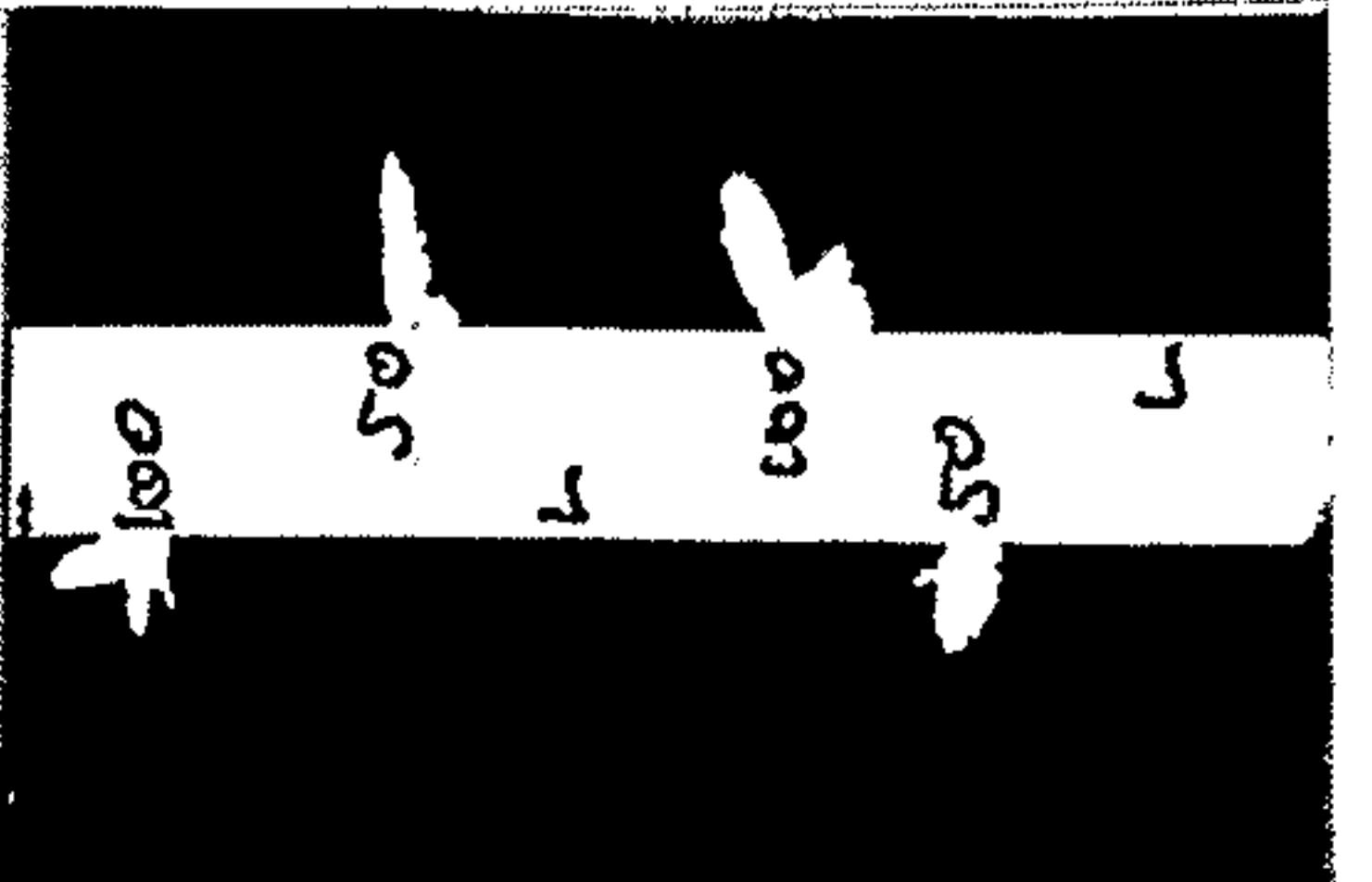
SIJA inter-coat adhesion of Desothane HS 70846X white ($30\pm5\text{ }\mu\text{m}$, CA8000C thinner) cured 40 hour at 120°F ($\sim 9\%$ RH) followed by 48 hour at 120°F (50% RH) followed by 24 hour at 160°F , activated and over-coated with Desothane HS S601X blue ($104\pm10\text{ }\mu\text{m}$).

			
Untreated	Sanded	1% acetic acid Ethyl acetate	1% acetic acid(pH~5.5) N-methyl pyrrolidinone

Activation Treatment : 30 min, horizontal application position (IPA wipe post treatment)

Example 2 : Oxidation Method

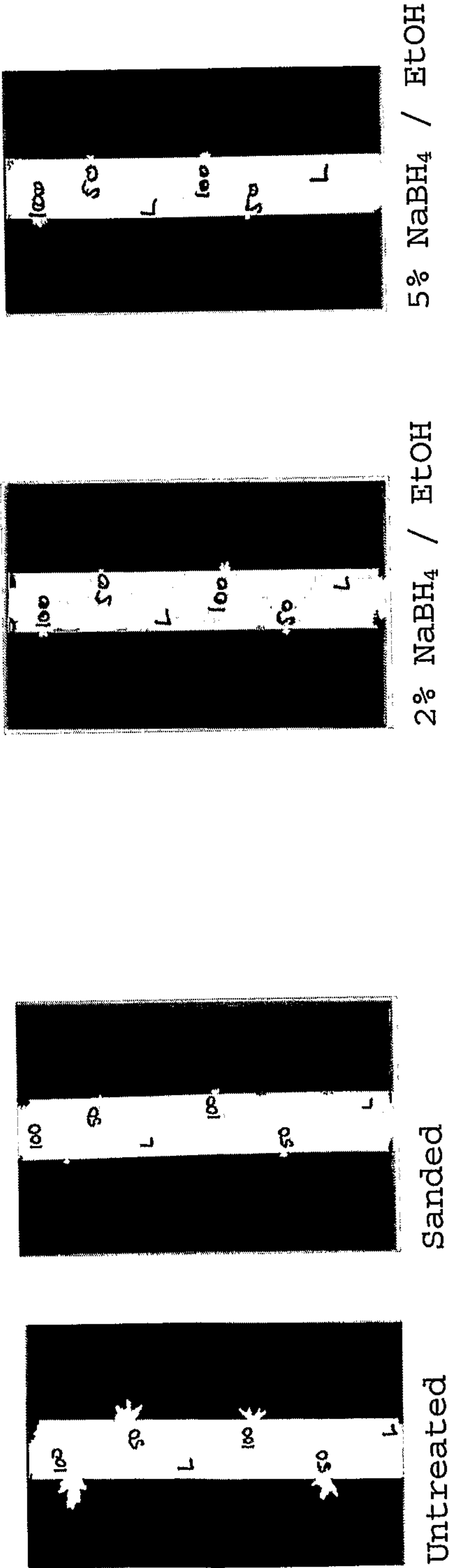
SIJA inter-coat adhesion of Desothane HS 70846X white (30±5 µm, CA8000C2 thinner) cured 40 hour at 120°F (~9% RH), followed by 48 hour at 120°F (50% RH) and 24 hour at 160°F, activated and over-coated with Desothane HS S601X blue (104±10 µm).

				
Untreated	Sanded	5% trichloroisocyanuric Acid Ethyl acetate	2%NaOCl/0.5% HCl DI water	2% NaOCl/0.5% HCl PEG 600, DI water

Activation treatment time 30 min, (IPA wipe post treatment)

Example 3 : Reduction Method

SIJA inter-coat adhesion of Desothane HS 70846X white (30±5 µm CA8000C2 thinner) cured 40 hour at 120°F (5% RH) followed by 48 hour at 120°F (50% RH) and 24 hour at 160°F, activated and over-coated with Desothane HS S601X blue (104±10 µm).

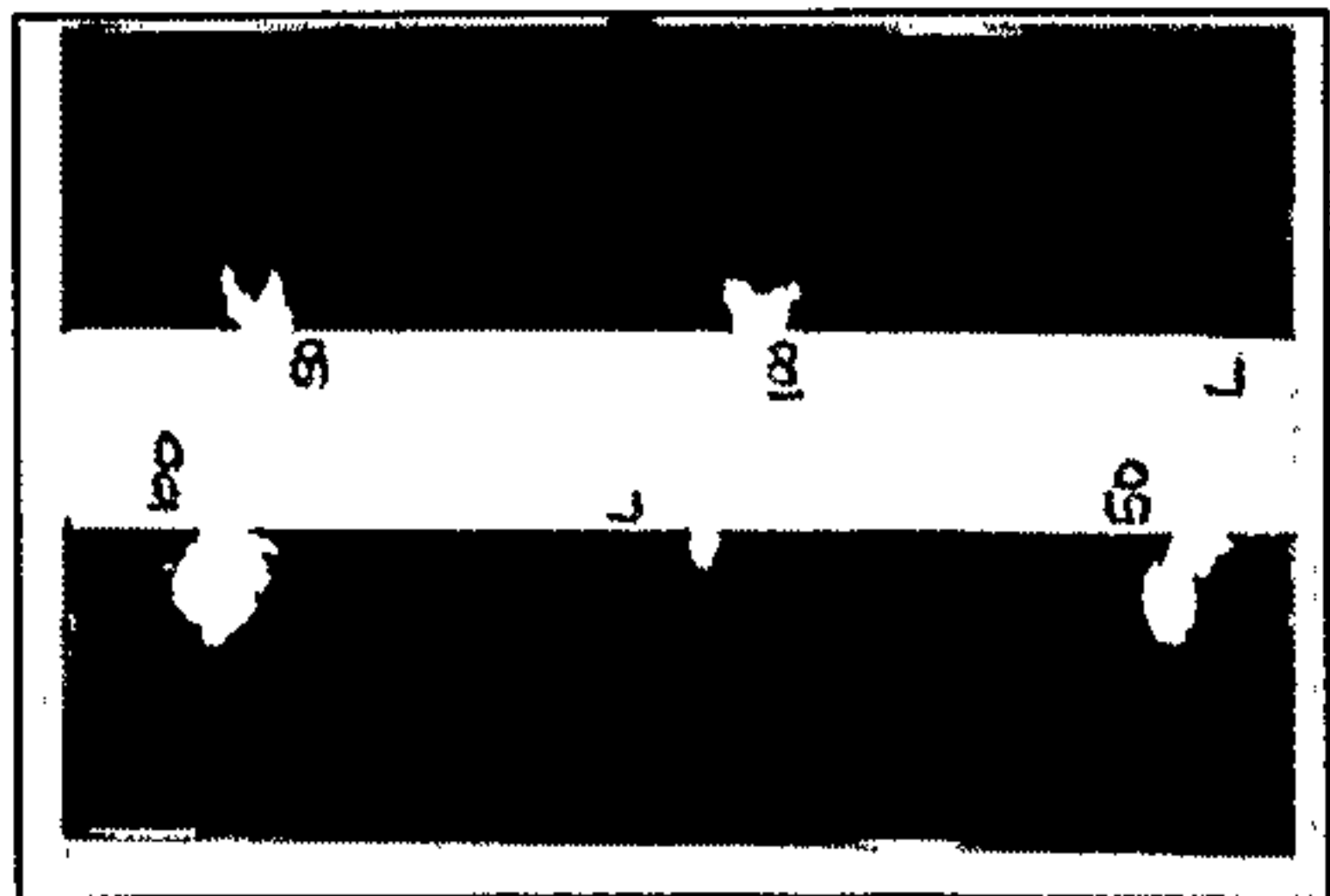


Treatment 30 min, (SOHO - post treatment).

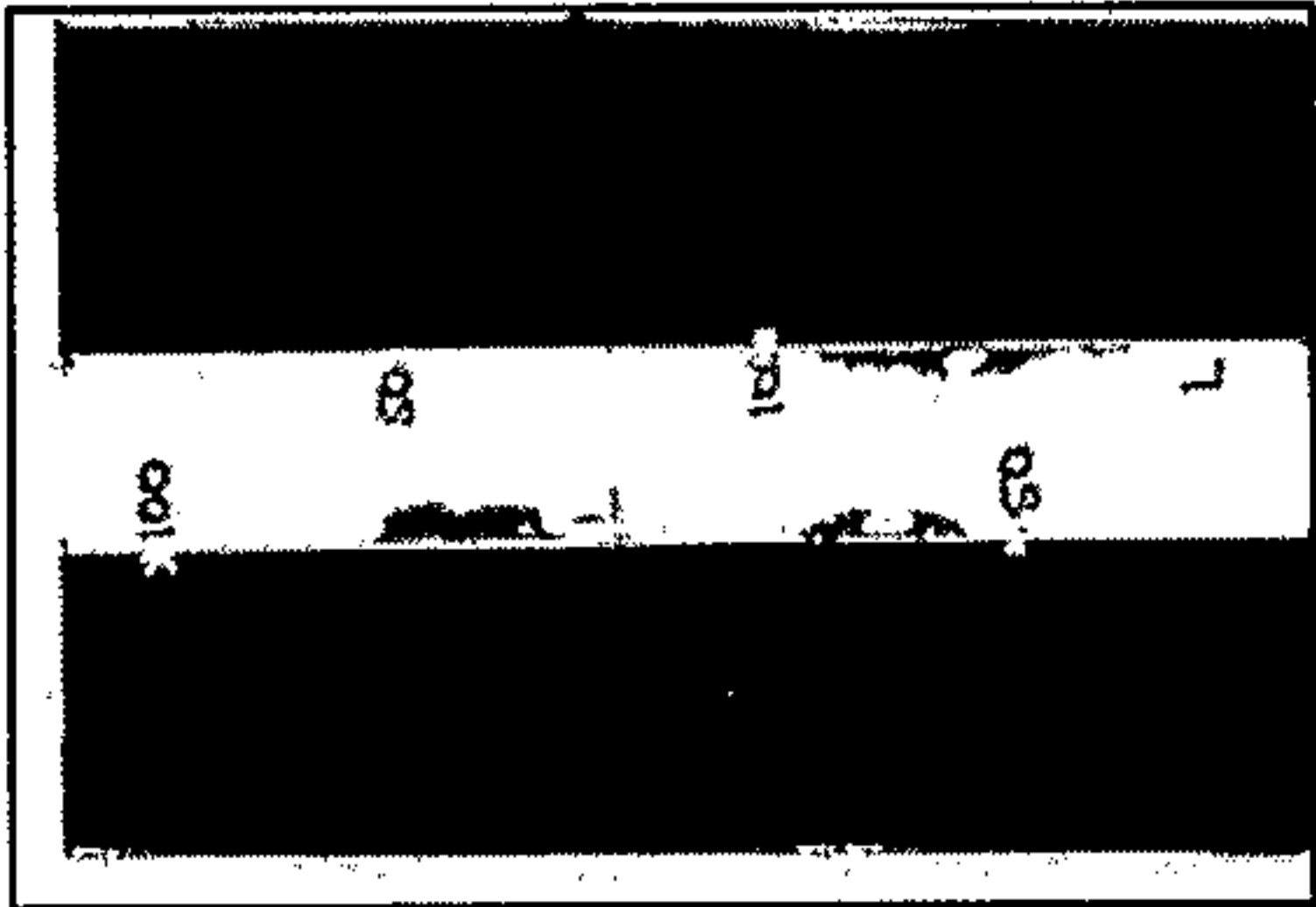
Example 4 : Light Grafting Method

SIJA inter-coat adhesion of Desothane HS 70846X white (30±5 µm, CA8000C-thinner) cured 40 hour at 120°F, (~9% RH), followed by 48 hour at 120°F, 50% RH and 24 hour at 160°F, activated 120 min, wiped (IPA) and over-coated with Desothane HS S601X blue (104±10 µm).

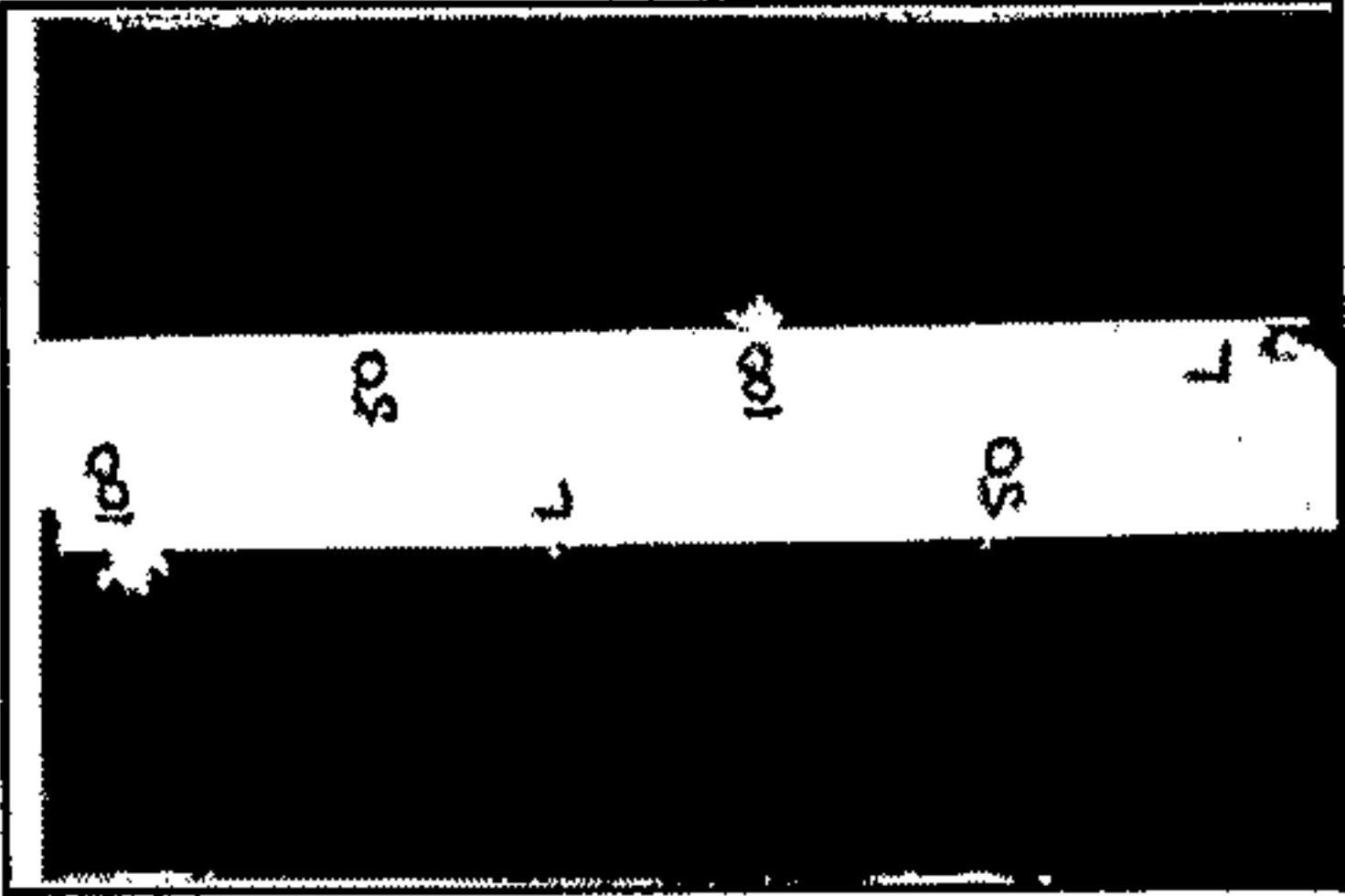
methylethylketone N-methyl pyrrolidinone methylethylketone



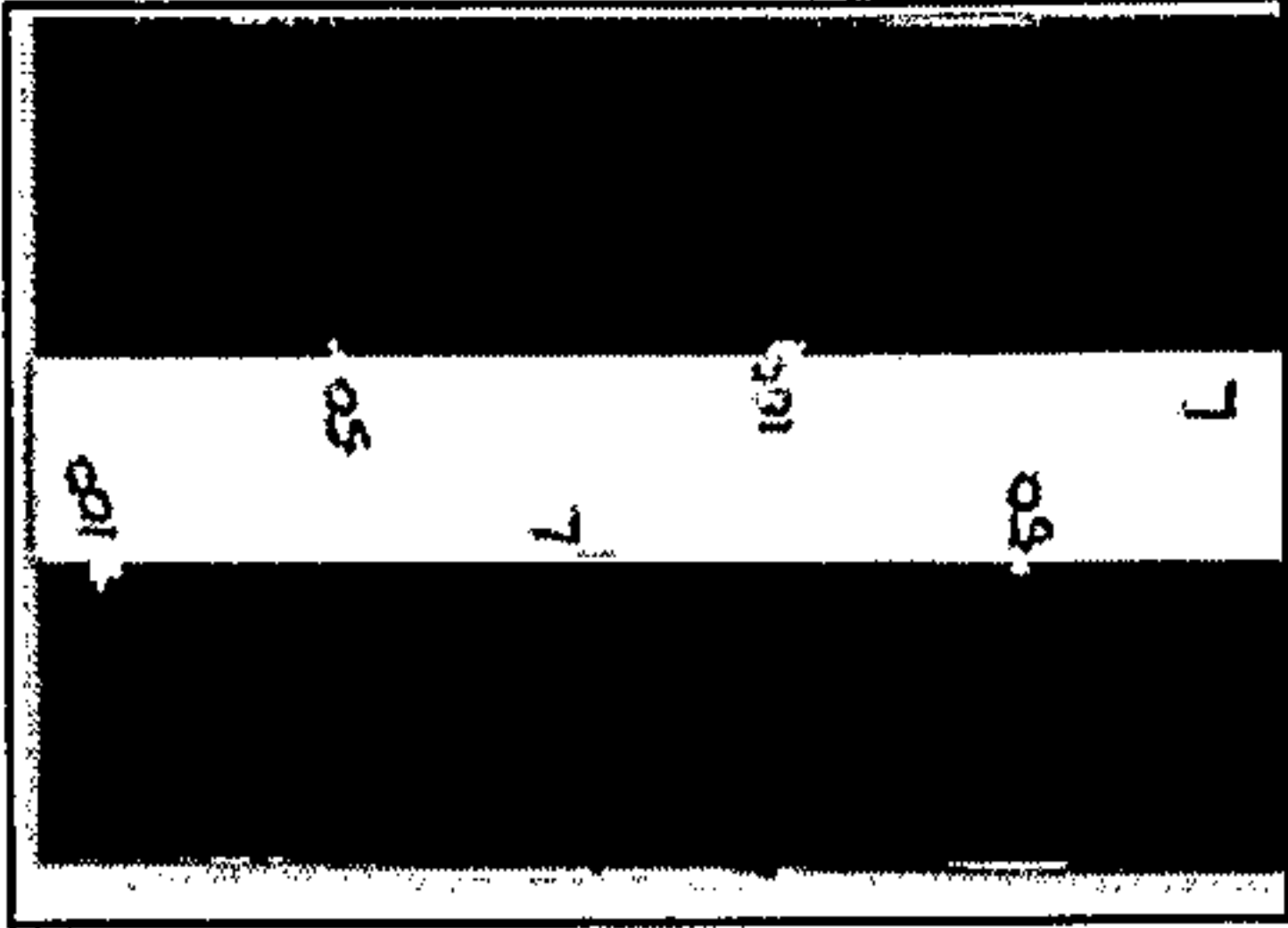
untreated



10% hydroxy
monomethacrylate



10% hydroxy
ethylacrylate

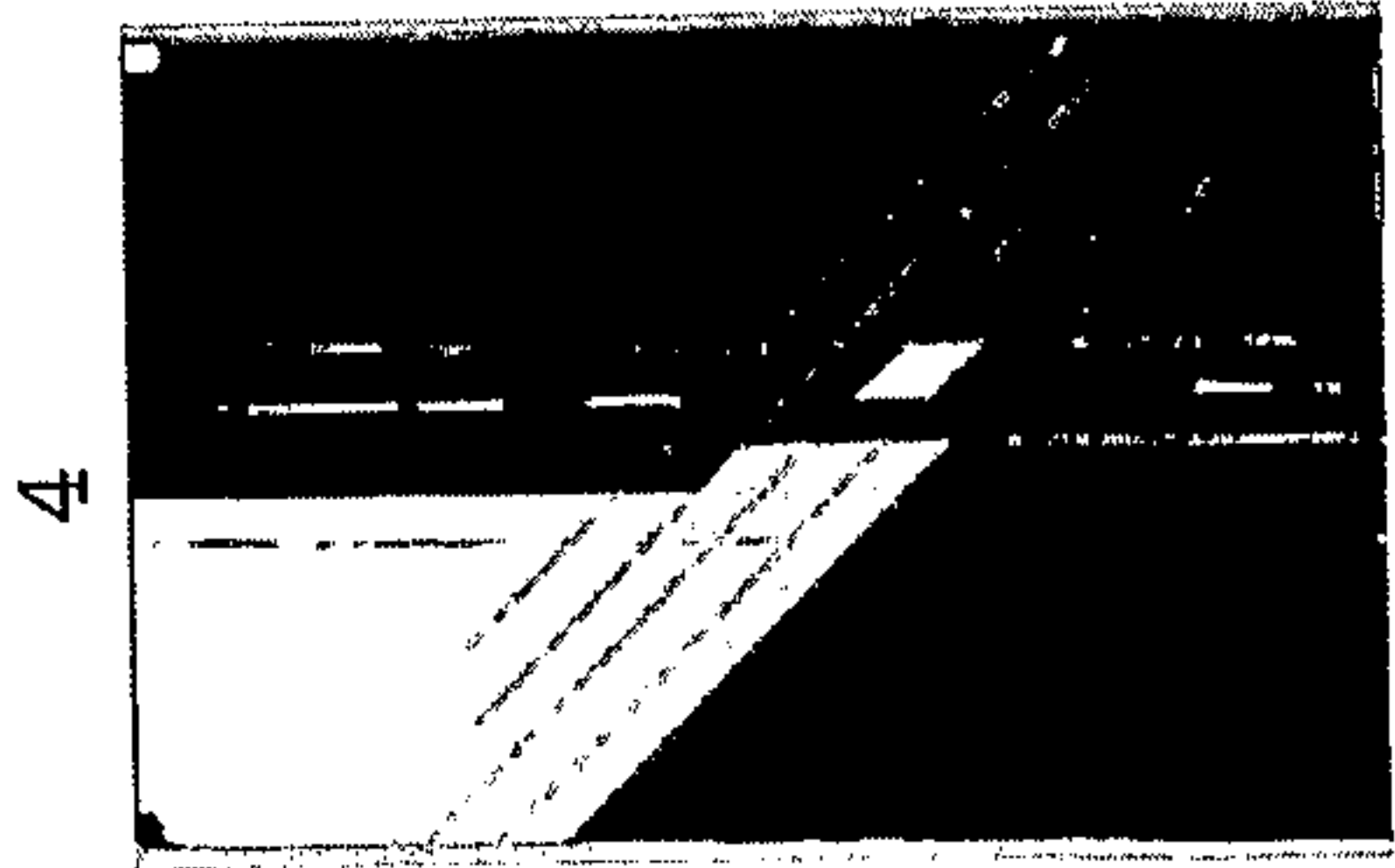


10% PEG -
ethylacrylate

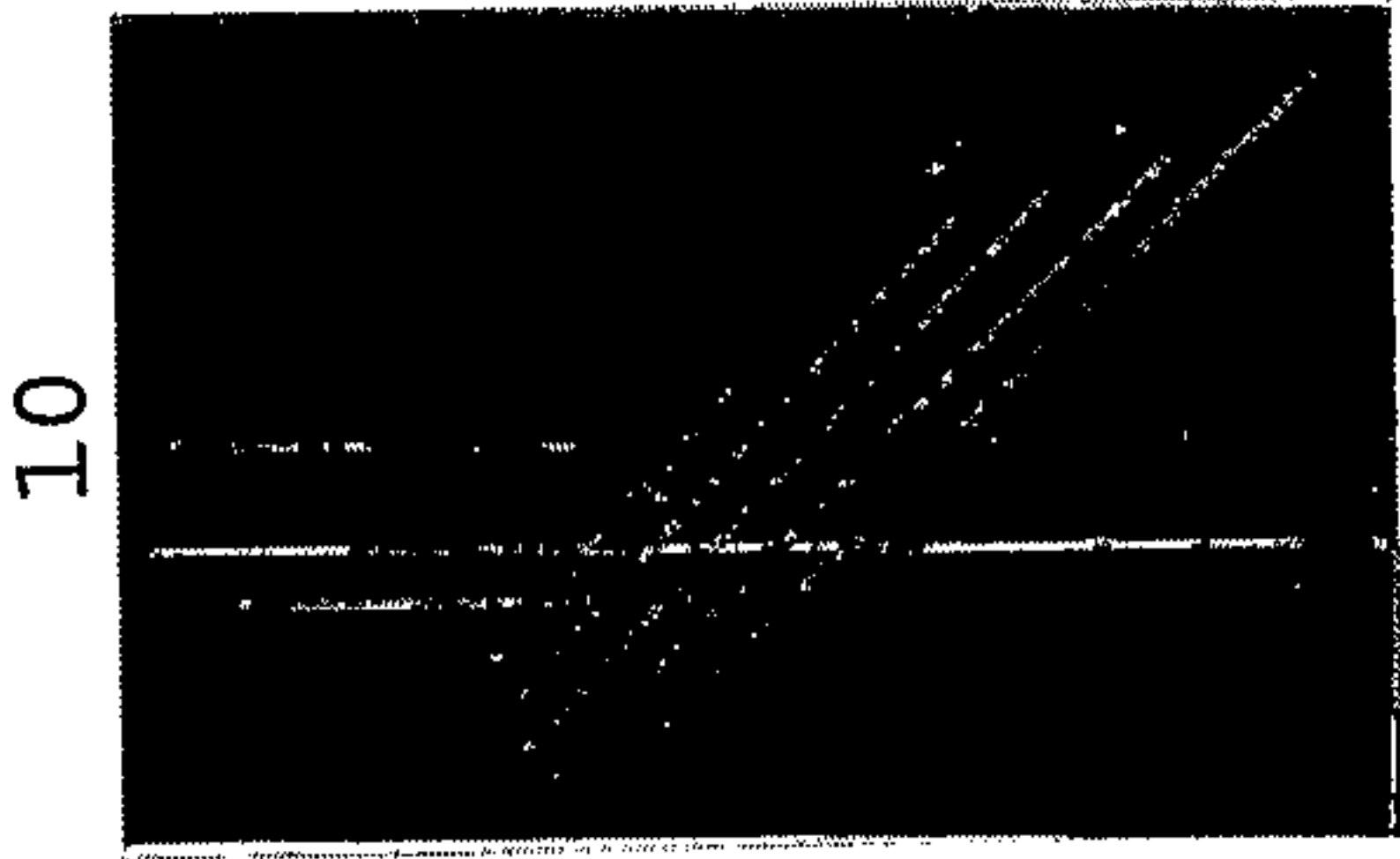
Initiator System : Camphorquinone (1% w/w based on acrylate), Dimethyltoluidine (120% w/w based on camphorquinone) system placed under an 2x18W fluorescent desk lamp.

Example 5 : Reduction Surface Activation Method - Green scribe adhesion

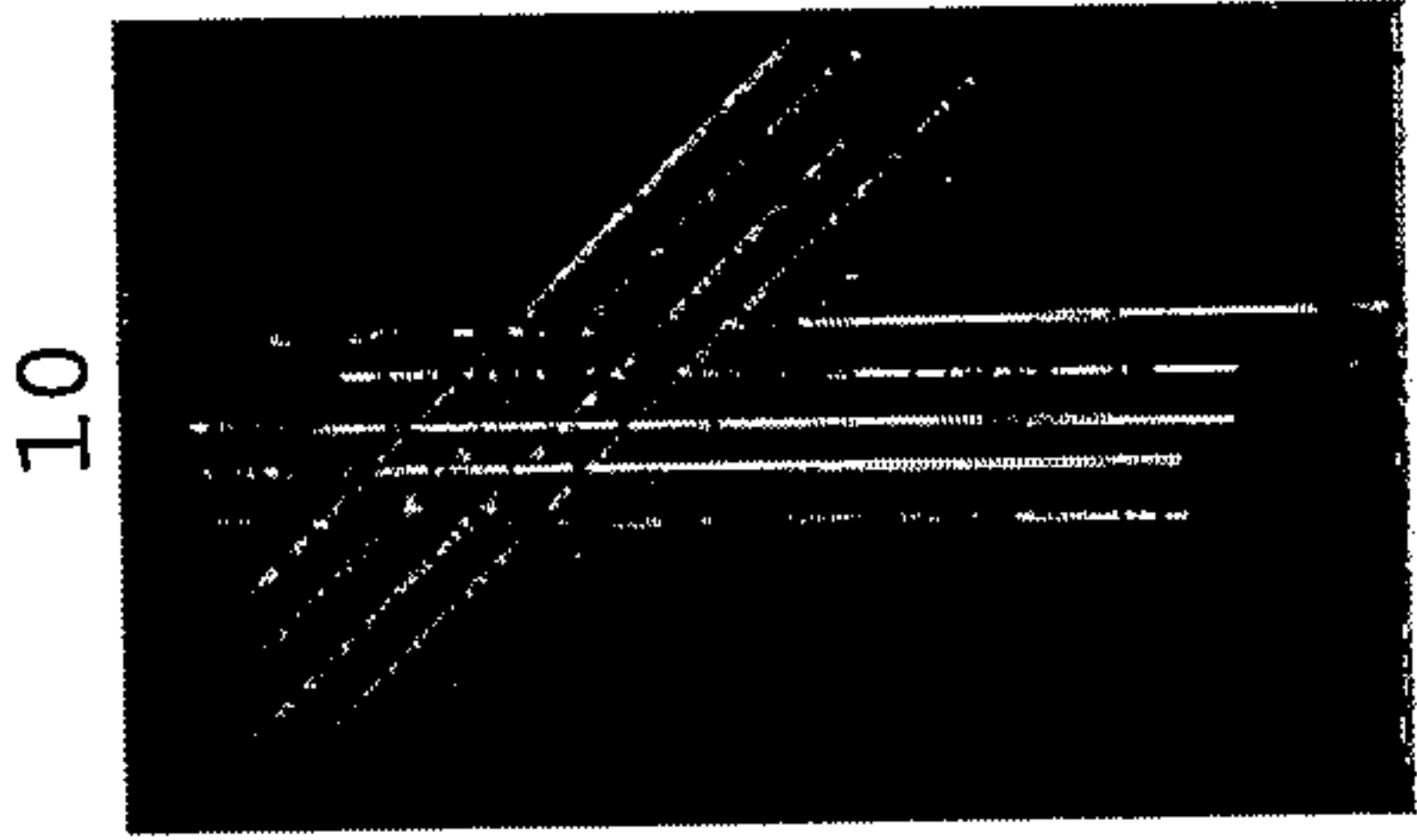
Green (scribe) inter-coat adhesion of Desothane HS 70846X white (30±5 µm CA8000C2 thinner) cured 40 hour at 120°F (~9% RH), followed by 48 hour at 120°F (50% RH) and 24 hour at 160°F, activated and over-coated with Desothane HS S601X blue (68±10 µm, 16h ambient cure). Green adhesion rating as per BSS7225.



Untreated

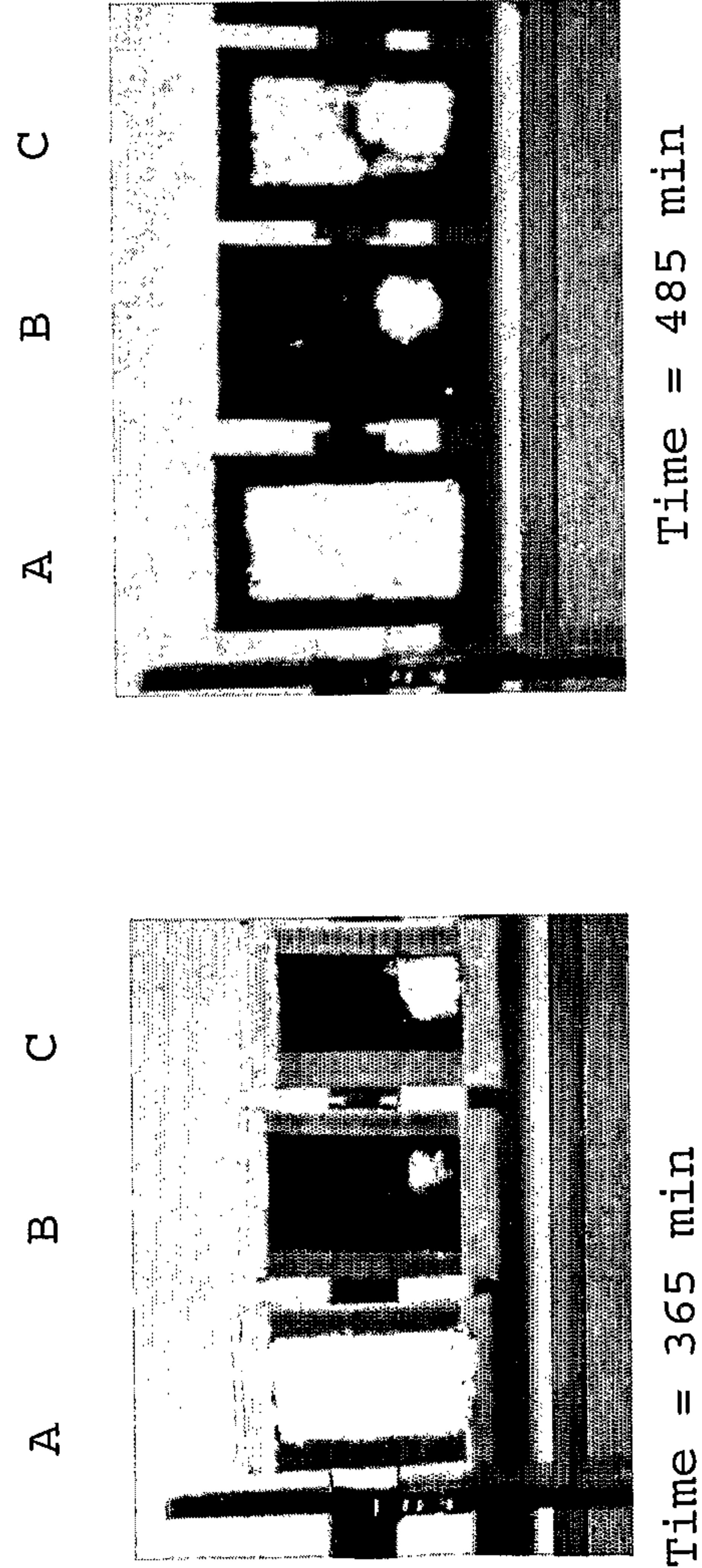
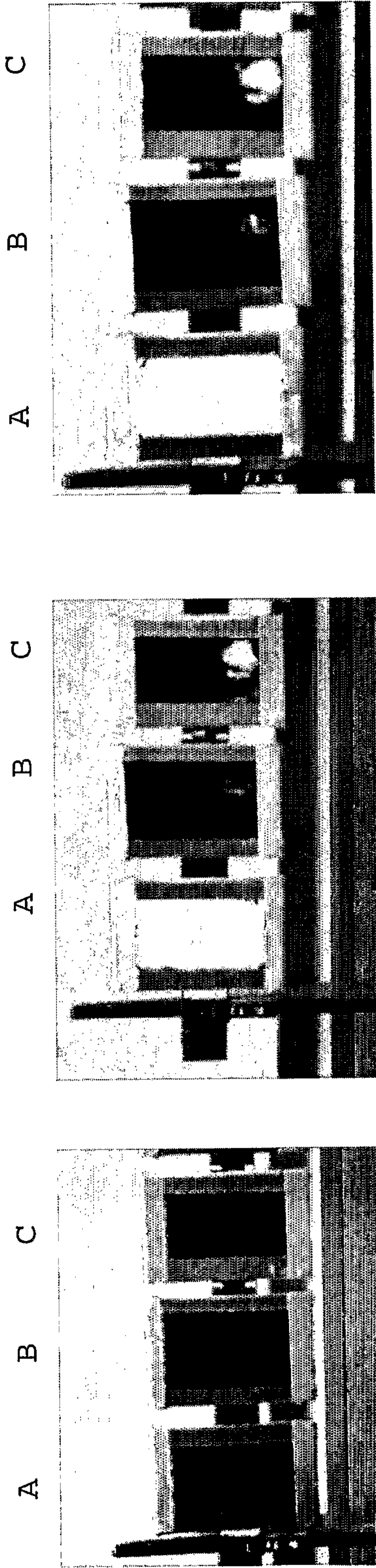


Sanded



2% NaBH₄ / EtOH

Example 6 : Reduction Activation Method - Stripping rate test



A - Untreated, B - Sanded, C - Treatment with 2% NaBH₄ in ethanol, 30 min

Example 7 : Evidence of Surface Energy Change

Surface energy results for activated surfaces employing a thermally aged Desothane HS 70846X substrate (CA8000C thinner)

Treatment	Conditions	Contact Angle (°)		Surface Energy (mJ/m2)	
		Water	CH ₂ I ₂	Specific γ_s^p	Dispersive γ_s^d
C Thinner					
Fresh		76.5	39.0	4.2	42.0
Aged Untreated		76.2	40.3	4.5	41.3
Aged IPA Wipe		75.8	35.0	4.0	44.0
Aged - 2% Sodium Borohydride	EtOH / EtOH wash	37.0	36.6	23.7	43.2
Aged - 1% Acetic Acid	EtOAc / IPA wipe	69.7	29.4	5.8	46.6
Aged - Camphorquinone (1% w/w based on acrylate), Dimethyltoluidine (120% w/w based on Camphorquinone) methylamylketone	2x18W fluorescent desk lamp, MAK wipe	65.2	43.5	8.5	43.5

Fresh - 4 hour at 120°F (~9% RH)
Aged - 40 hour at 120°F (~9% RH), 48 hour at 120°F (50% RH) and 24 hour at 160°F

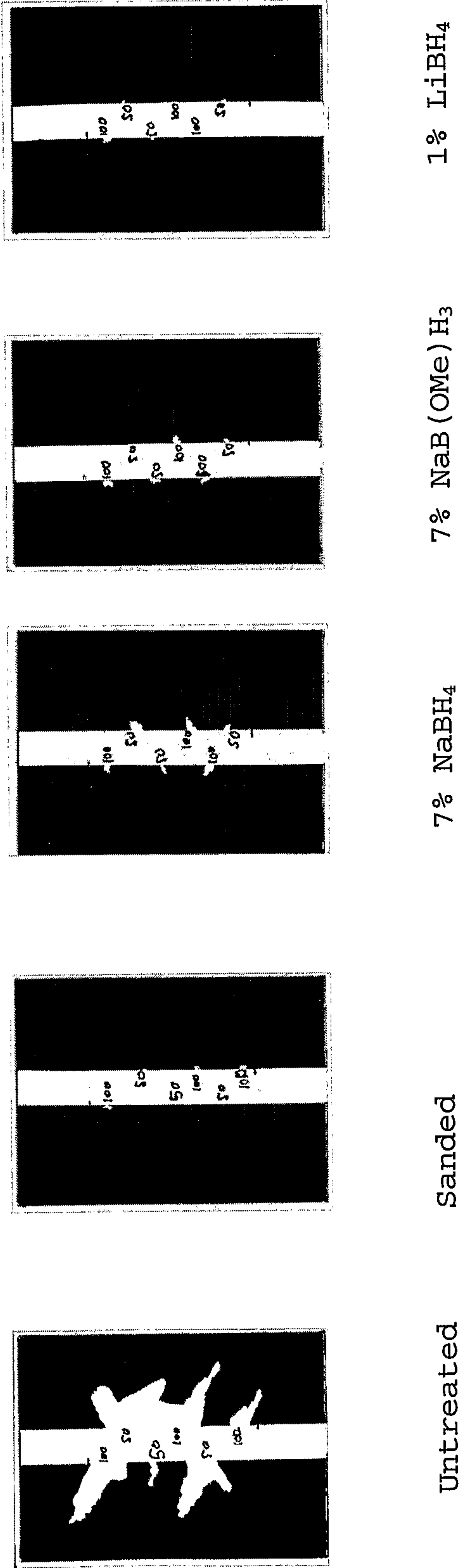
Example 8 : Evidence of Surface Energy Change

Surface energy results for activated surfaces employing a thermally aged Desothane HS 70846 substrate (C2 thinner)

Treatment	Conditions	Contact Angle (°)		Surface Energy (mJ/m2)	
		Water	CH ₂ I ₂	Specific γ_s^p	Dispersive γ_s^d
C2 Thinner					
Fresh		71.4	27.6	5.0	47.3
Aged Untreated		74.6	45.5	5.7	38.5
Aged IPA Wipe		73.9	36.3	4.9	43.4
Aged - 2% Sodium Borohydride	EtOH / EtOH wash	42.6	32.2	19.7	45.3
Aged - 1% Acetic Acid	EtOAc / IPA wipe	67.9	28.7	6.5	46.9
Aged - Camphorquinone (1% w/w based on acrylate), Dimethyltoluidine (120% w/w based on Camphorquinone) methylamylketone	2x18W fluorescent desk lamp, MAK wipe	68.6	27.3	6.0	47.4

Fresh - 4hour at 120°F (~9% RH)
Aged - 40hour at 120°F (~9% RH), 48 hour at 120°F (50% RH) and 24 hour at 160°F

Example 9. SIJA inter-coat adhesion of aged Desothane HS 70846X white (C2) reactivated under the conditions specified for 30min (SOHO) and over-coated with Desothane S400X red 3 hours following hose-off with water.



Treatment solutions prepared in propylde (dipropylene glycol dimethyl ether) .

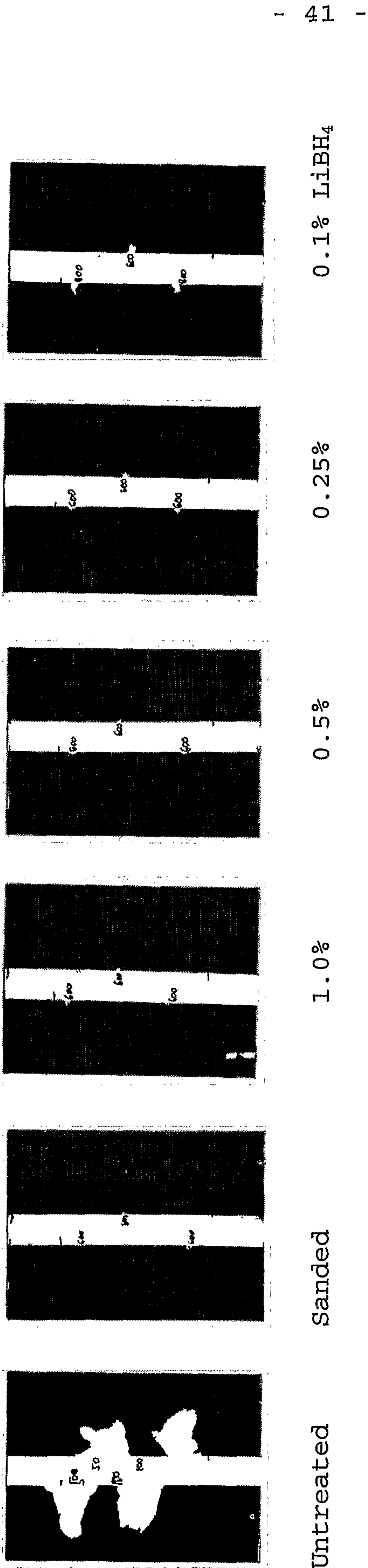
Results indicated that improved inter-coat adhesion is possible employing "mild" reducing agents such as NaBH₄ and LiBH₄.

Example 10. SIJA inter-coat adhesion of aged Desothane HS 70846X white (C2) reactivated under the conditions specified for 30min (SOHO) and over-coated with Desothane HS S601X blue 3 hours following hose-off with water.

Untreated	Red-Al	K-selectride	Lithium pyrrolidinoborohydride

Borane-THF complex Lithium dimethylaminoborohydride
 Treatment solutions prepared in dipropylene glycol dimethyl ether at 0.2% concentration.
 Results indicate that reducing agents with different strengths may be employed for the purpose of reactivation.

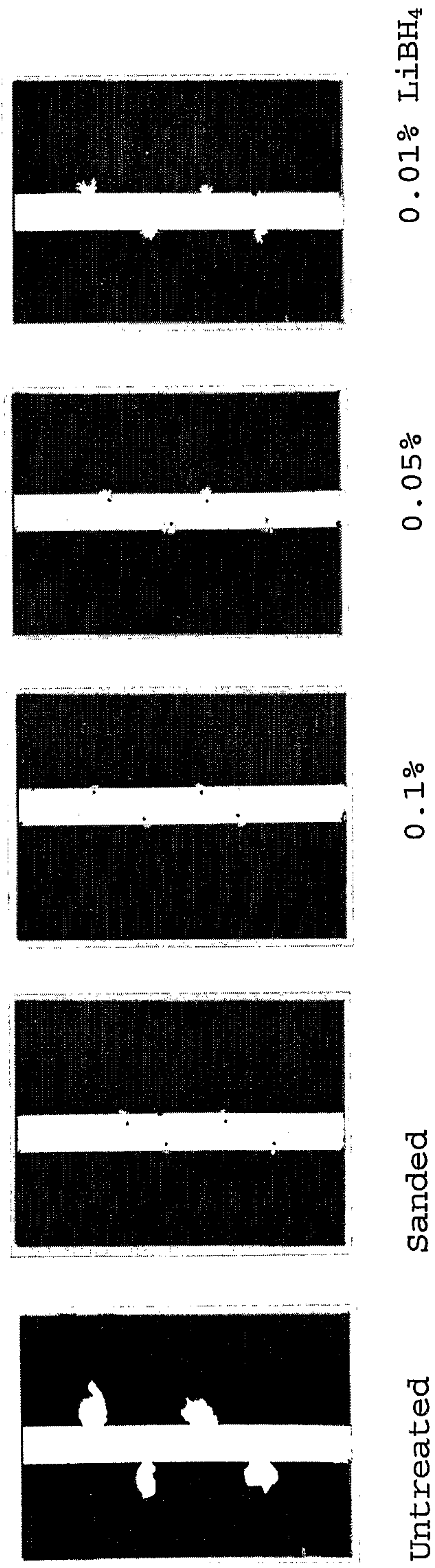
Example 11. SIJA inter-coat adhesion of aged Desothane HS 70846X white (C2) reactivated under the conditions specified for 30min (SOHO) and over-coated with Desothane S400X red 3 hours following hose-off with water.



Treatment solutions prepared in dipropylene glycol dimethyl ether.

Example illustrates that a variety of different concentrations may be employed to "activate" the surface of polyurethane based coatings towards over-coating to provide improved adhesion.

Example 12. (i) SIJA inter-coat adhesion of aged Desothane HS 70846X white (C2) reactivated under the conditions specified (SOLO) for 3h and over-coated with Desothane HS 5070X blue.

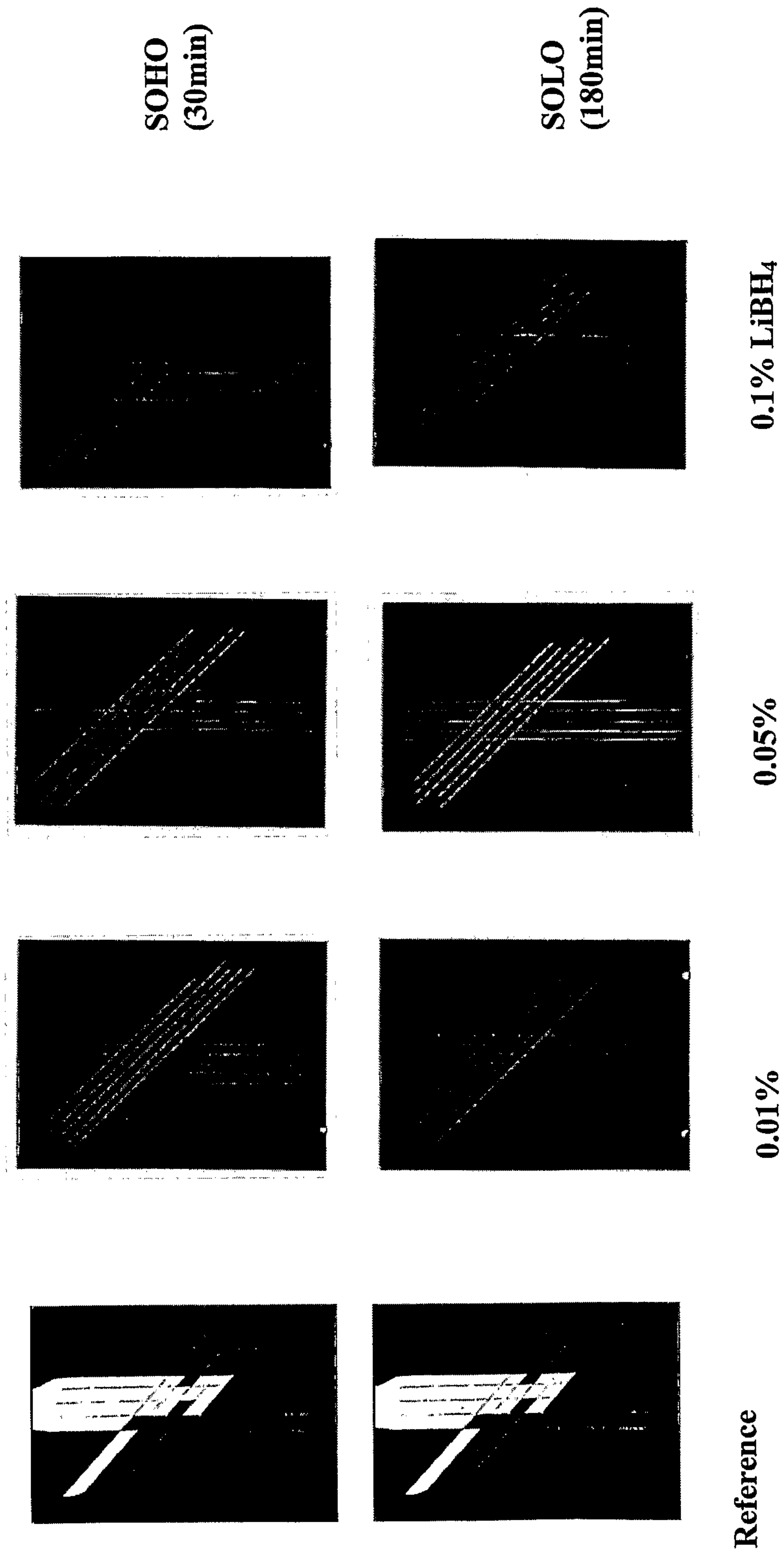


Treatment solutions prepared in dipropylene glycol dimethyl ether.

Example illustrates that very low concentrations of the reducing agent may be employed to "activate" the surface of polyurethane based coatings towards over-coating using a spray on - leave on approach.

- 43 -

(ii) Scribe adhesion of aged Desothane HS 70846X white reactivated under the conditions specified and over-coated with Desothane HS 5070X blue. The over coat was allowed to cure under ambient conditions for 16h prior to conducting the test.

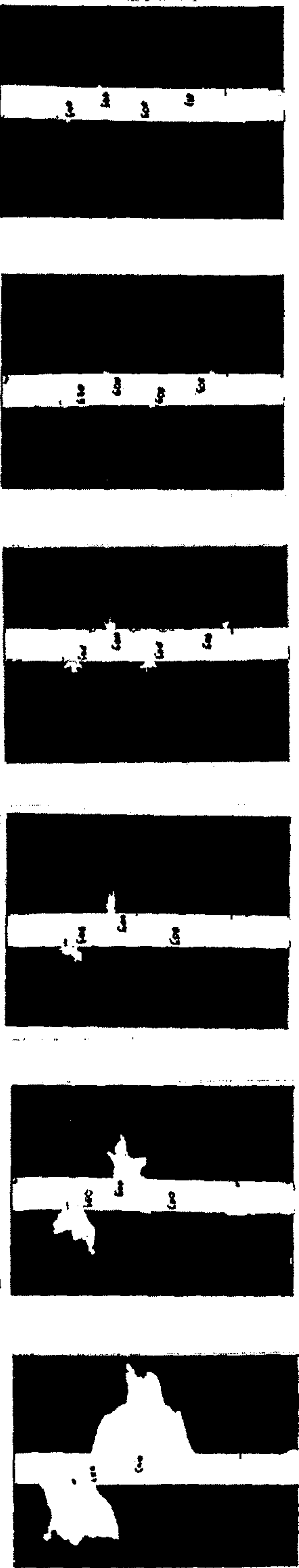


The example illustrates that excellent scribe adhesion results are possible employing low concentrations of reducing reagent under various application conditions.

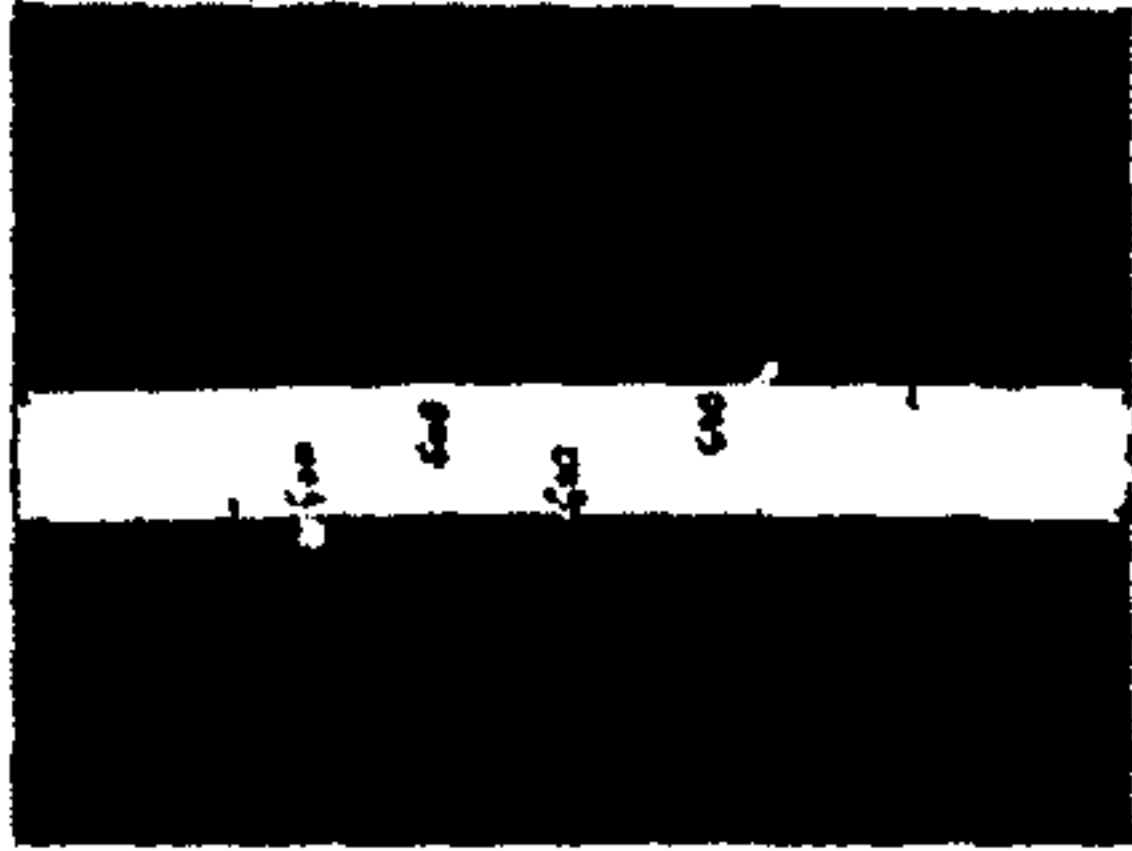
WO 2006/086828

PCT/AU2006/000070

Example 13. (i) SIJA inter-coat adhesion of aged Eclipse™ BAC70846 white reactivated under the conditions specified (SOLO) for 3h and over-coated with Desothane HS 5070X blue.



Untreated

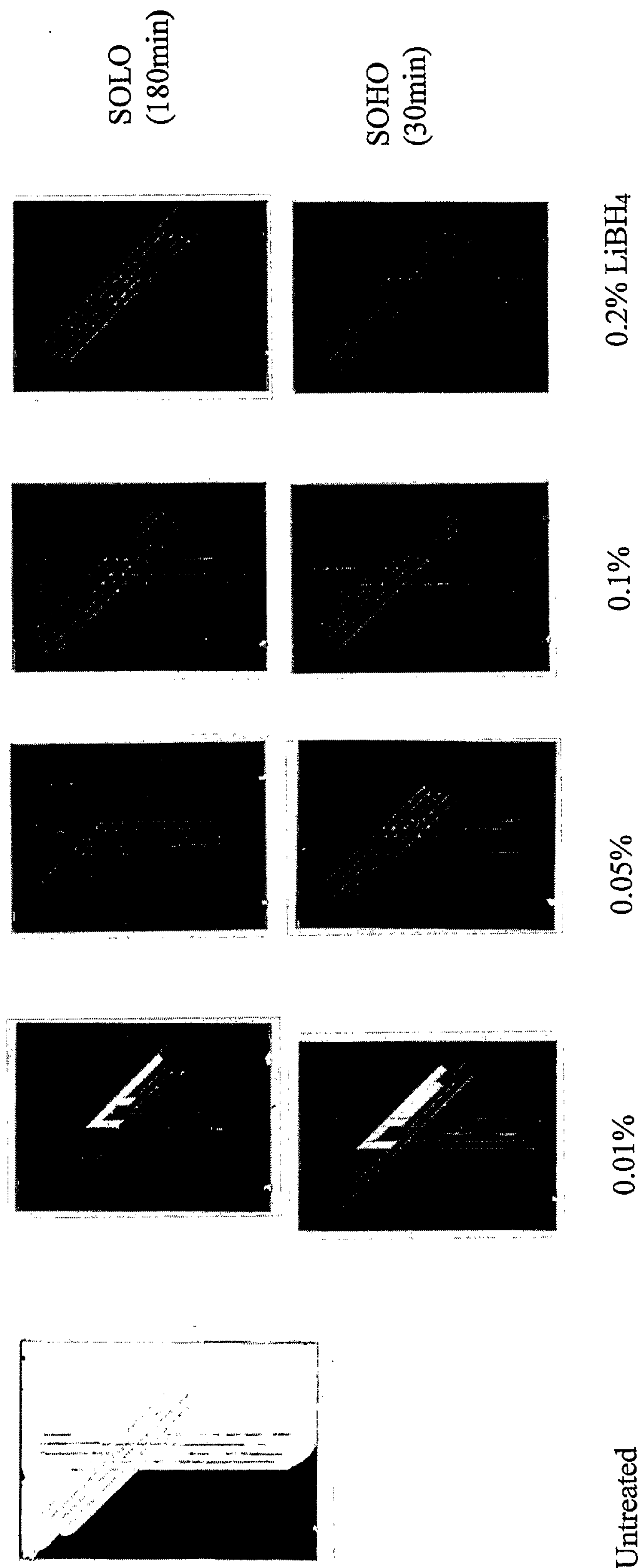


Sanded

Treatment solutions prepared in Progylde (dipropylene glycol dimethyl ether) using LiBH_4 as the reducing agent. Example illustrates that a variety of different reducing agent concentrations may be employed to "activate" the surface of polyurethane based coatings towards over-coating from different manufacturers and polyurethane chemistries.

- 45 -

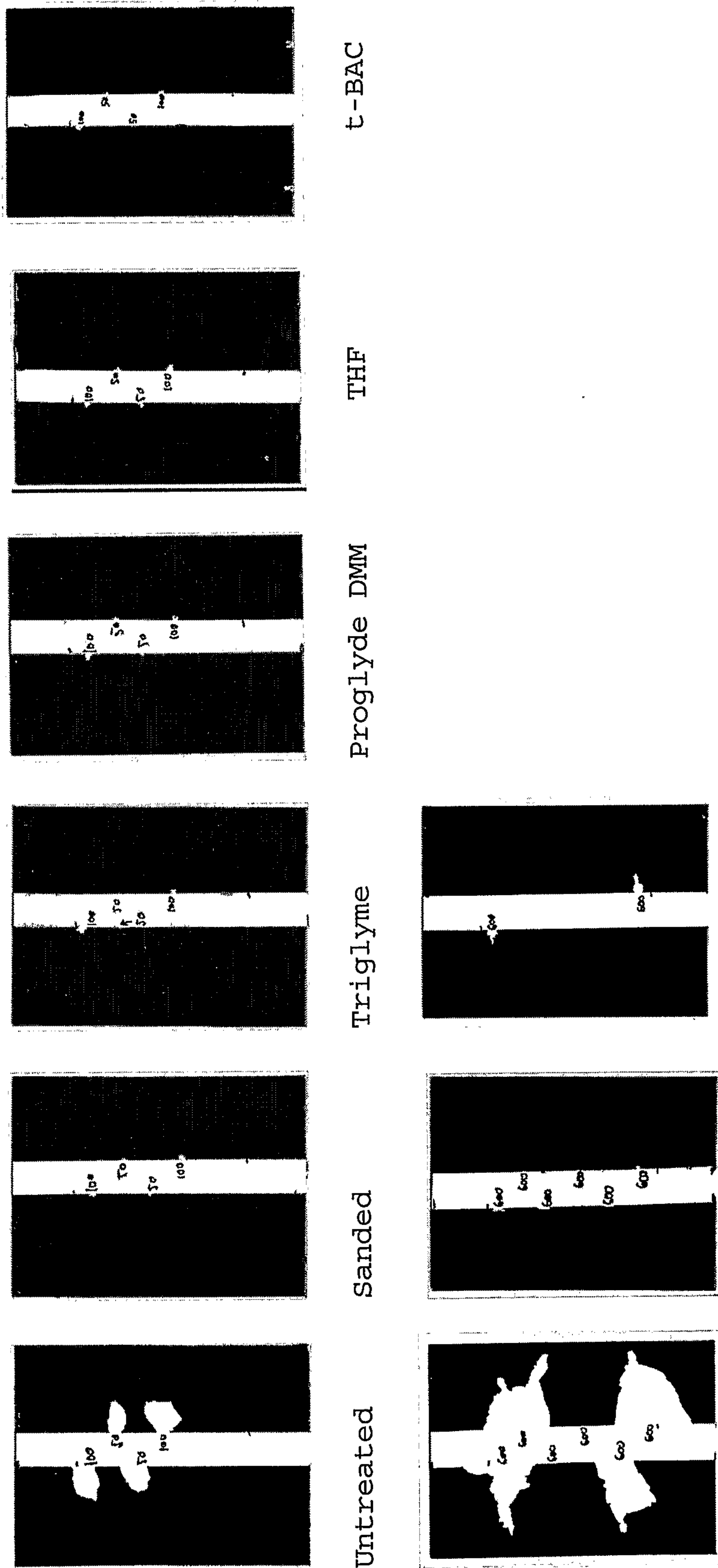
(ii) Scribe adhesion of aged Eclipse BAC70846 white reactivated under the conditions specified and over-coated with Desothane HS 5070X blue. The over coat was allowed to cure under ambient conditions for 16h prior to conducting the test.



The example illustrates that improved scribe adhesion results were possible employing low concentrations of reducing reagent to reactivate different types of polyurethane topcoats under various application conditions.

- 46 -

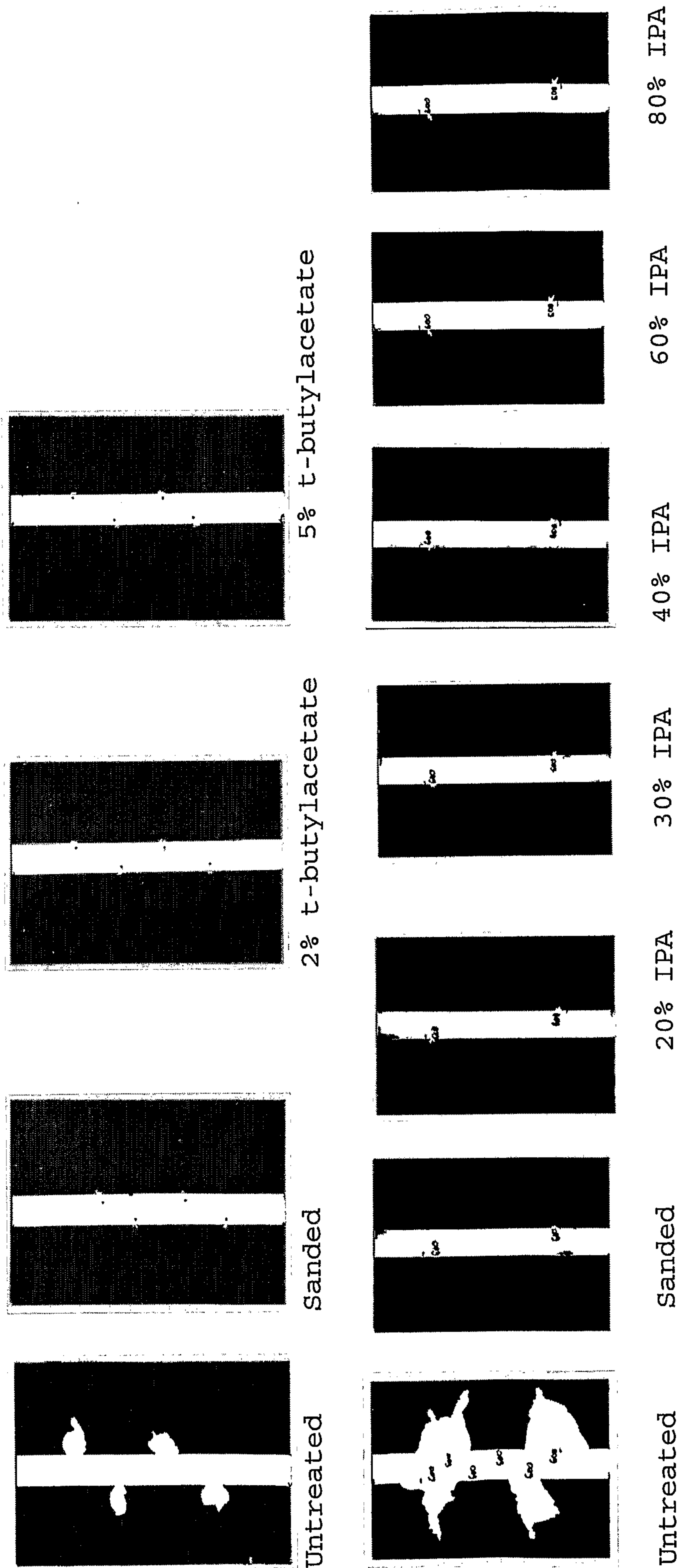
Example 14. SIJA inter-coat adhesion of aged Desothane HS70846X white reactivated with LiBH_4 (0.2 wt%) in the solvent/s specified (SOLO) for 3h and over-coated with various coloured Desothane HS polyurethane topcoats.



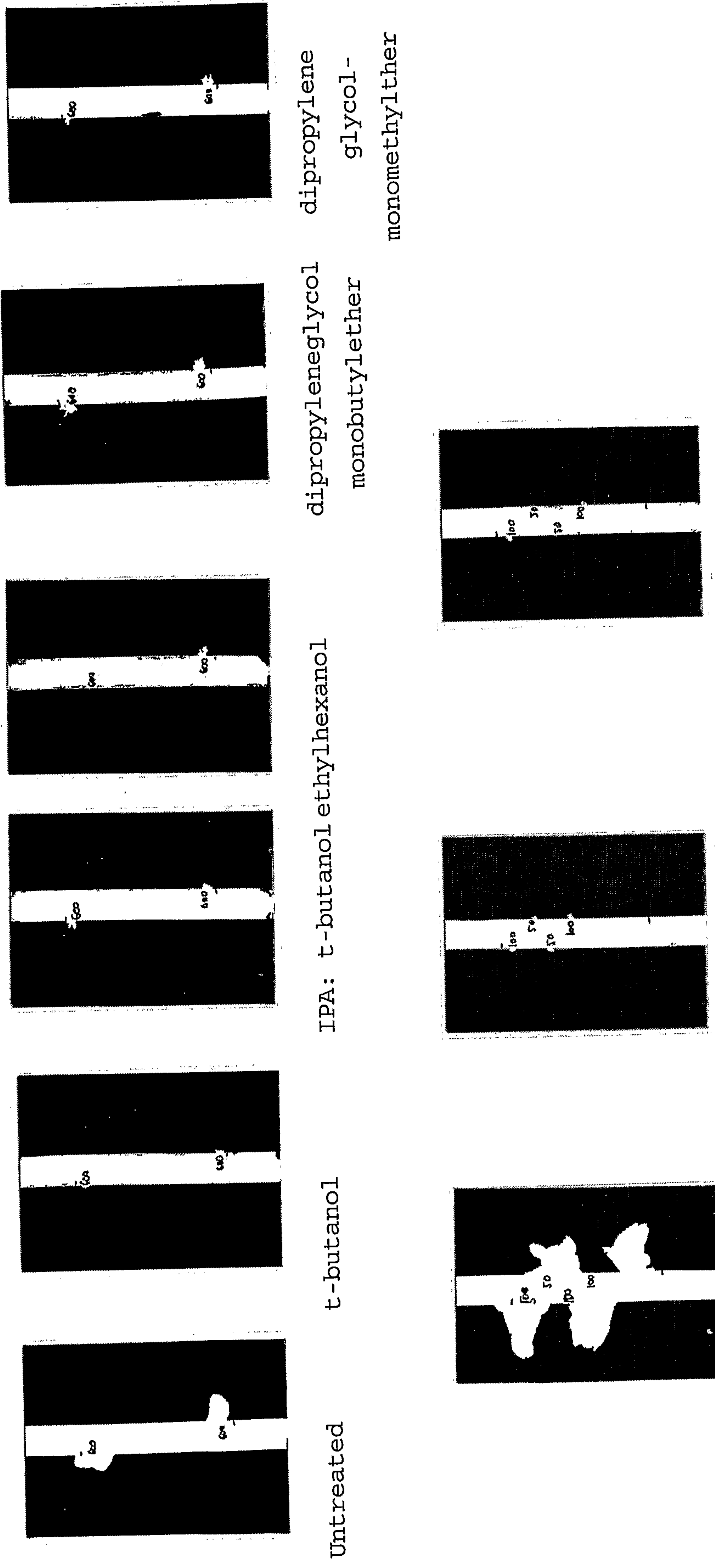
Untreated Sanded IPA
Results indicate that different solvents may be employed for reactivation using reducing agents under appropriate conditions.

- 47 -

Example 15. (i) SIJA inter-coat adhesion of aged Desothane HS 70846X white reactivated with LiBH_4 (0.2 wt%) in Progylde DMM and co-solvent specified (SOLO) for 3 hours and over-coated with various coloured Desothane HS polyurethane topcoats.



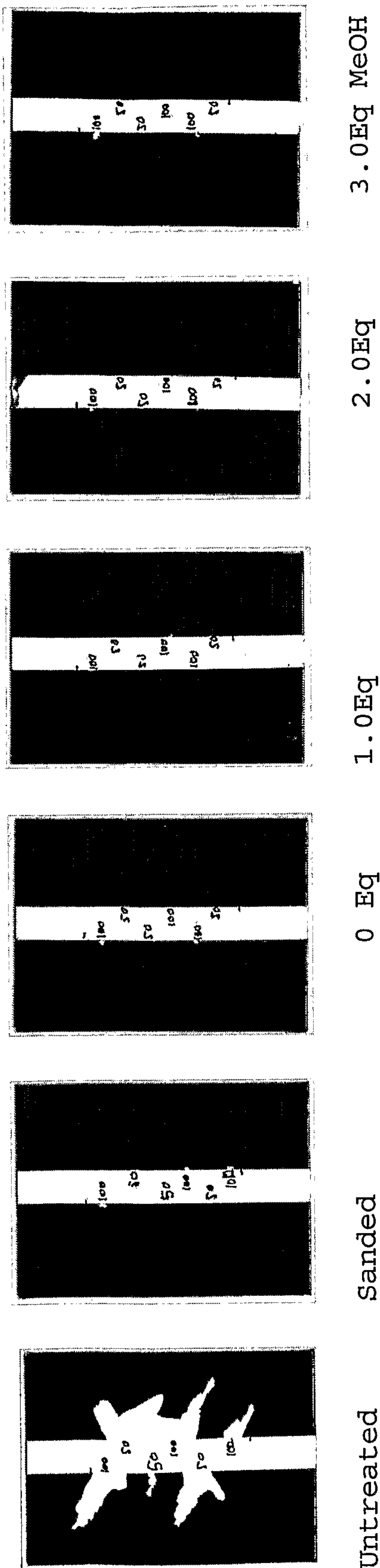
(ii) Example incorporating different alcohols (40%) and alcohol combinations (20:20%).



Results indicate that under appropriate conditions a variety of solvent combinations may be employed for the purpose of reactivation with appropriate reducing agents.

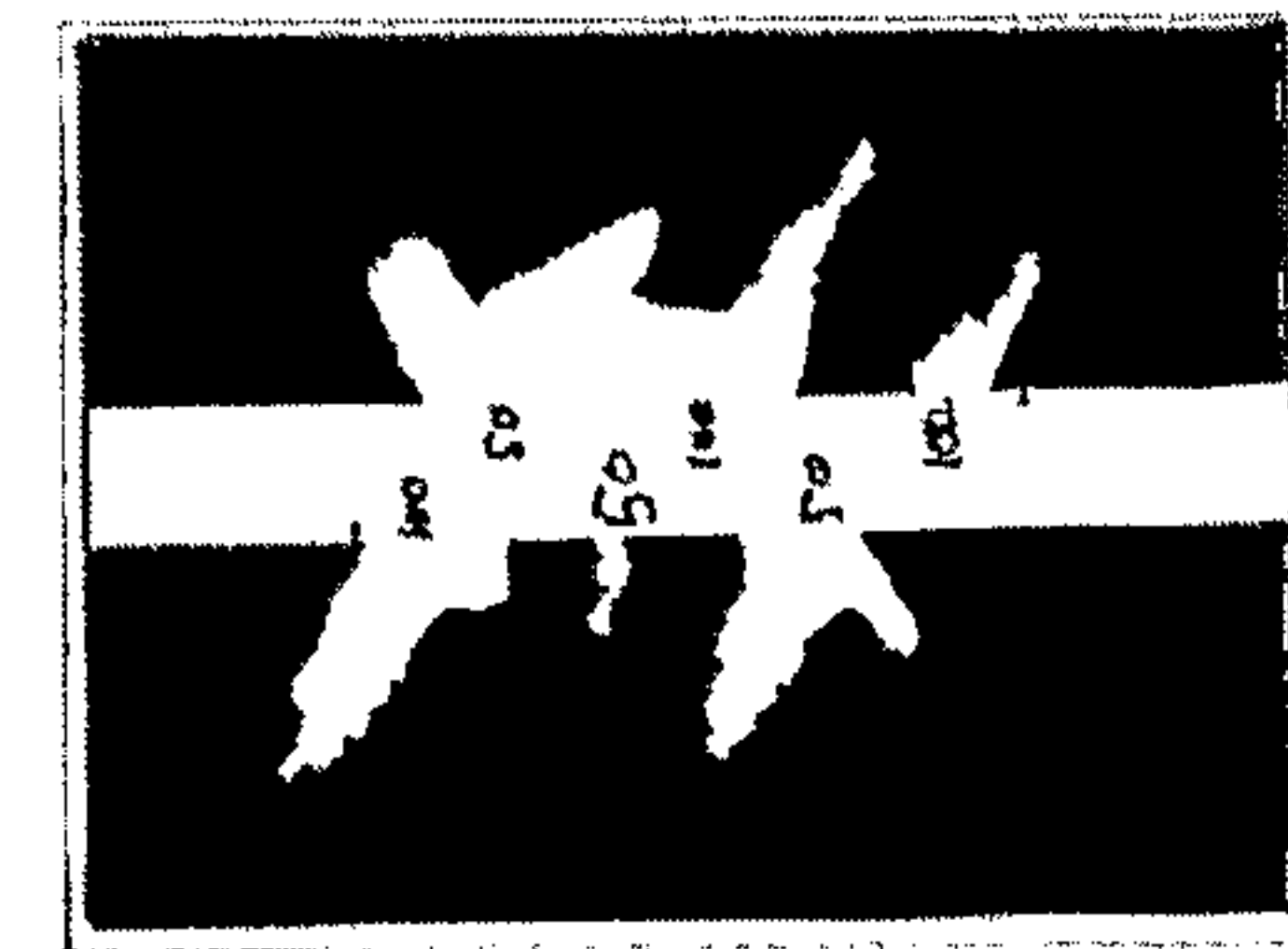
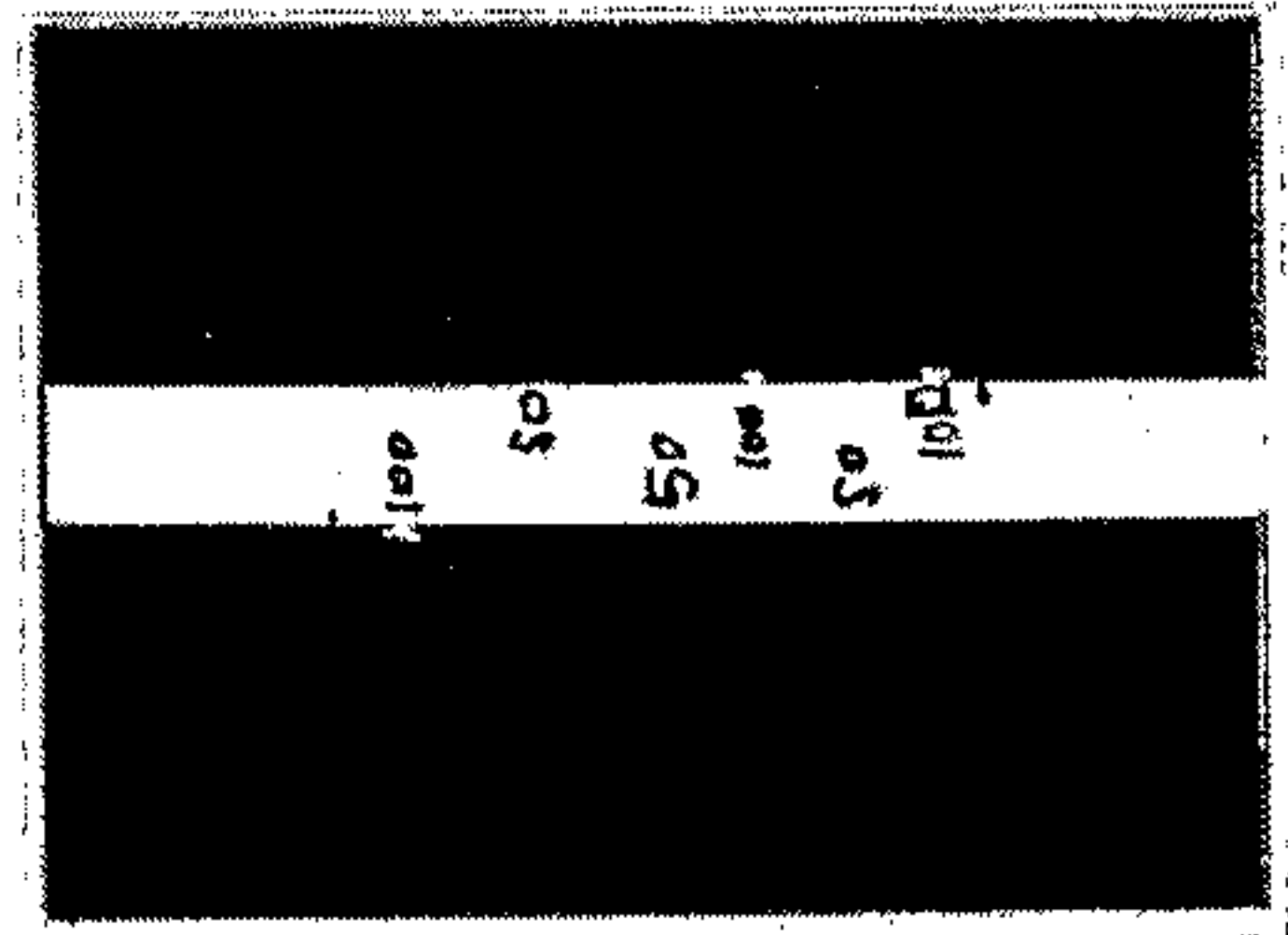
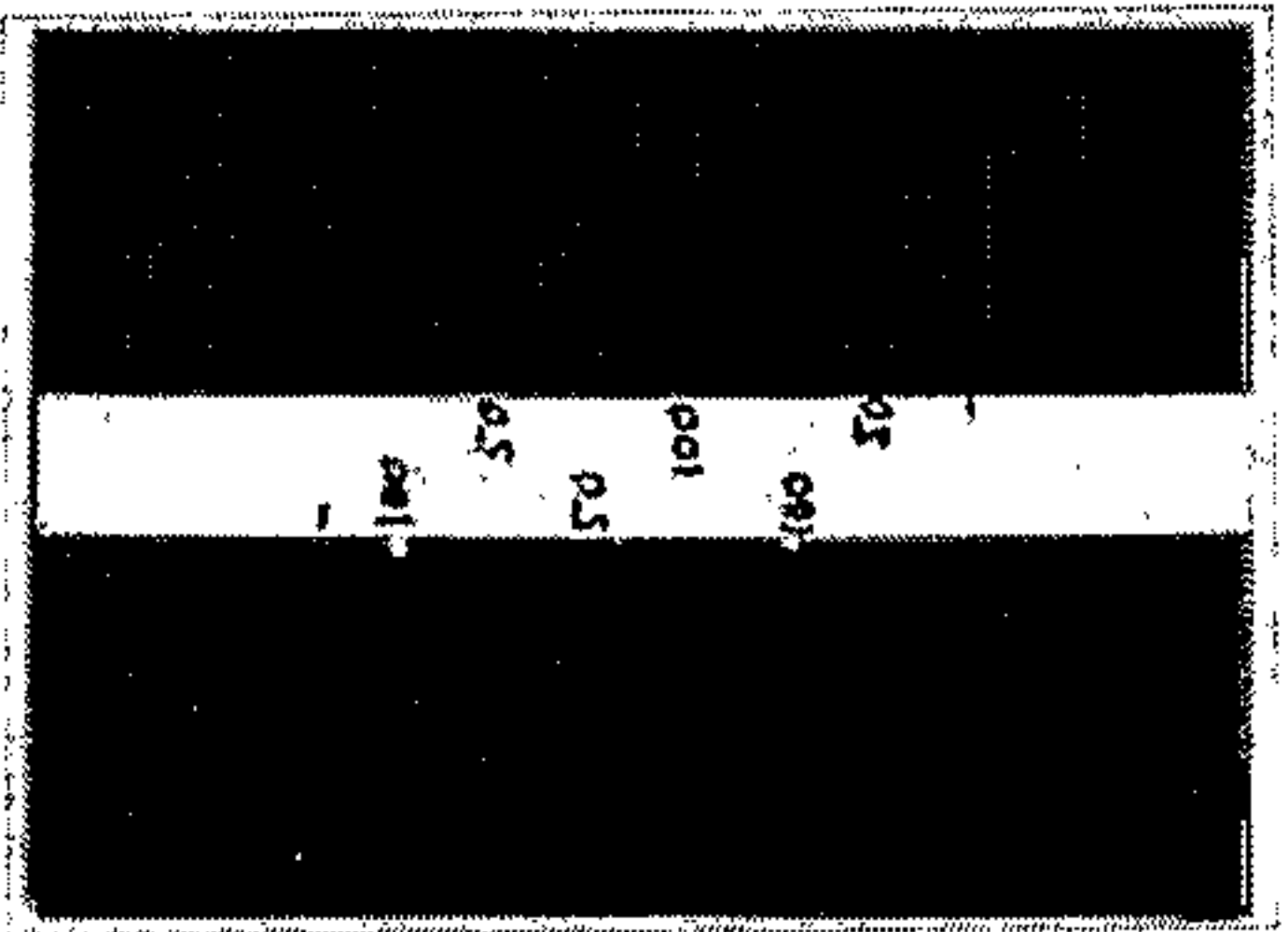
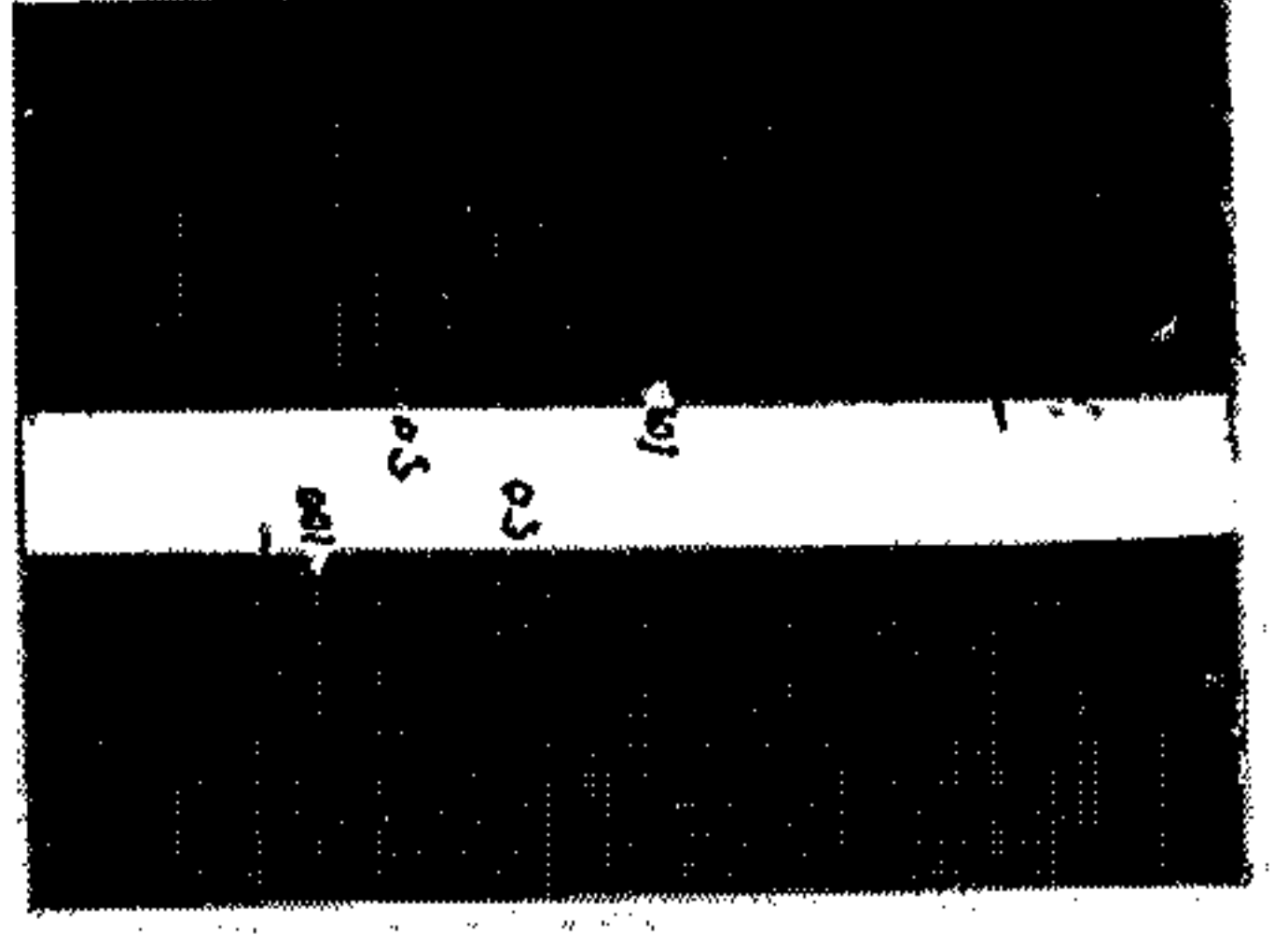
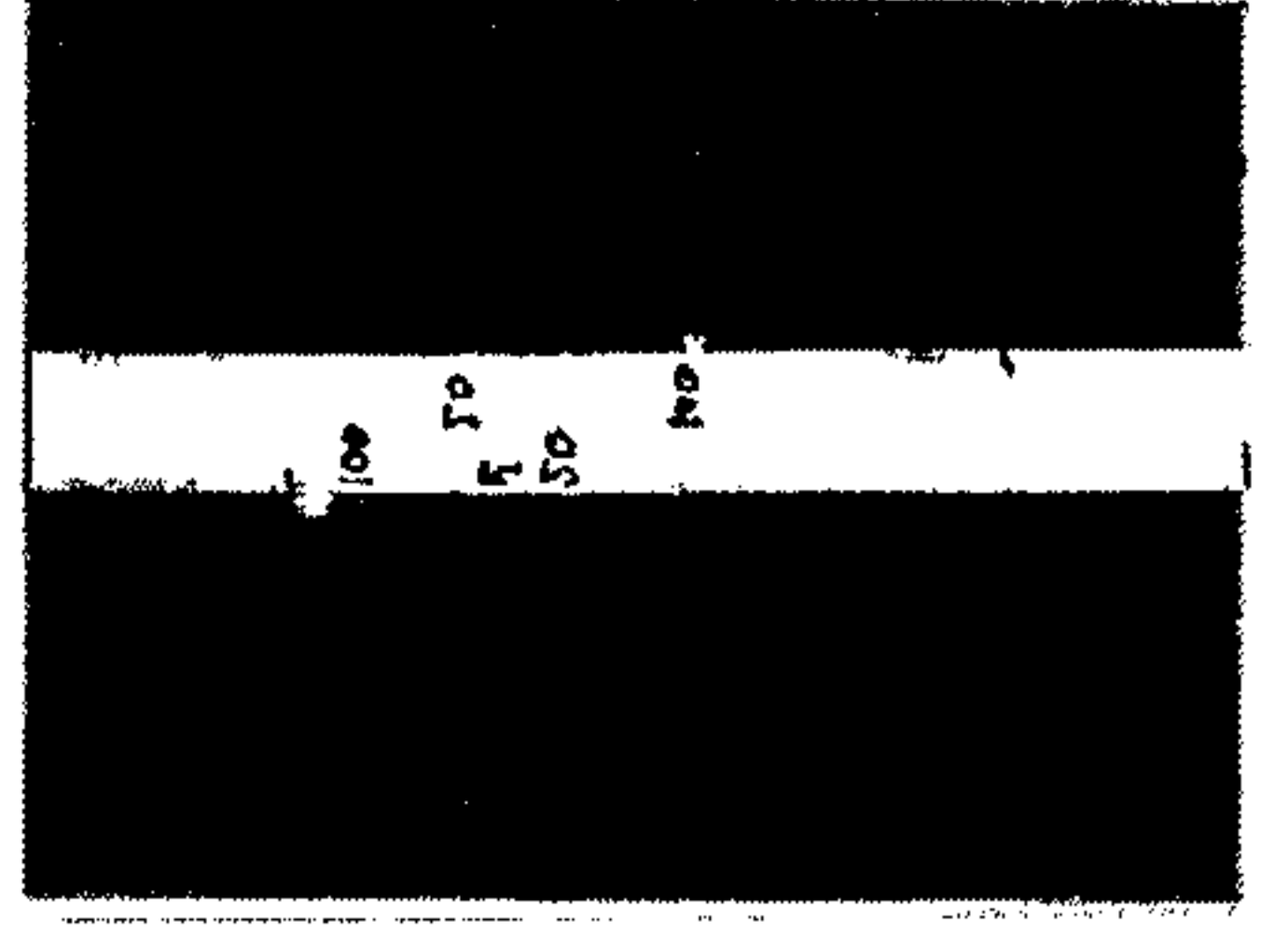
Example 16. SIJA inter-coat adhesion of aged Desothane HS 70846X white (C2) reactivated under the conditions specified for 30min (SOHO) and over-coated with Desothane S400X red 3 hours following hose-off with water.

1.0% $\text{Li}(\text{OCH}_3)_x\text{BH}_4$ -x in Proglyde prepared by addition of 0 (x=0), 1 (x=1, major component)), 2 (x=2, major component), and 3 (x=3, major component) equivalents (Eq) respectively of methanol "in-situ".



Example illustrates that the active agent may be prepared "in situ" and that reactivation can be conducted in the presence of more than one different type of reducing reagent.

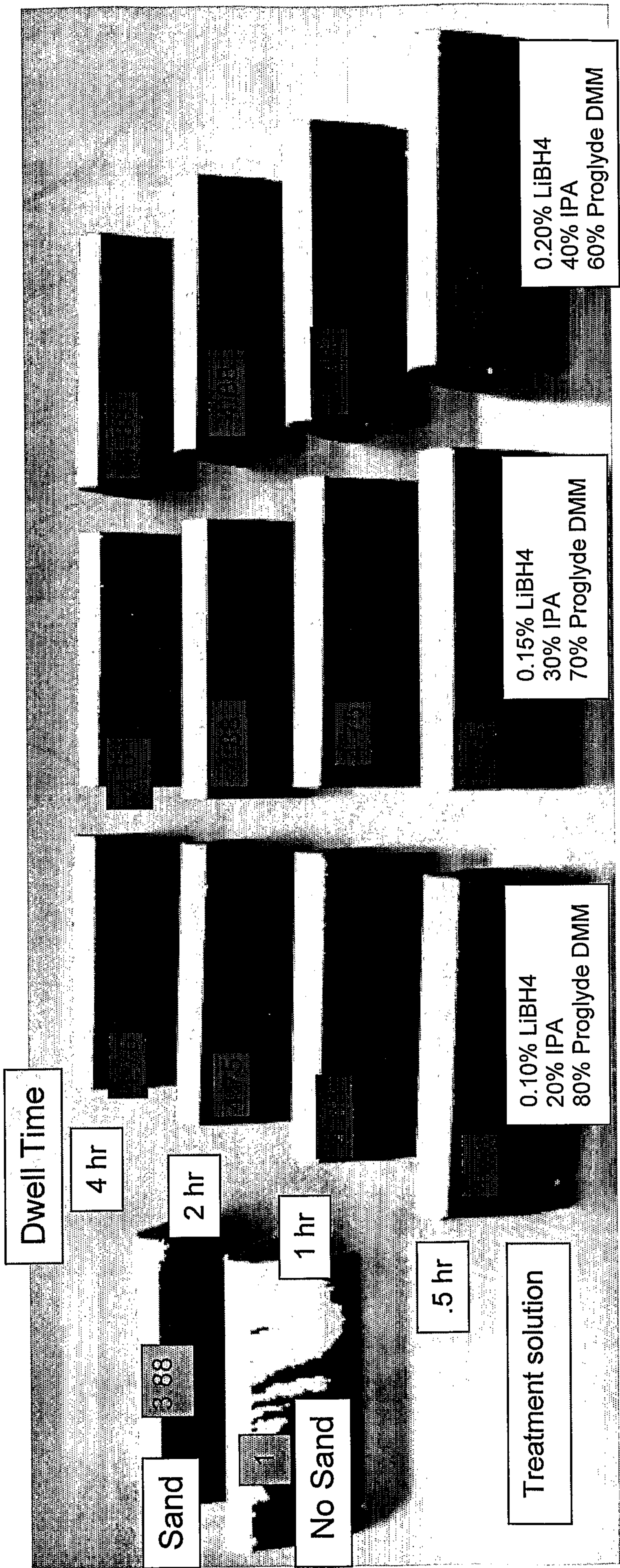
Example 17. SIJA inter-coat adhesion of aged Desothane HS 70846X white (C2) reactivated under the conditions specified for 30min (SOHO) and over-coated with Desothane S400X red 3hours following hose off with water.

				
Untreated	Sanded	0.5wt% LiBH ₄ from 5wt% THF stock solution diluted with proglyde	0.5wt% LiBH ₄ prepared from solid LiBH ₄ in proglyde	0.5wt% LiBH ₄ prepared in- situ from NaBH ₄ and LiCl in triglyme

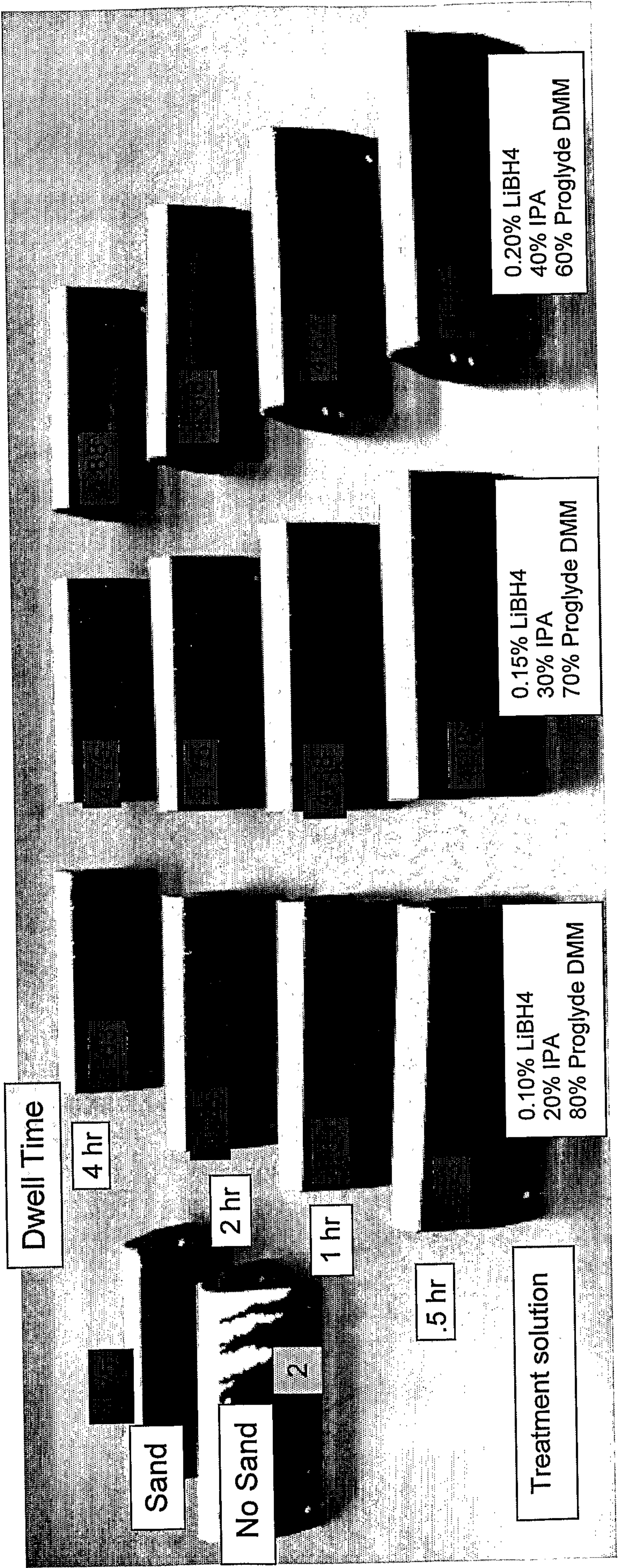
Example illustrates that different treatment solution preparation methods can be employed to manufacture the reduction based reactivations formulation taking into consideration the different ways in which reducing agents are packaged and sold commercially. In certain circumstances the reactive agent may be generated "in situ" if required.

Example 18. Rain erosion adhesion results for Desothane HS 70846X white (C2) aged as specified. Reactivated using the formulations and treatment time specified before over-coated with Desothane HS 50103X blue.

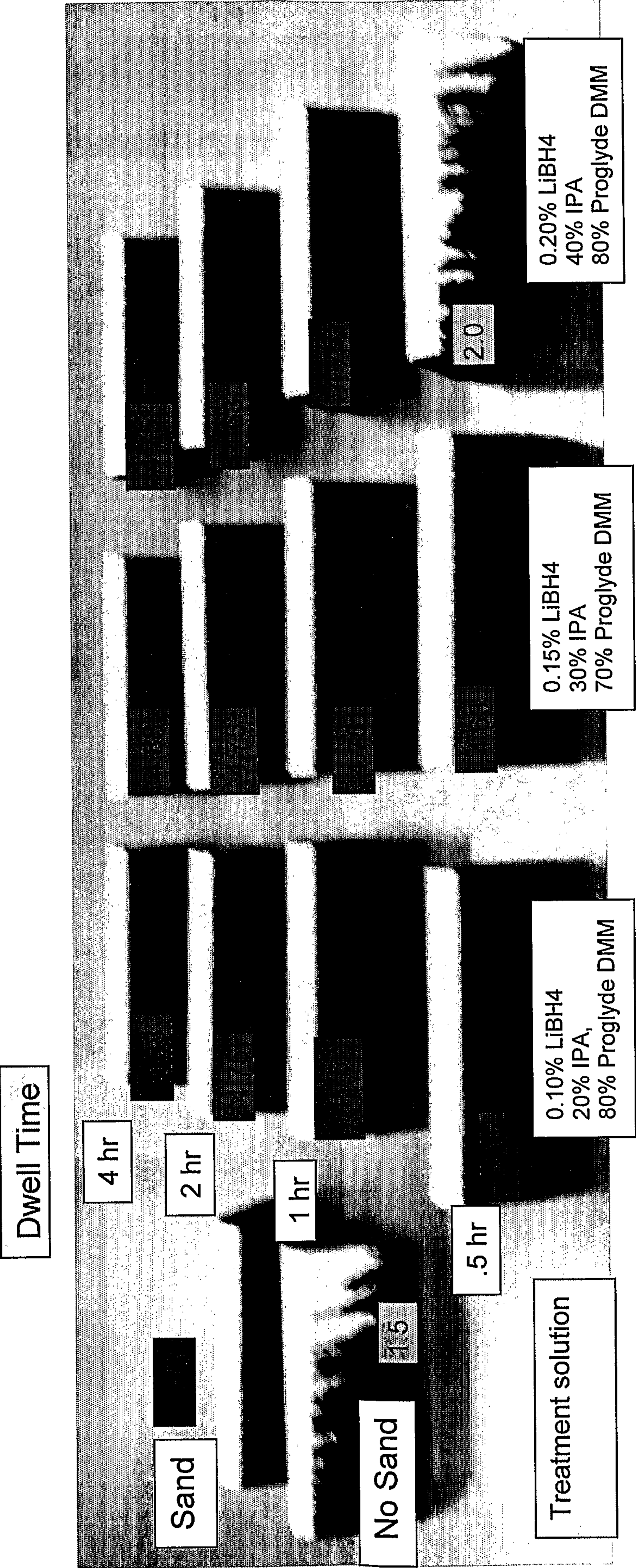
(i) Ageing protocol: 4h (120F, 2-3% RH). SOLO based reactivation method



(ii) Ageing protocol: 5 Days (120F, 2-3% RH) SOLO based reactivation treatment

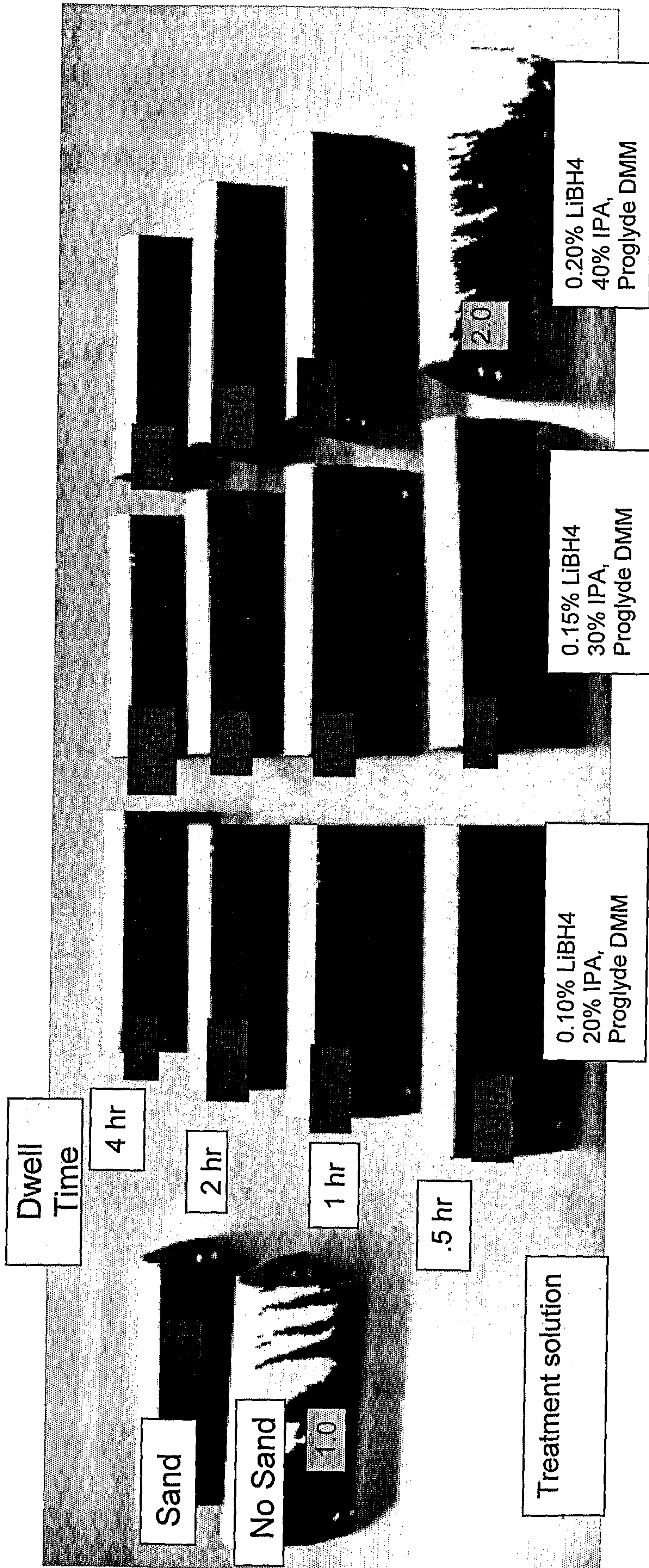


(iii) Ageing protocol: 4h (120F, 2-3% RH) SOHO based reactivation method



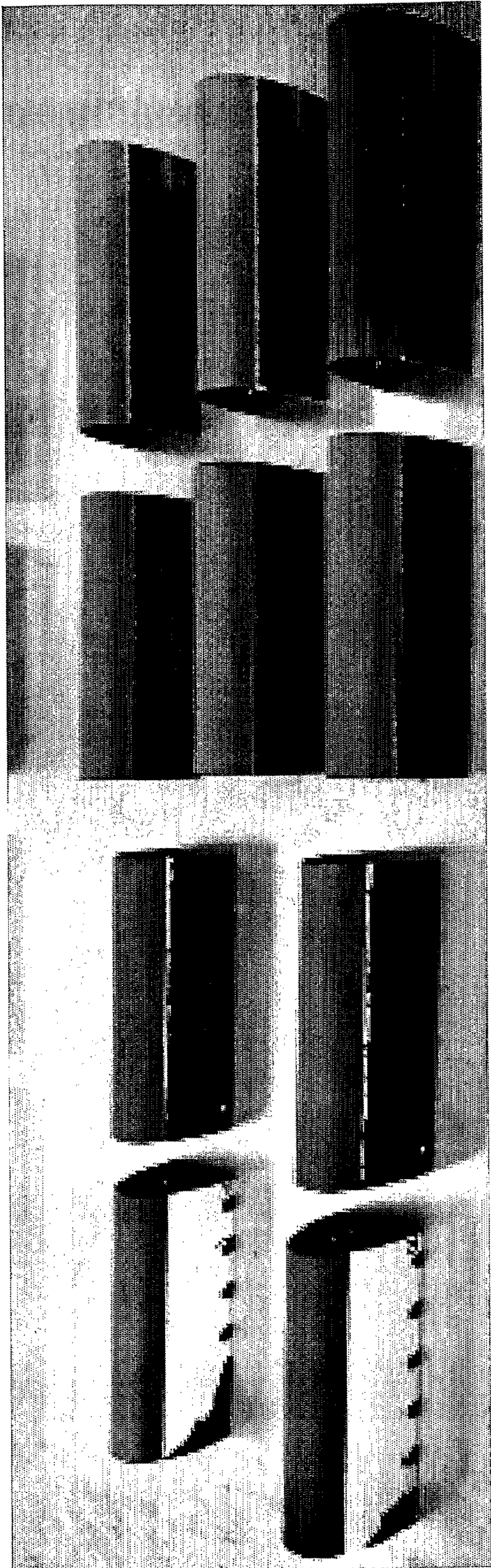
- 54 -

(iv) Ageing protocol: 5 days (120F, 2-3% RH) SOHO based reactivation method



Results illustrate that improved inter-coat adhesion is possible using reducing agents mixed into various reactivation treatment formulations and applied under various treatment times and protocols for substrates aged under various protocols.

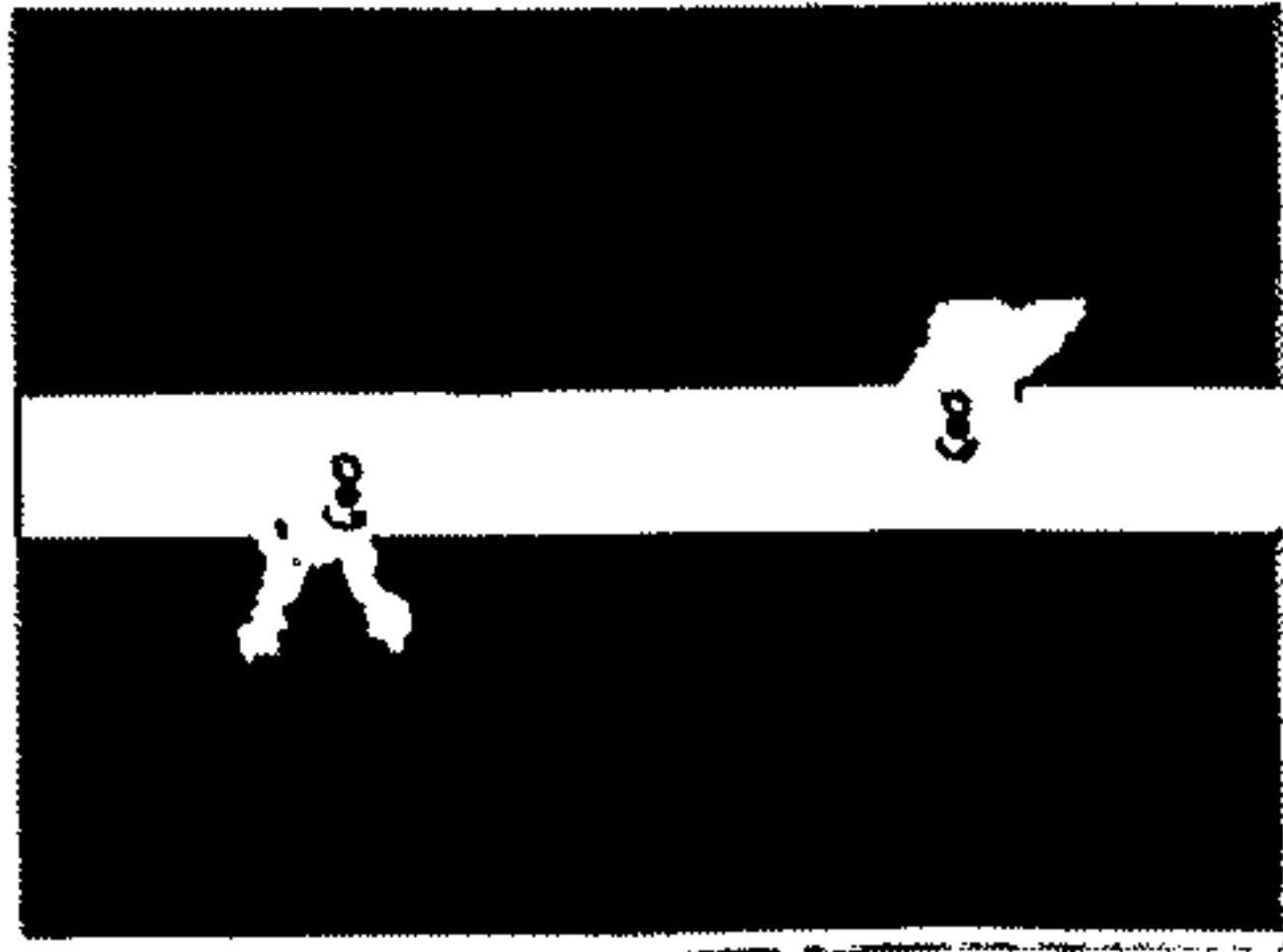
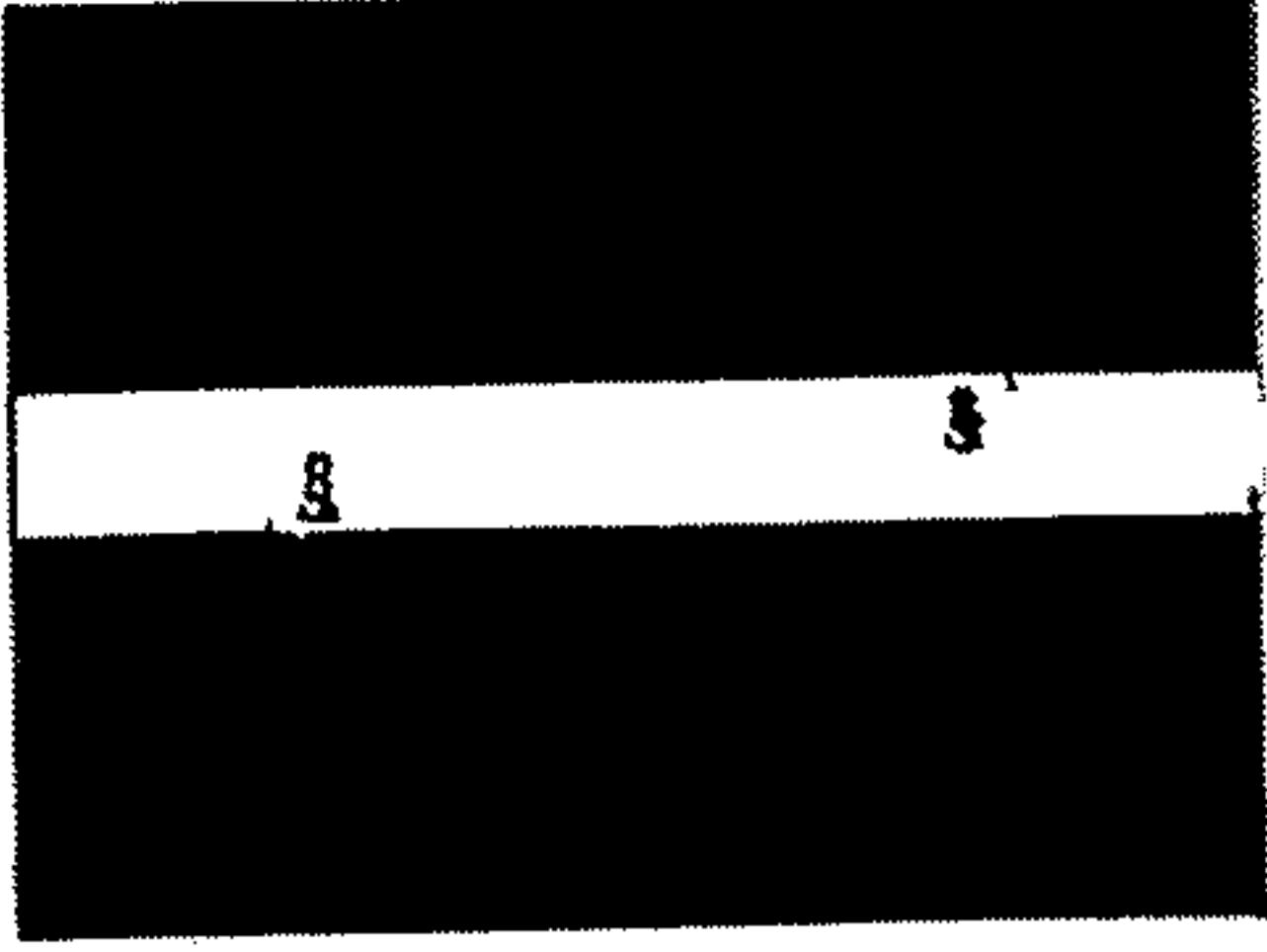
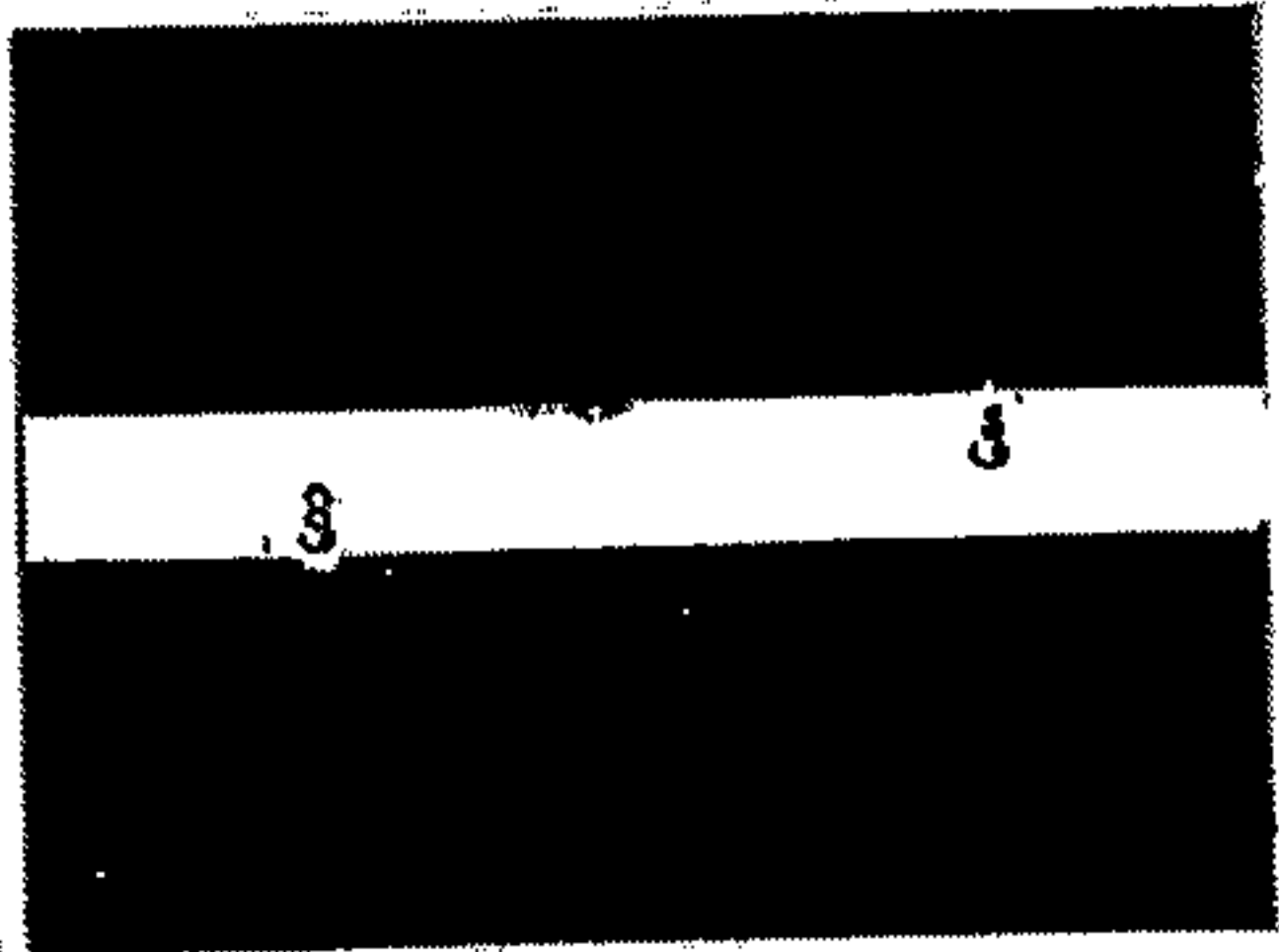
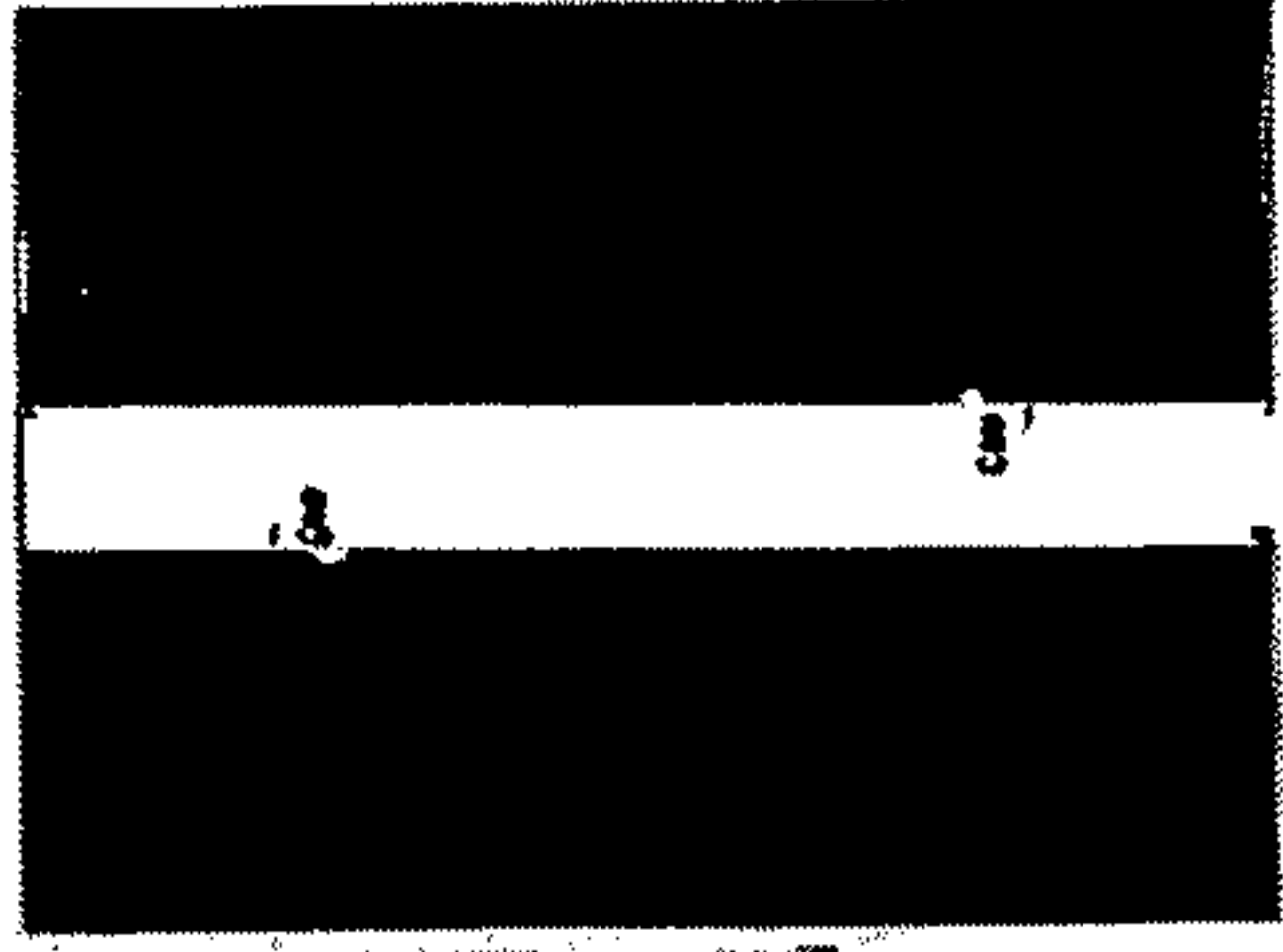
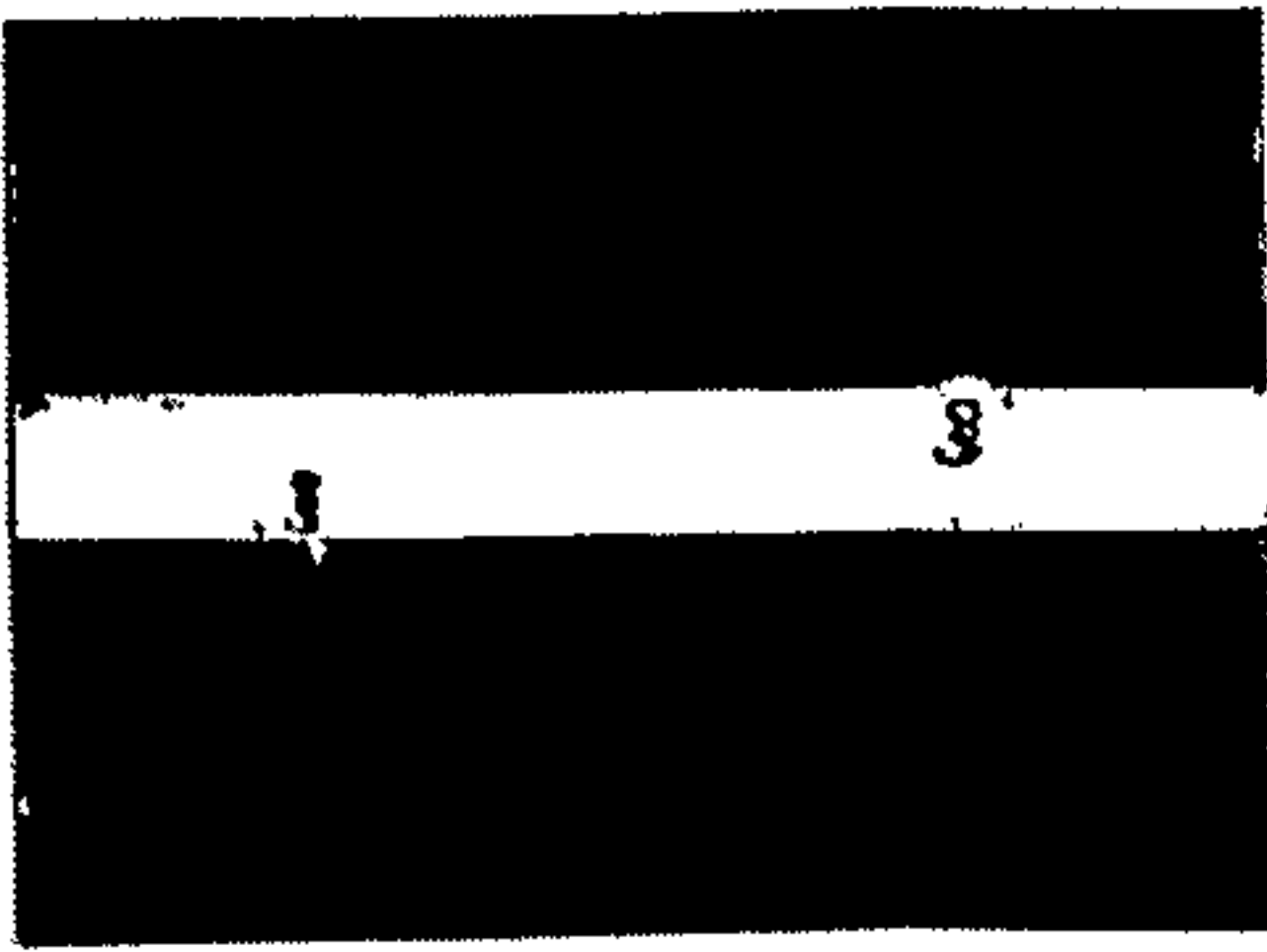
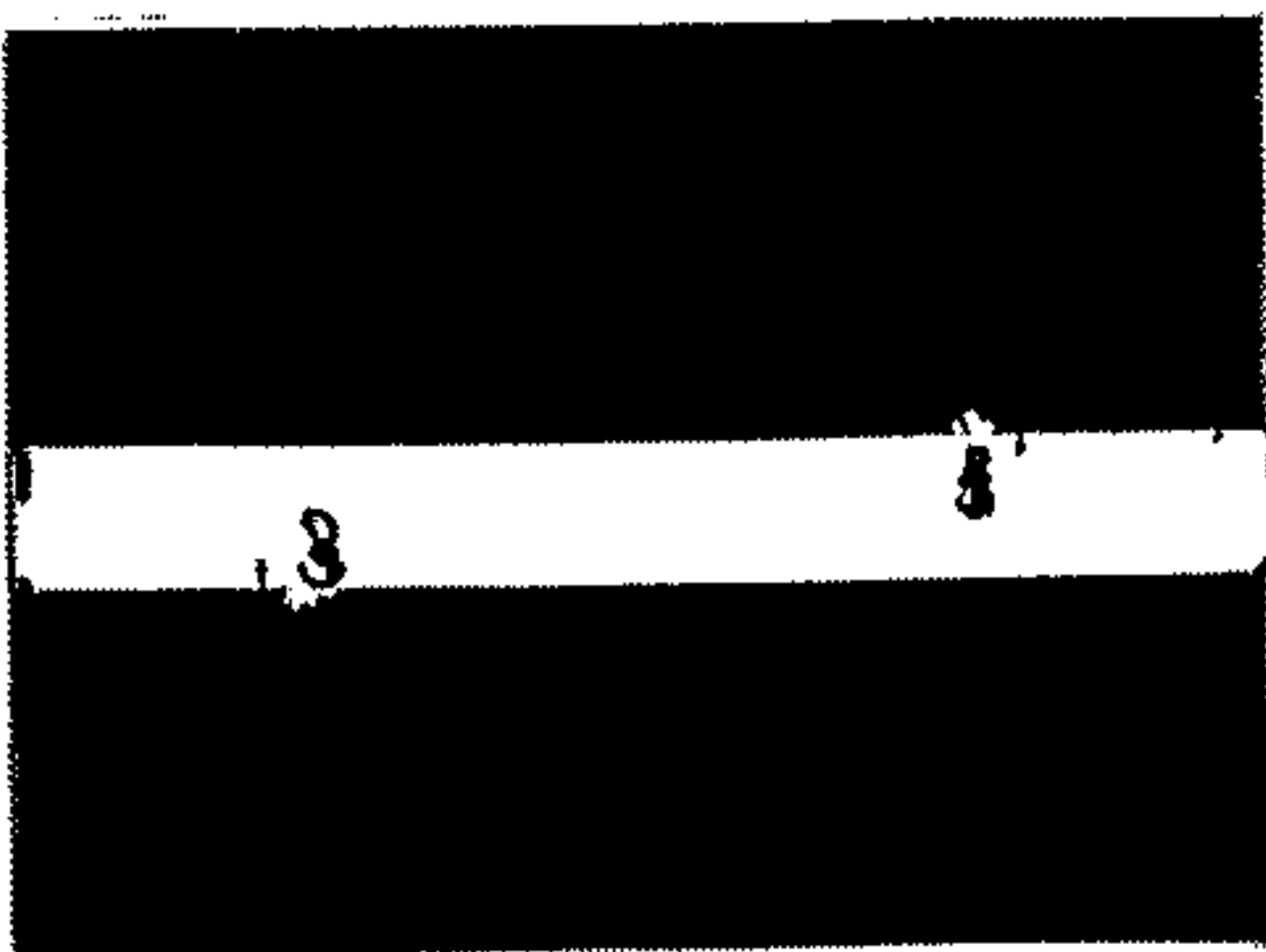
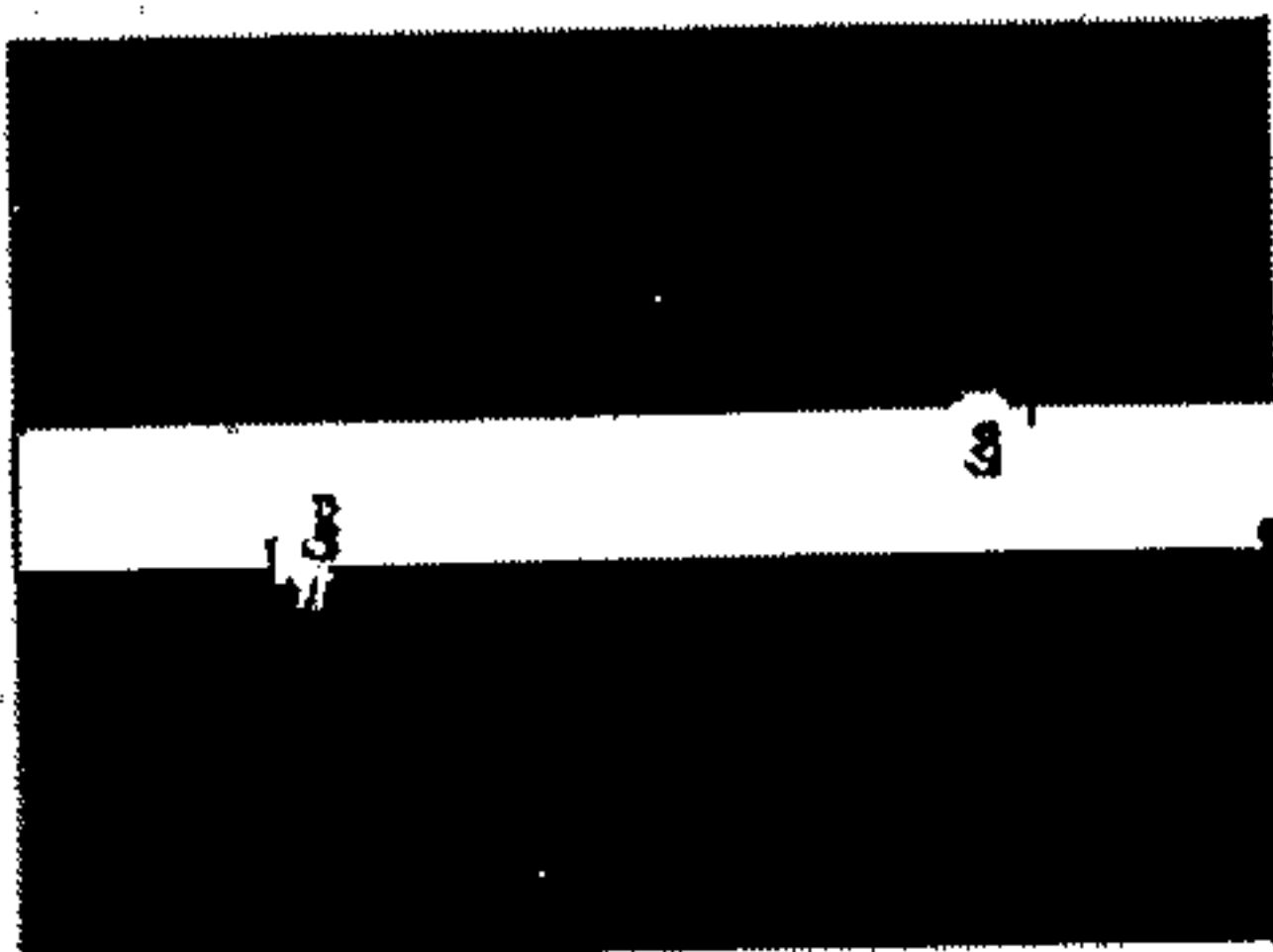
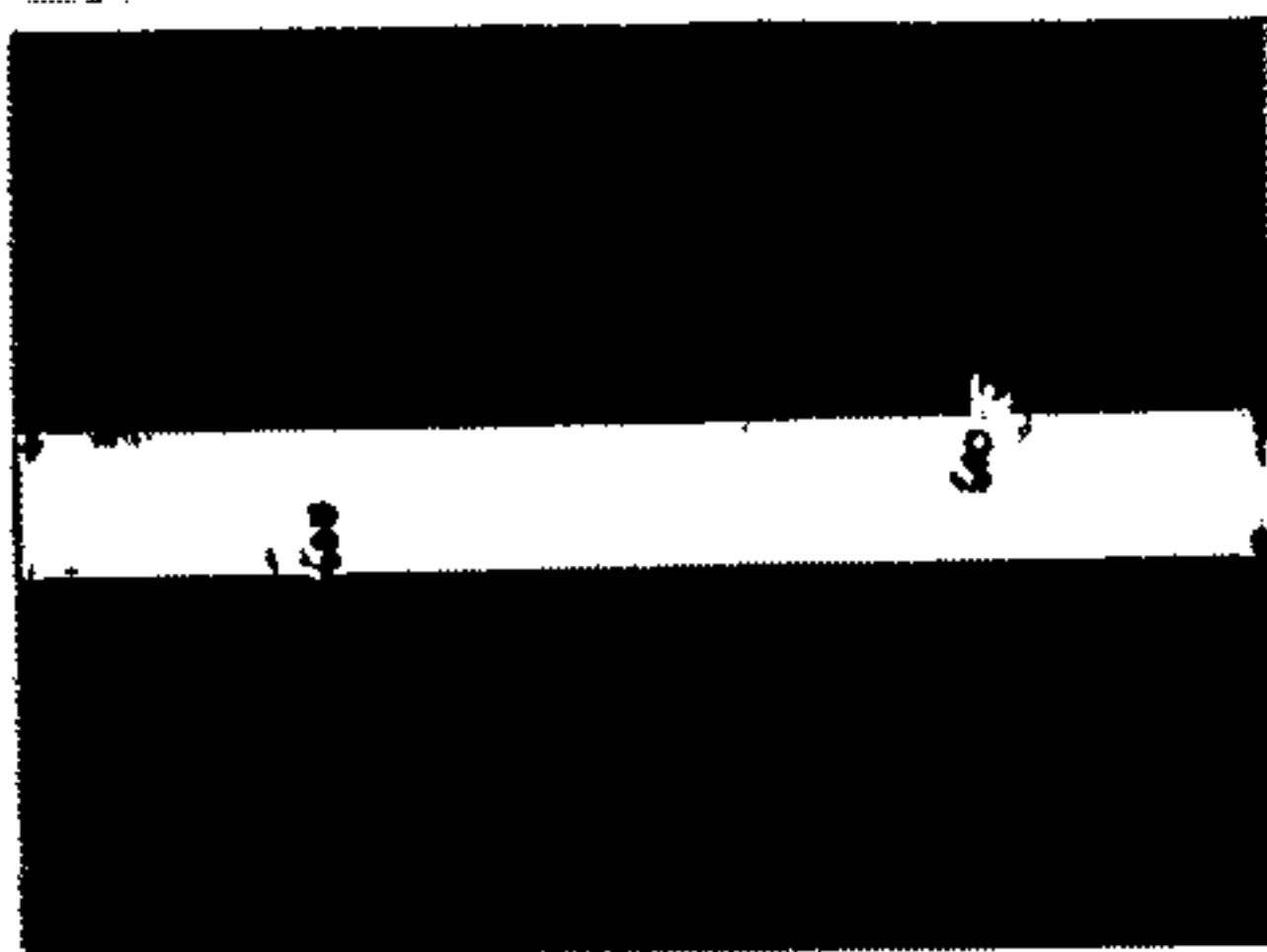
Example 19. Rain erosion adhesion results for aged Desothane HS 70846X white (C-thinner) applied onto epoxy-carbon fibre composite incorporating primer, intermediate and topcoat layers reactivated under the conditions specified before being over-coated with Desothane HS S601X blue.

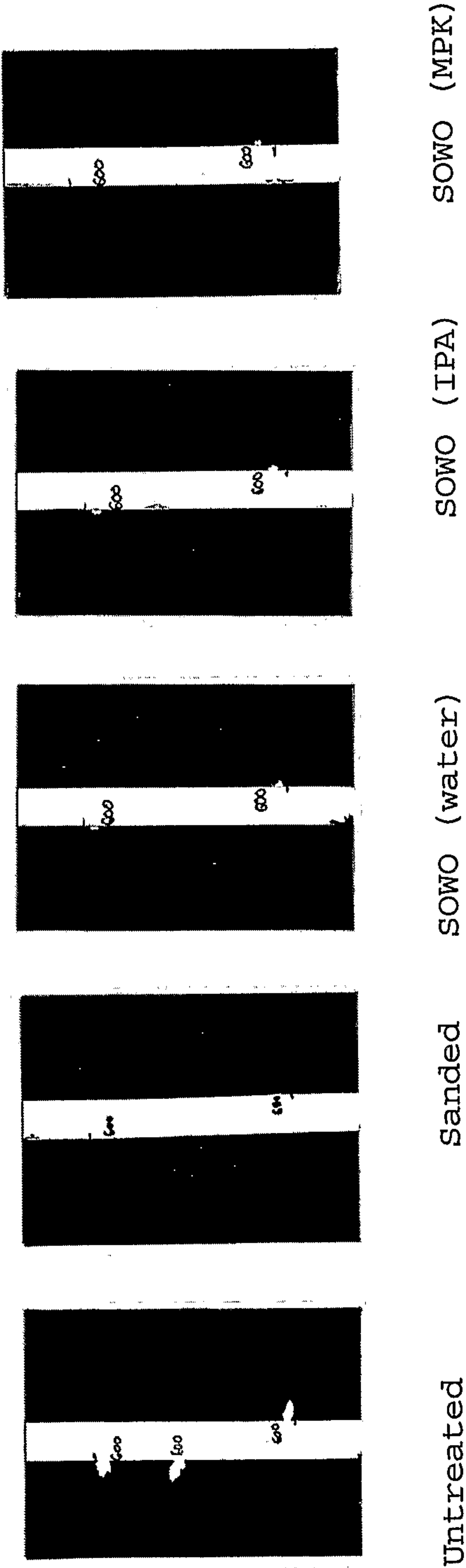


Example illustrates that reactivation of aged polyurethane topcoats can be completed using the reducing methodology on "composite substrates" incorporating paint lay-ups including selectively strippable intermediate coating layers beneath the polyurethane topcoat.

Note: sanded and untreated reference in duplicate, chemically reactivated in triplicate

Example 20. SIJA inter-coat adhesion of aged Desothane HS 70846X white (C2) reactivated with LiBH_4 (0.2 wt% in Proglyde DMM) for 2h under the post treatment conditions specified before being over-coated with Desothane HS S601X blue.

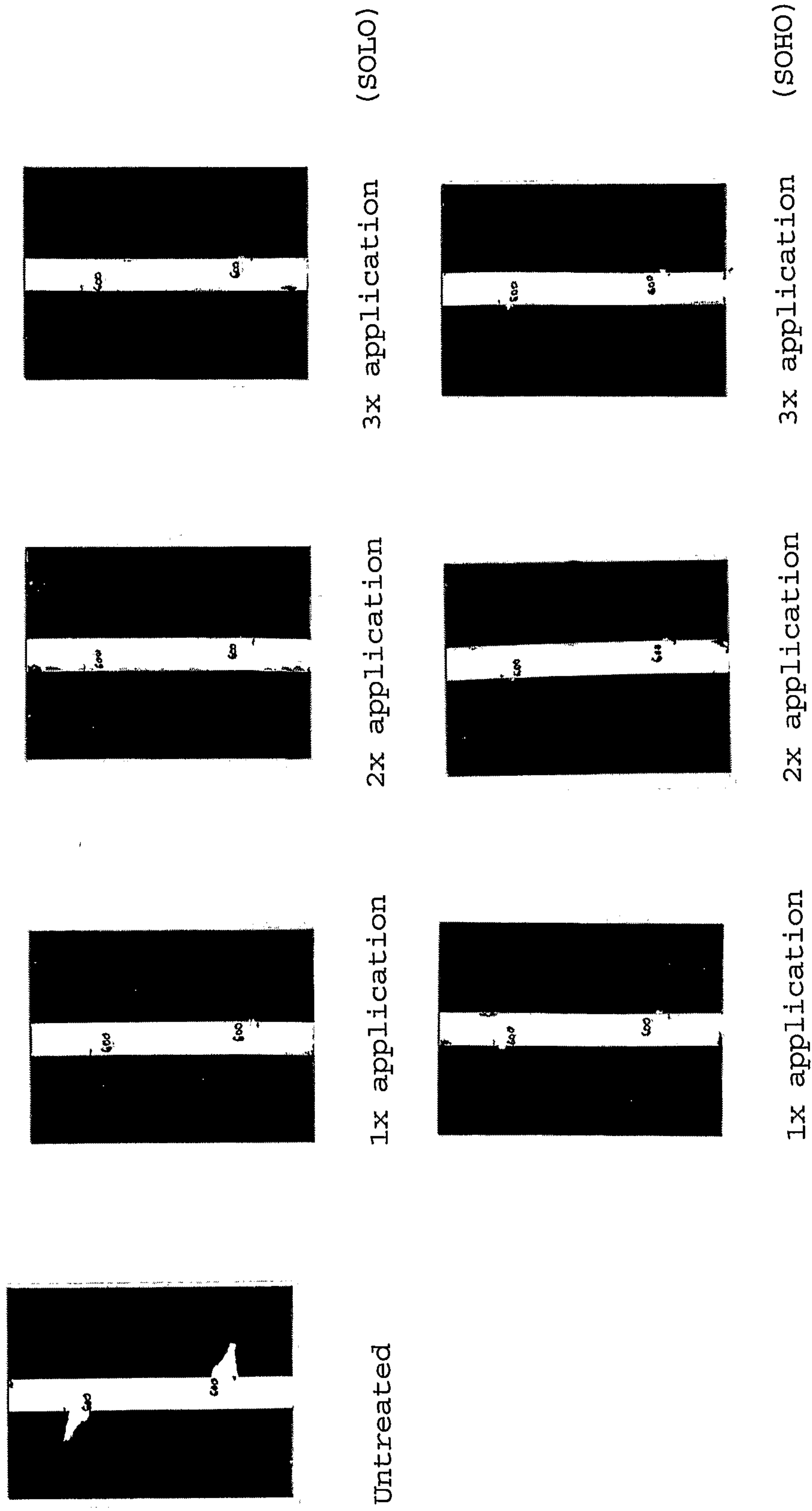
			
Untreated	Sanded	SOLO	SOLO with dry tack rag wipe
			
SOHO (water)	SOHO (Water 0.1% FC4430 surfactant)	SOHO (IPA)	SOHO (IPA: water, 20:80)



Example illustrates that various "post treatment" protocols may be employed depending on the application / process requirements without negatively impacting adhesion.

- 58 -

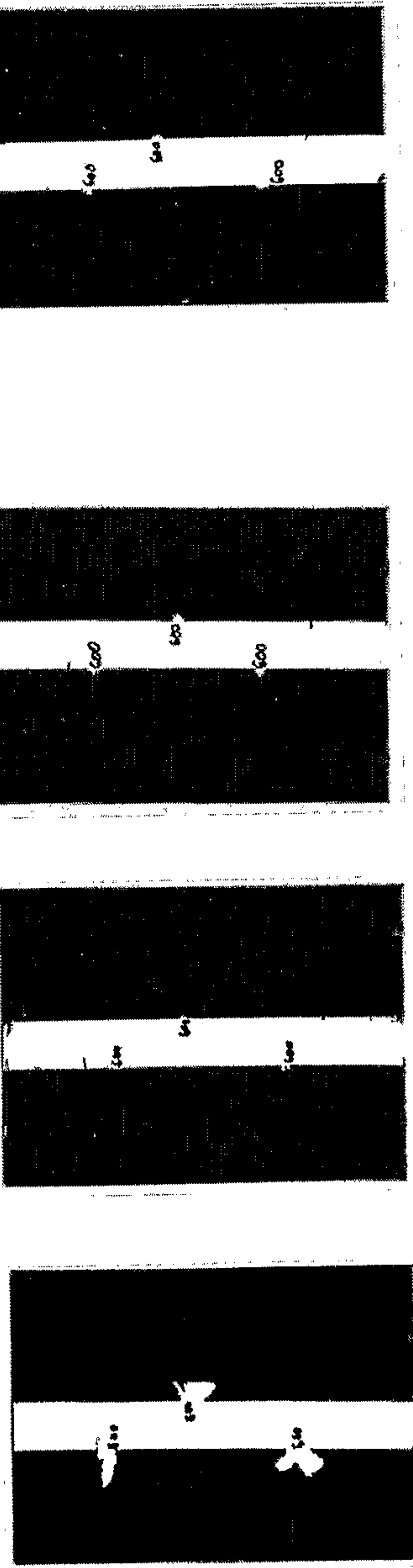
Example 21. SIJA inter-coat adhesion of aged Desothane HS 70846X white (C2) reactivated with LiBH_4 (0.1 wt% in Proglyde DMM) multiple times 30min apart under the conditions specified before being over-coated with Desothane HS S601X blue.



Example illustrates that multiple applications of the reactivation treatment solution does not diminish adhesion performance.

Example 22. SIJA inter-coat adhesion of aged Desothane HS 70846X white (C2) reactivated with LiBH_4 (0.1 wt% in Proglyde DMM) for (i) one hour before being subjected to the conditions specified and then washed (water) allowed to dry or (ii) for the treatment time specified before being over-coated with Desothane HS S601X blue or S400X red.

(i)



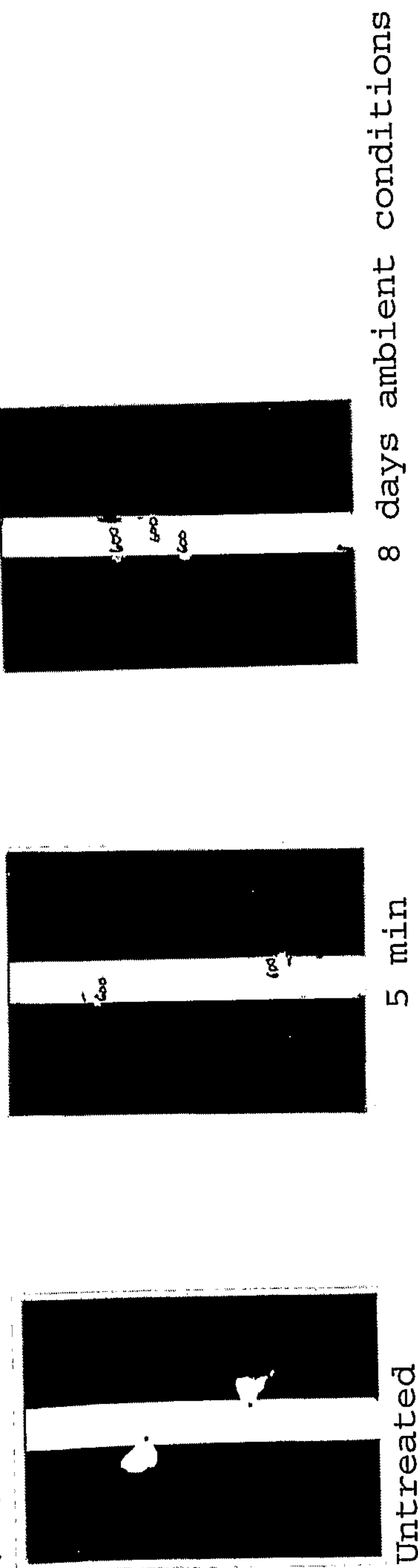
Untreated

Sanded

4h bake at 70°F

24h at ambient conditions

(ii)



Untreated

5 min

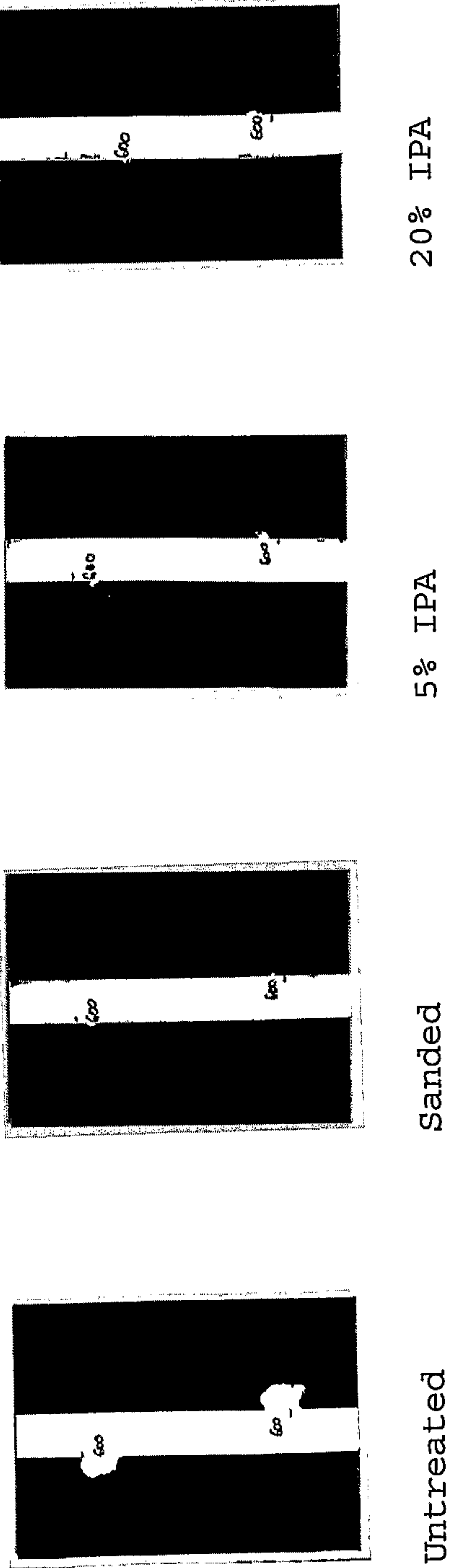
8 days ambient conditions

The example demonstrates that reactivation can be conducted for a short (5min) or extended period (8 days) and that the reactivated surface retains its reactivity towards subsequent paint layers under a variety of conditions.

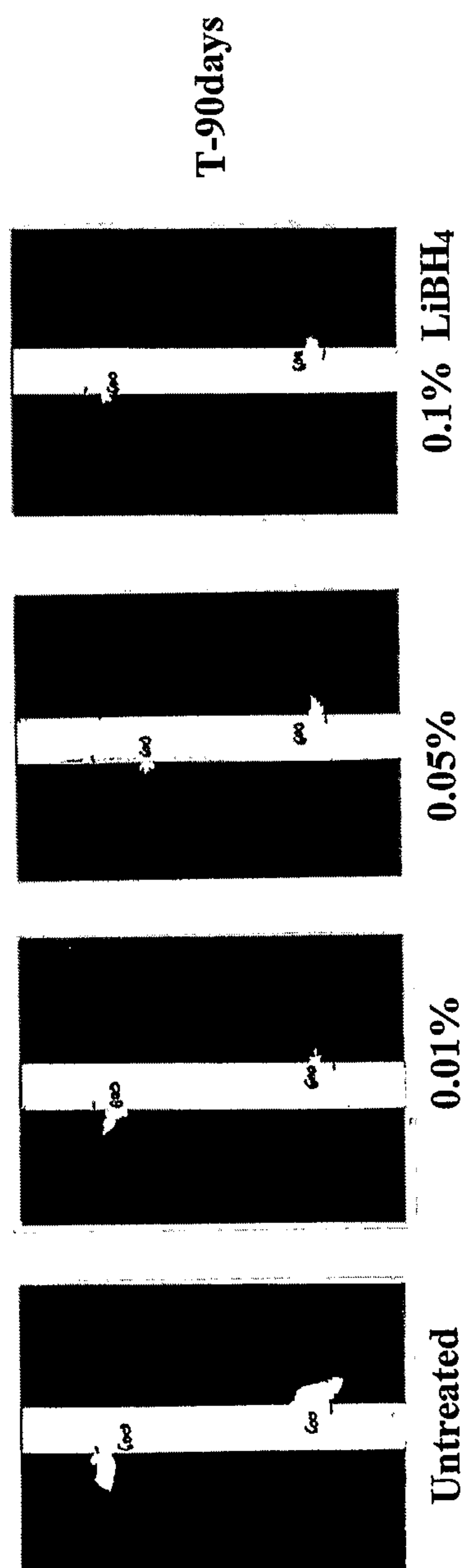
- 60 -

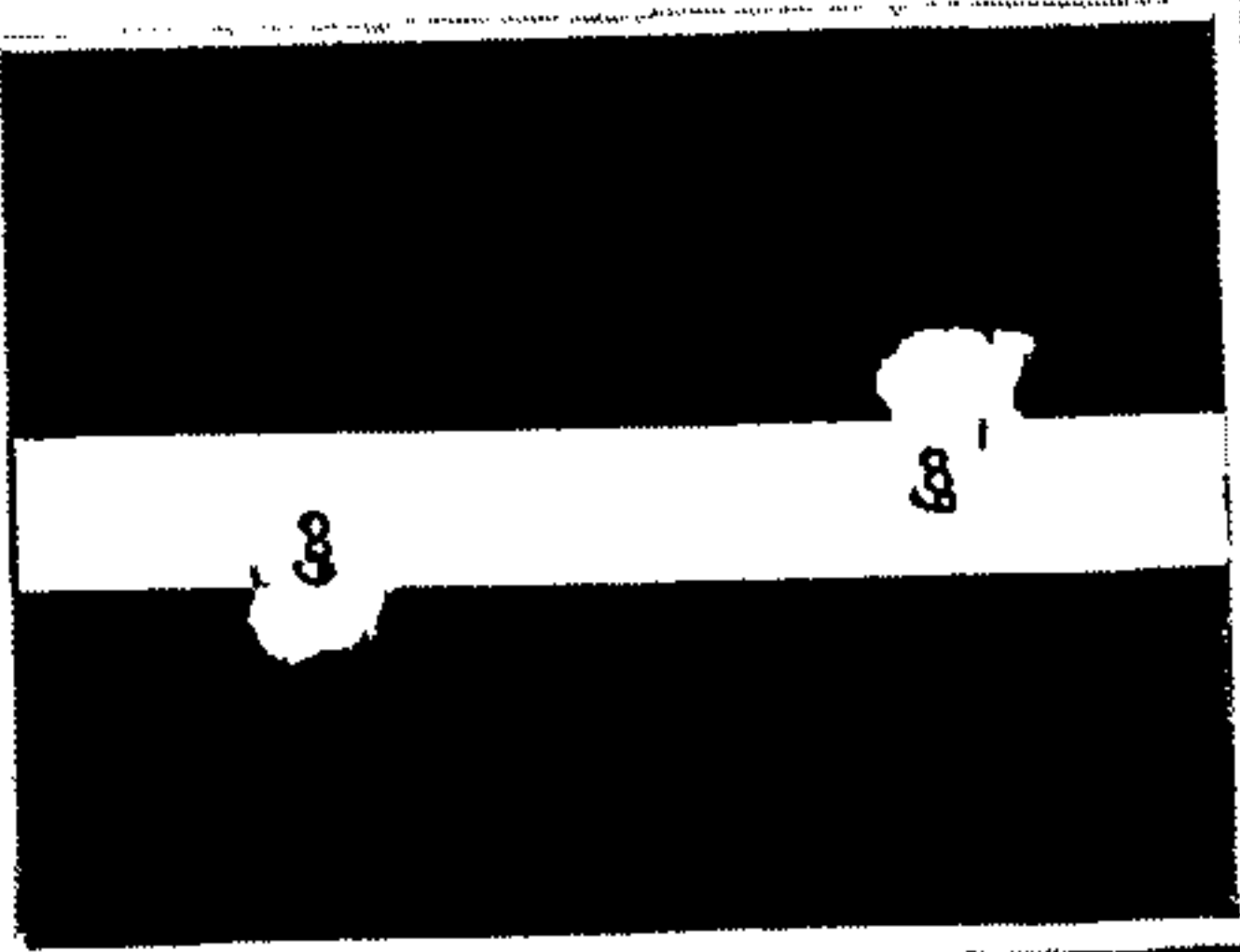
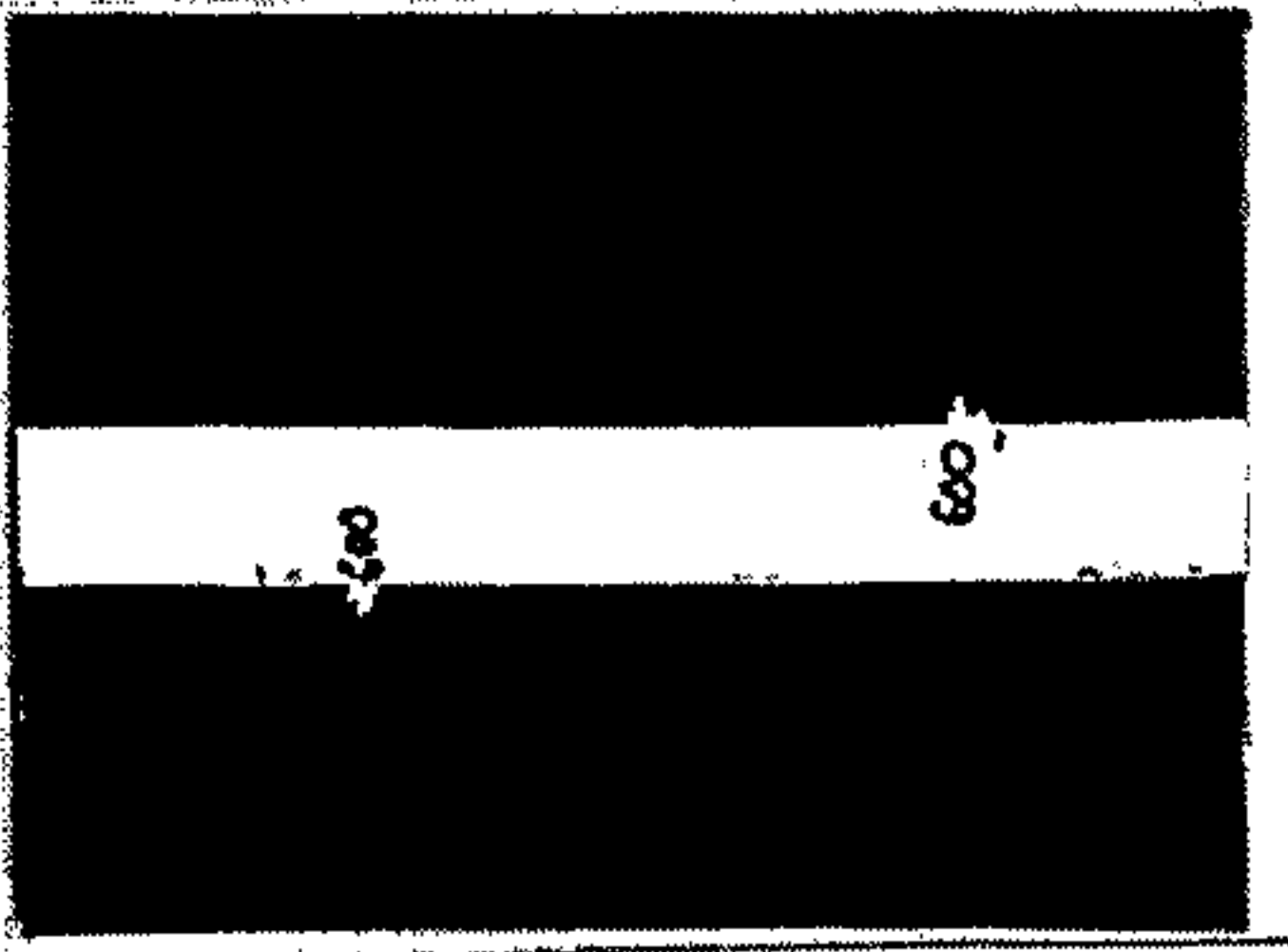
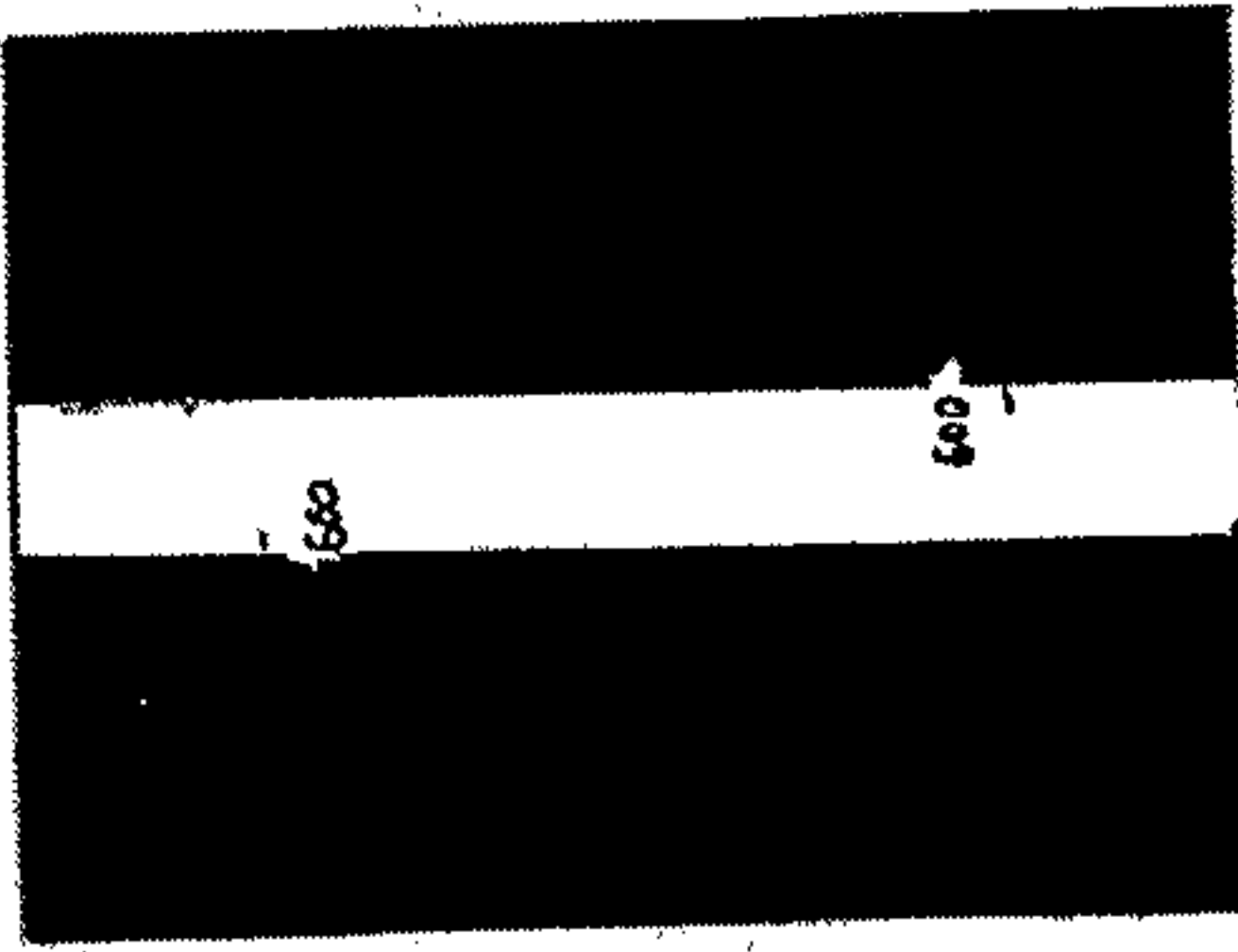
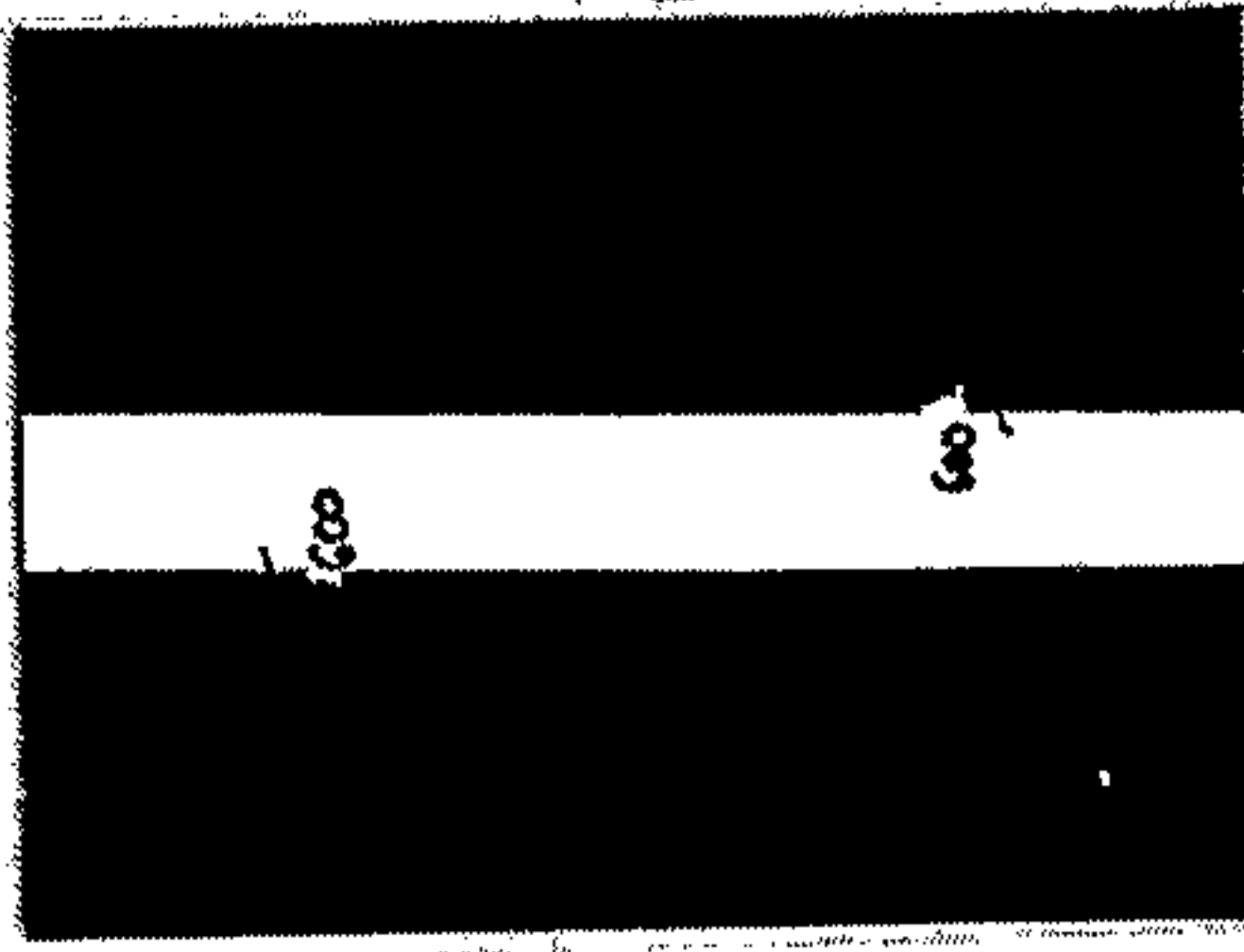
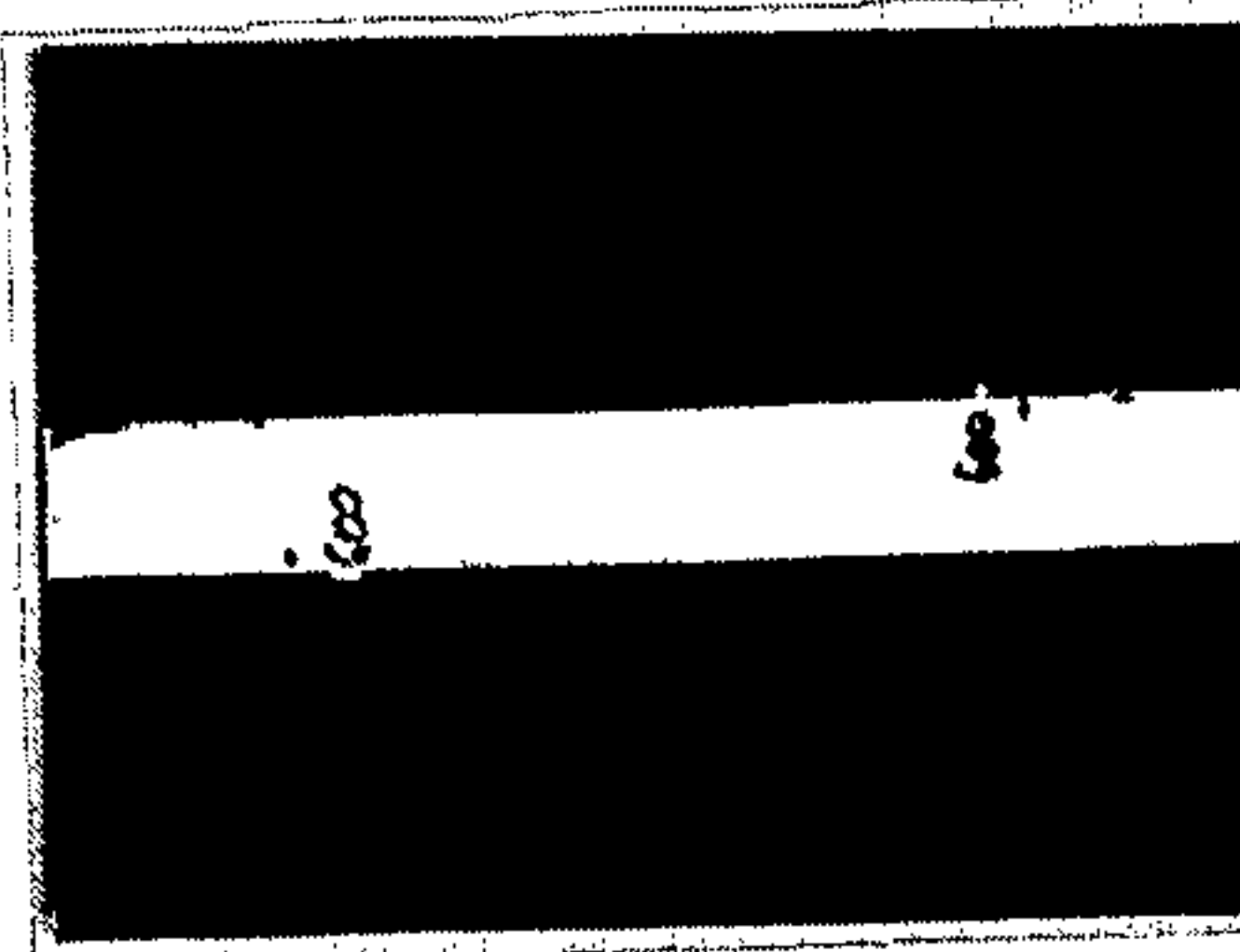
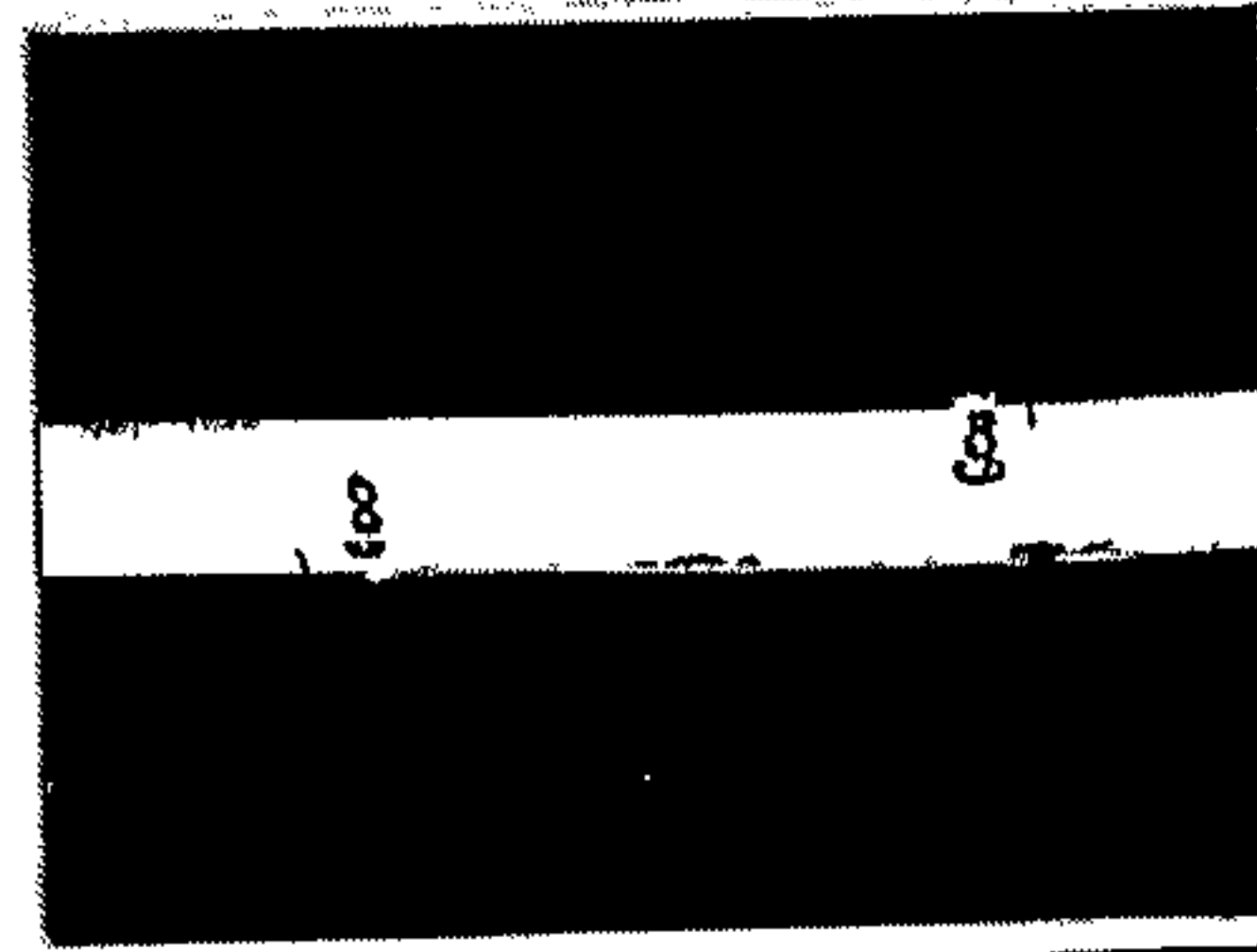
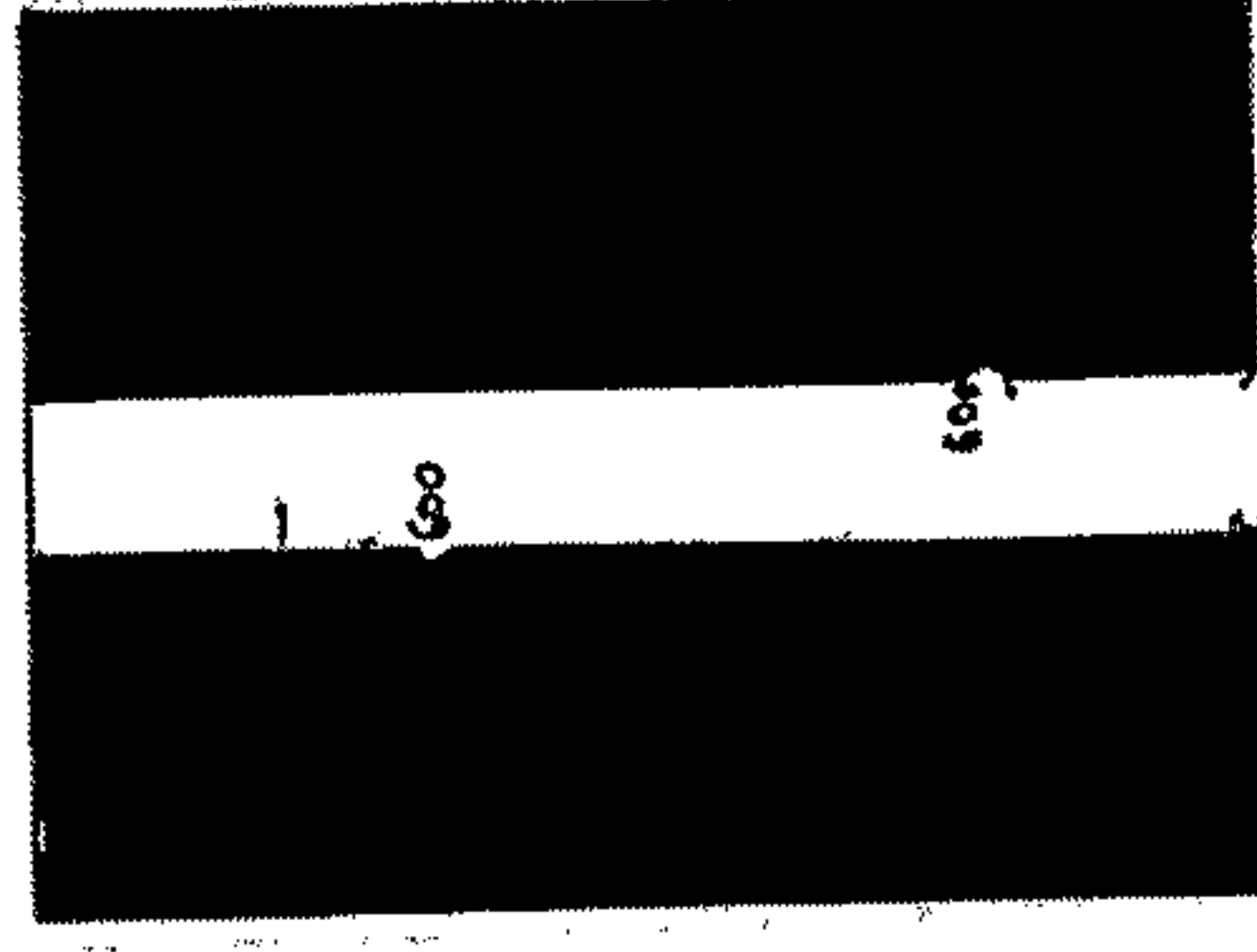
Example 23. SIJA inter-coat adhesion of aged Desothane HS 7084X6 white (C2) reactivated with LiBH_4 solutions themselves previously aged under ambient conditions for the period specified before being over-coated with Desothane HS S601X blue.

(i) Treatment solutions: 0.2% LiBH_4 in Propylde DMM + the percentage IPA indicated stored for 50 days before being used to reactivate the aged polyurethane topcoat.



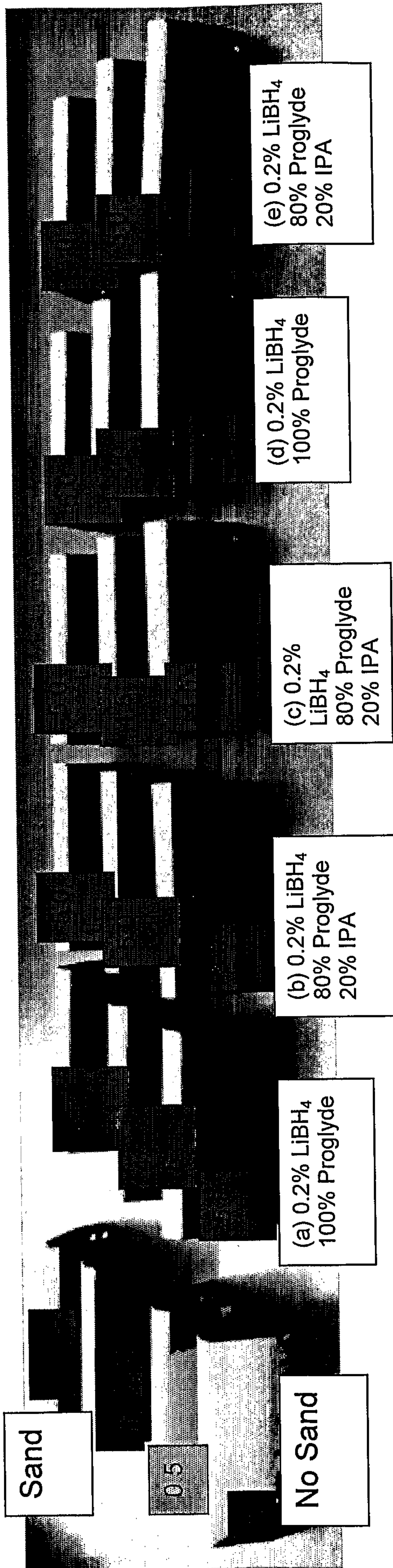
(ii) Treatment solutions: Various LiBH_4 concentrations stored in Progylde DMM / 2% tBAC for 90 days prior to application



Untreated	0% IPA	20% IPA	40% IPA
			
	LiBH_4	LiBH_4	LiBH_4
	0.15%	0.2%	
			
	Sanded		

(iv) Rain erosion adhesion data from Desothane HS 70846X white (C) cured at 120F (10%RH) 4 days prior to reactivation and over-coating with Desothane HS S601X blue. NOTE: Reactivated samples in triplicate, benchmark untreated and sanded in duplicate.

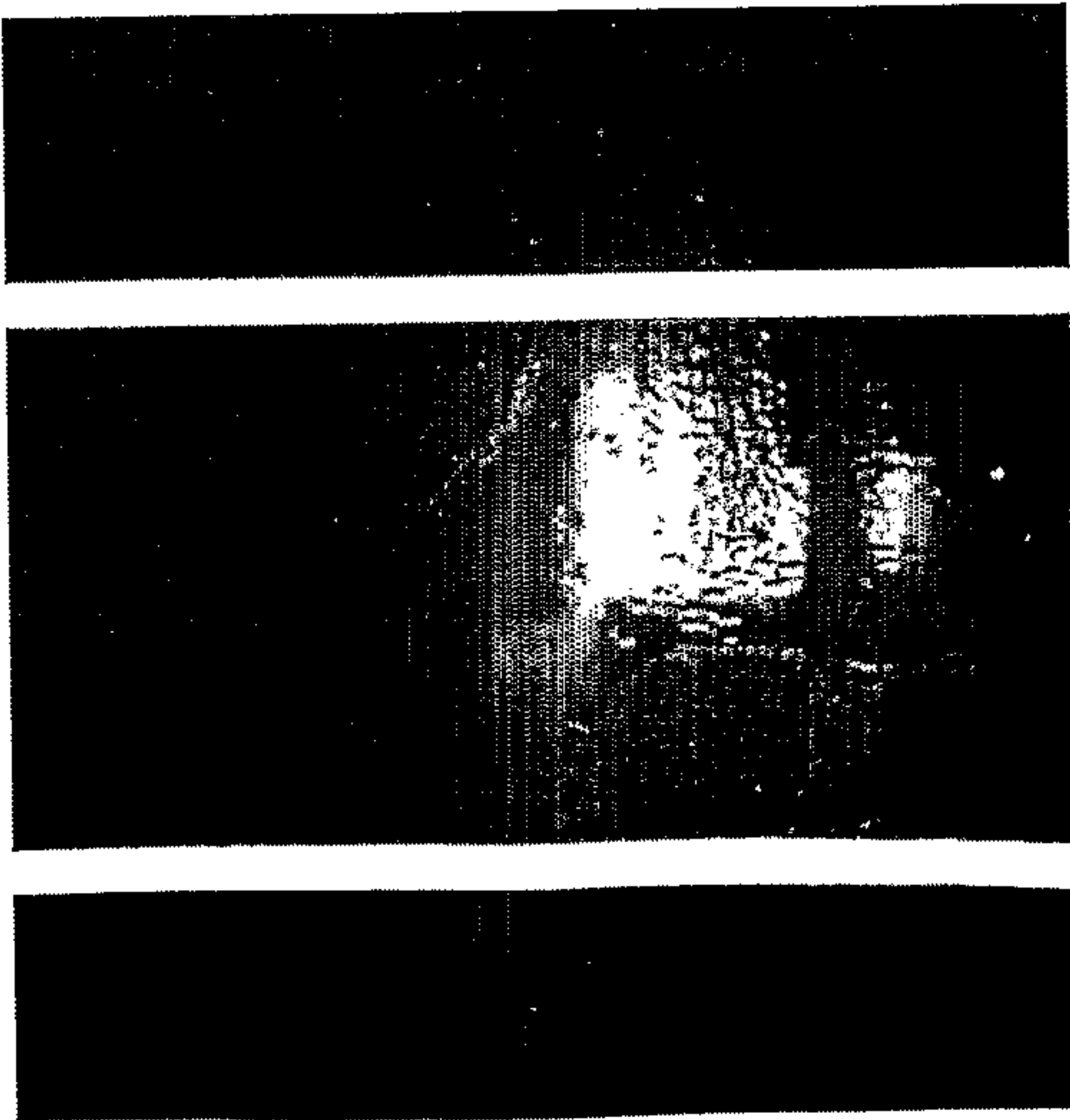
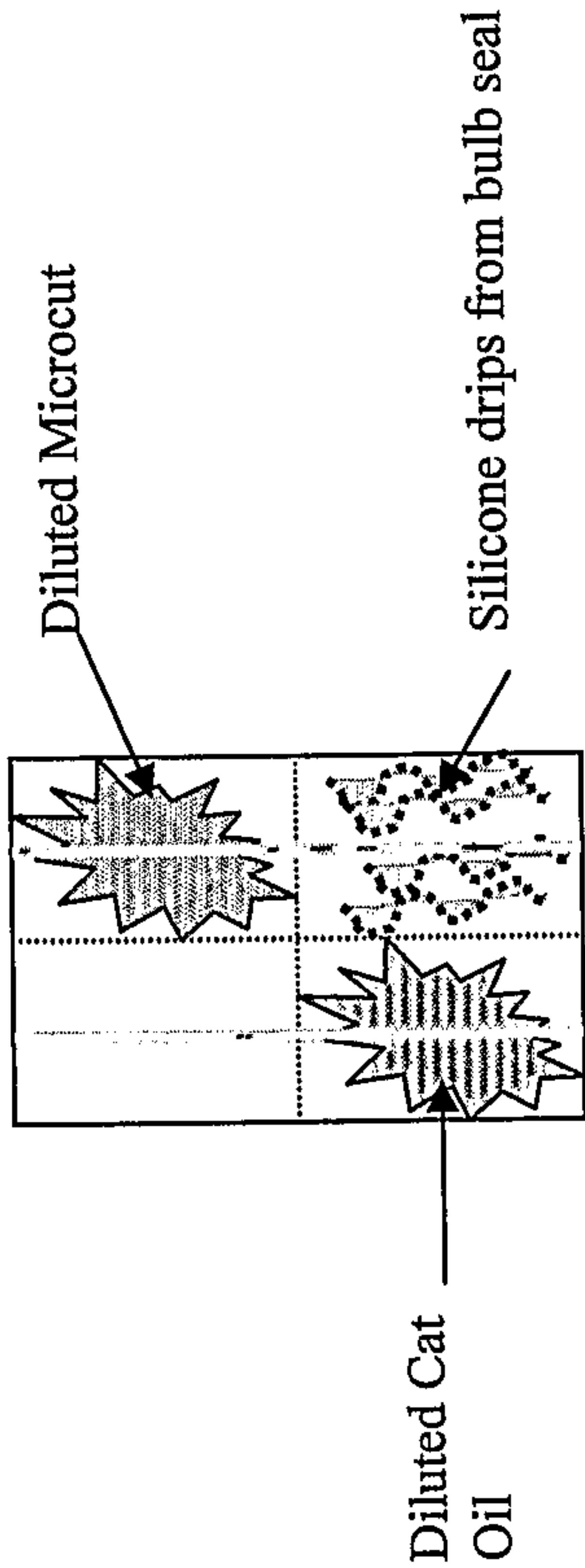
Treatment solutions (a) Aged for 25 days (b) Aged for 25 days (c) Stock solution in Progylde DMW aged for 25 days and IPA added just prior to application to provide the given concentration (d) prepared fresh (e) prepared fresh.



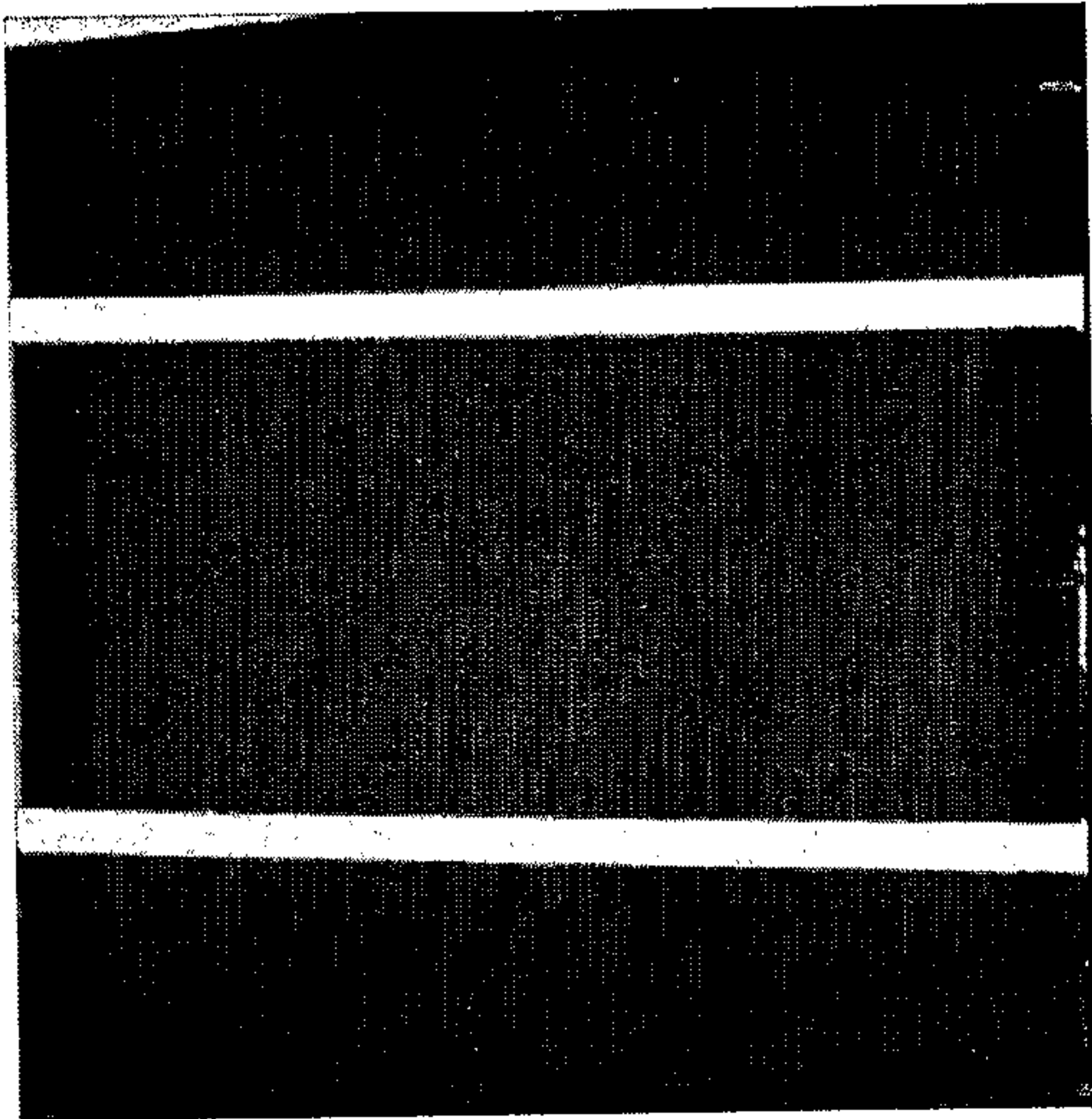
Examples illustrate that reactivation treatment solutions stored under ambient conditions retain their activity thus providing shelf life and pot-life robustness.

Example 24. Example demonstrates that application of the treatment solution can assist in the mitigation of common surface contaminants (residues), produced by the manufacturing assembly which can reduce both the visual appearance and inter-coat adhesion particularly when the reactivation treatment solution is applied as a SOHO or SOWO application technique.

(i) Illustration of application of common surface contaminates to the surface of an aged Desothane HS 70846X white topcoat prior to reactivation and over-coating with Desothane HS 5070X blue.



Paint appearance untreated



Paint appearance following reactivation with 1.0% LiBH₄ solution in Progylde DMM (30min) SOHO.

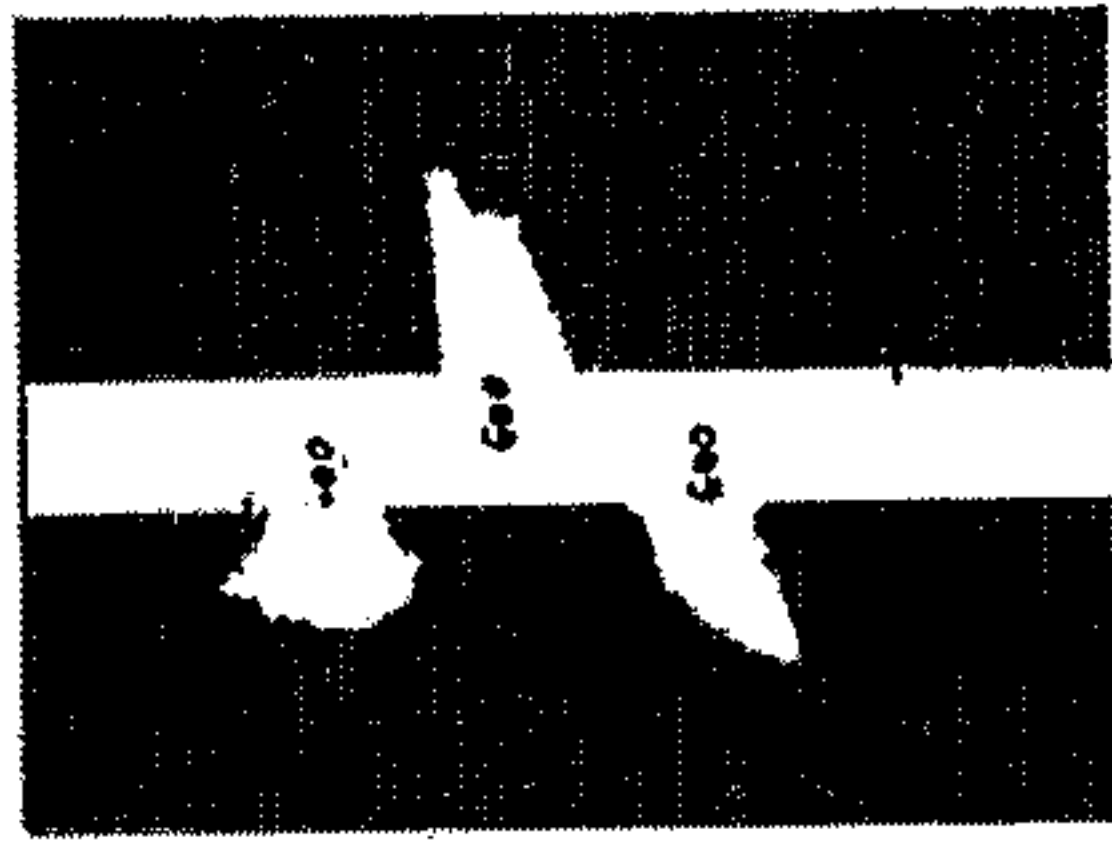
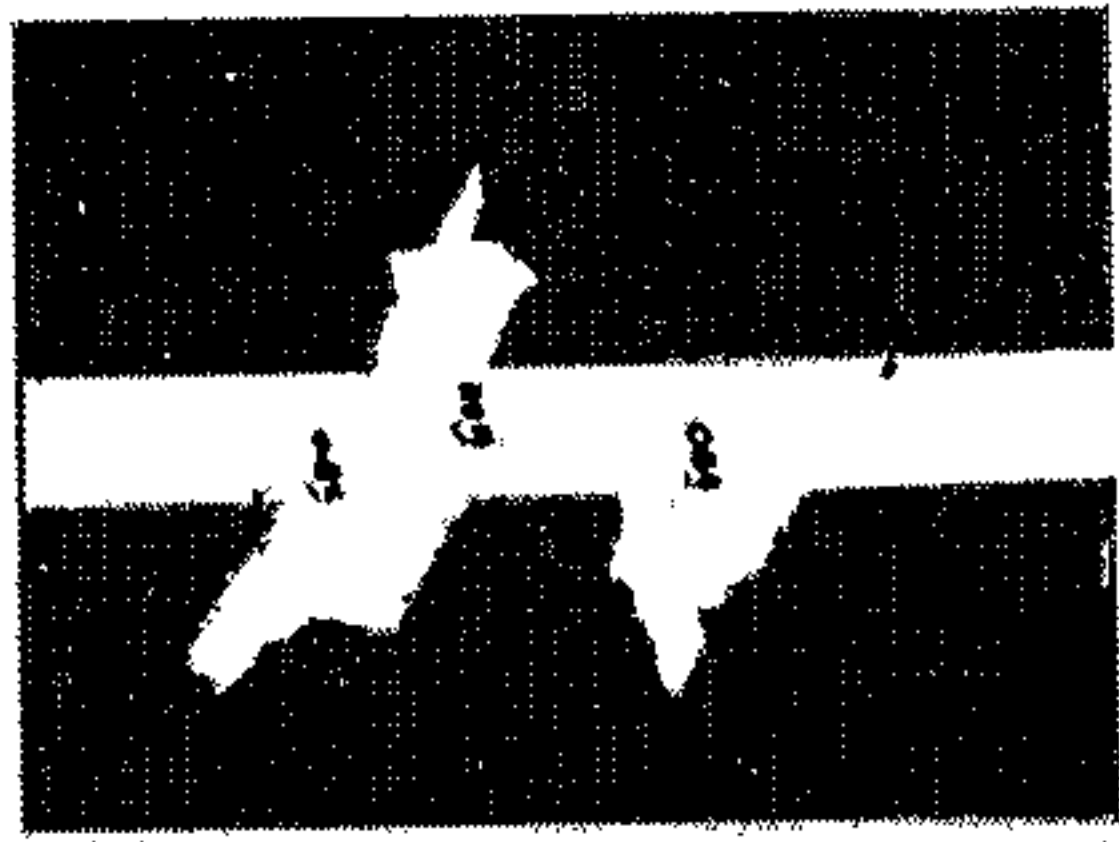
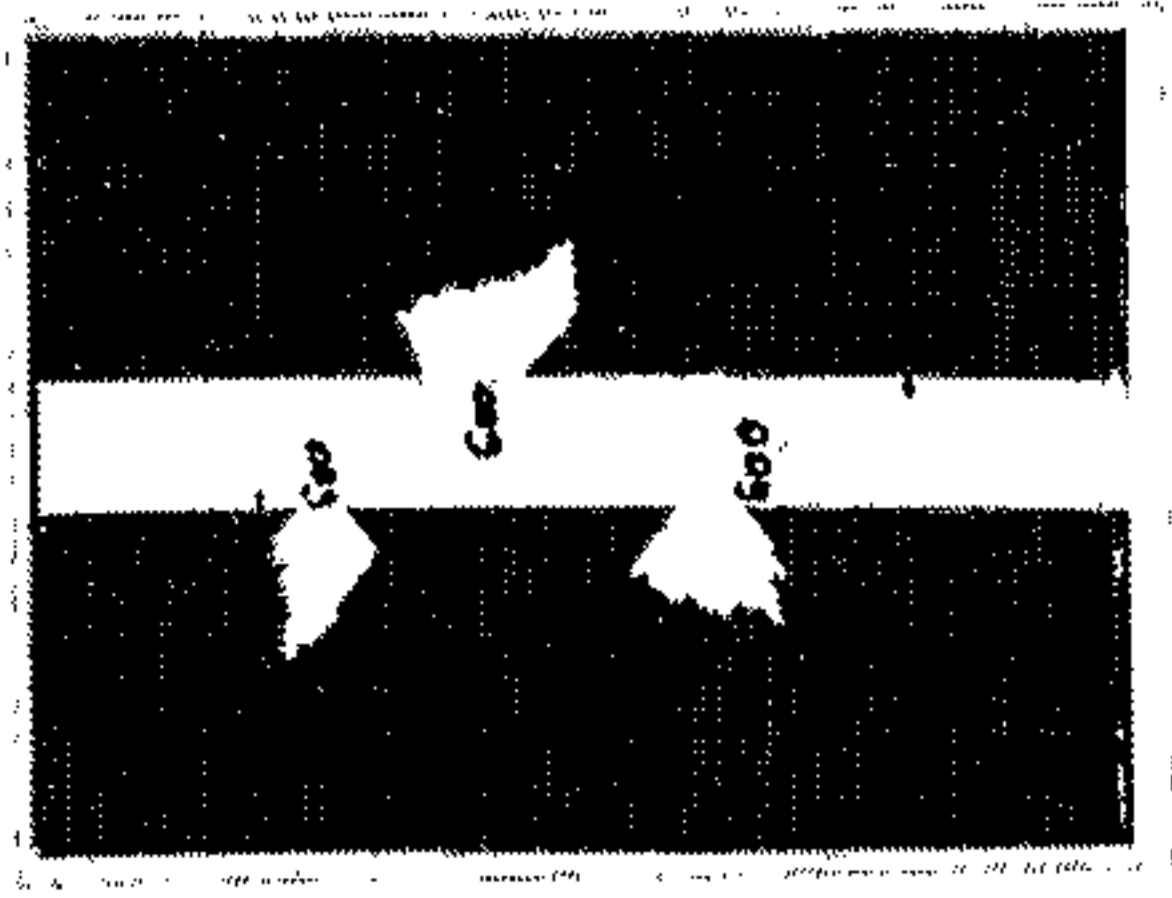
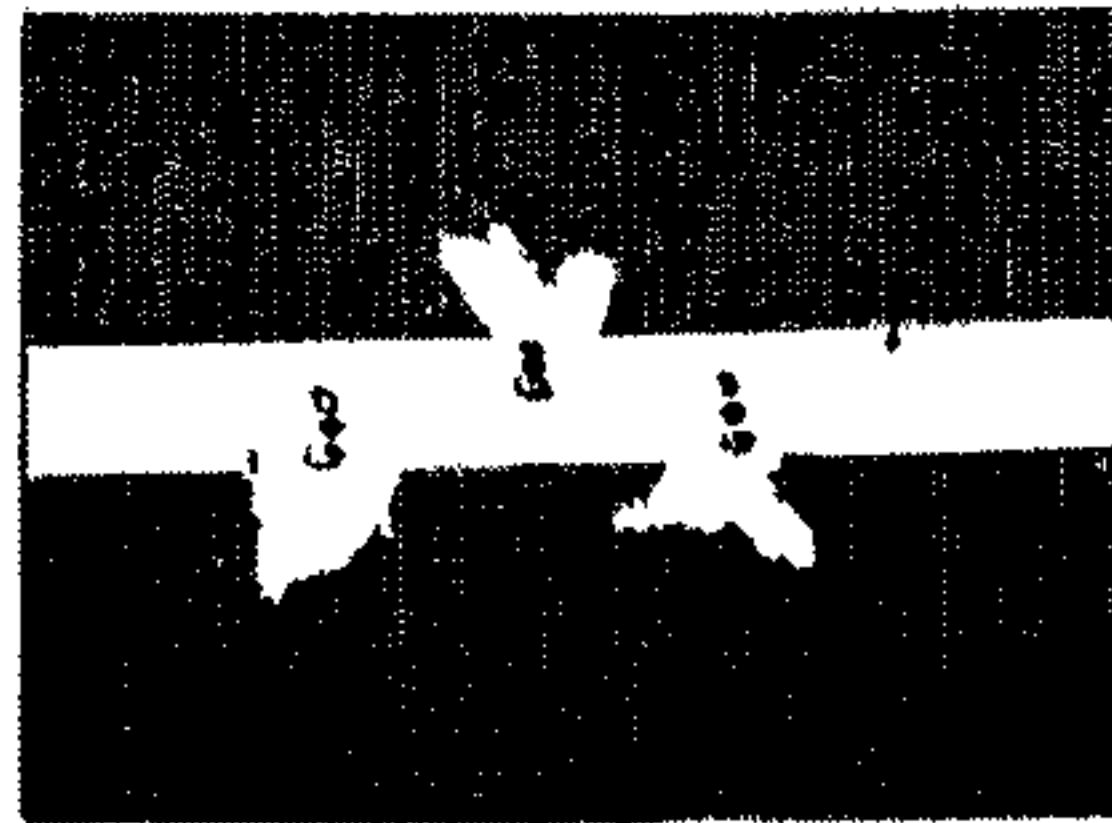
Corresponding SIJA inter-coat adhesion results from contaminant quadrants

Quadrant: Blank

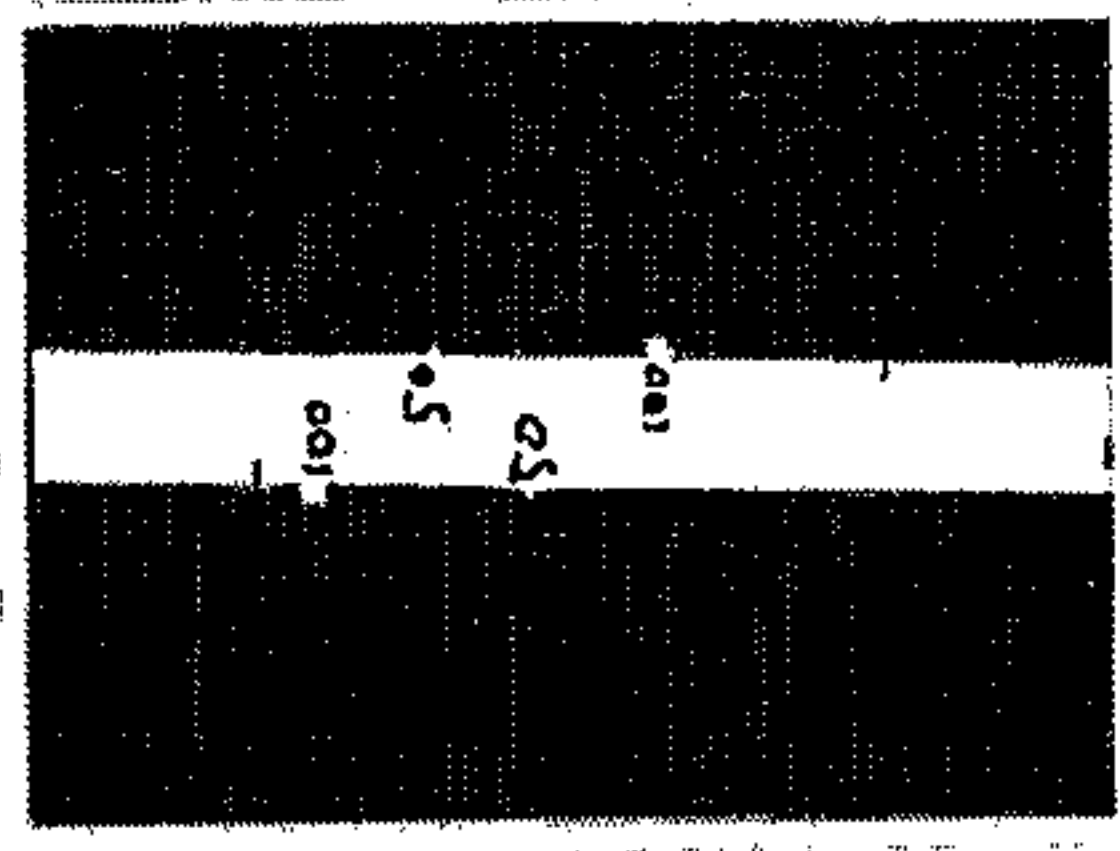
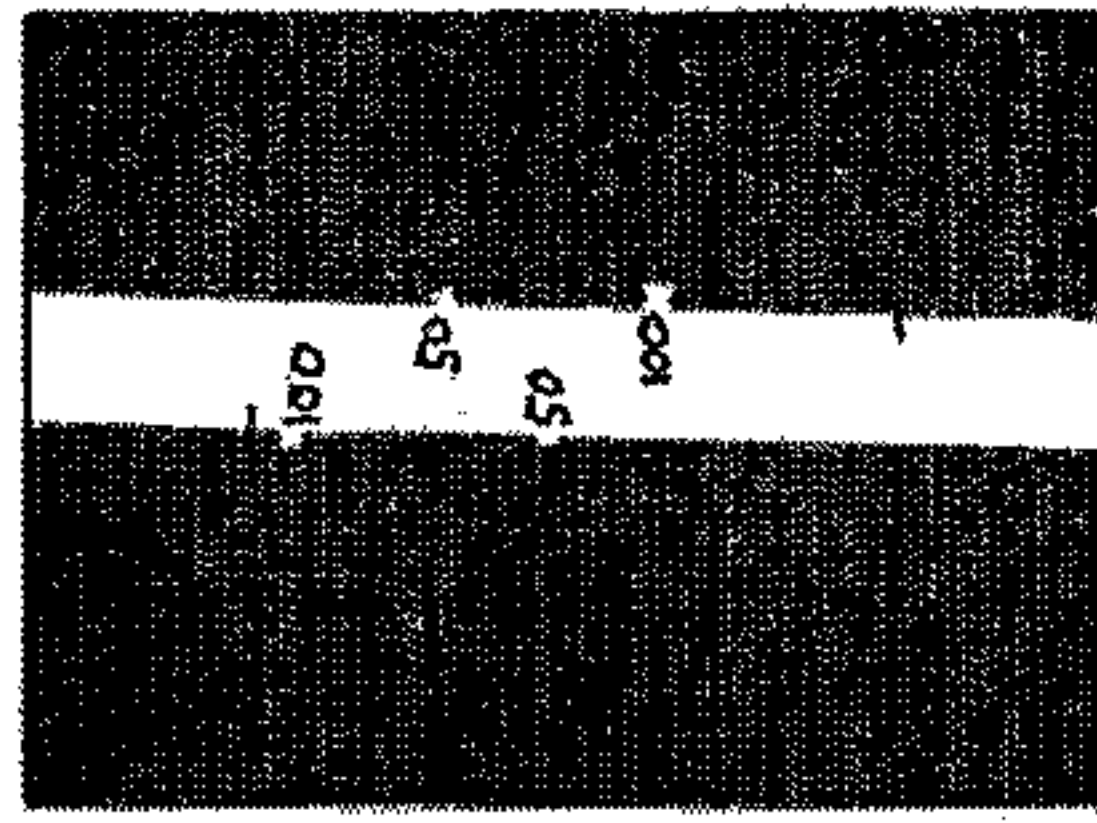
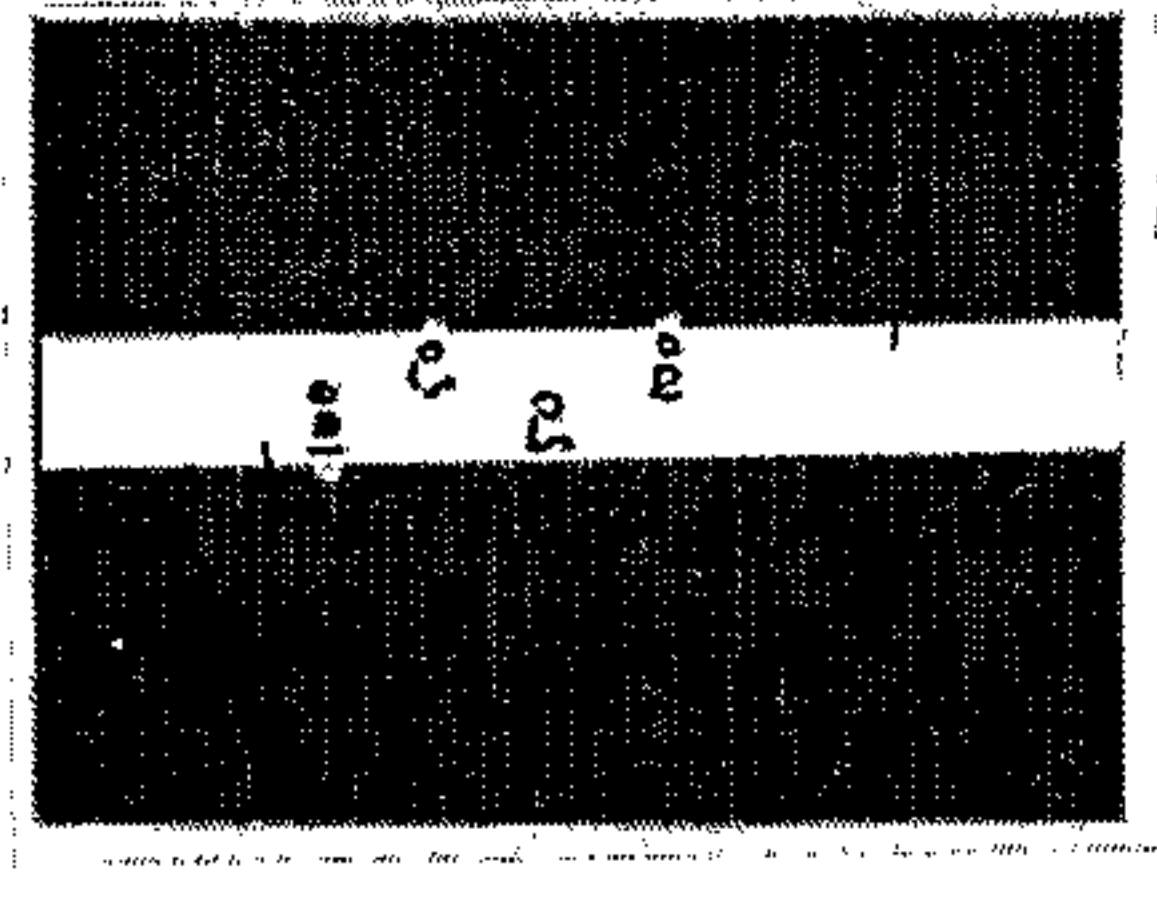
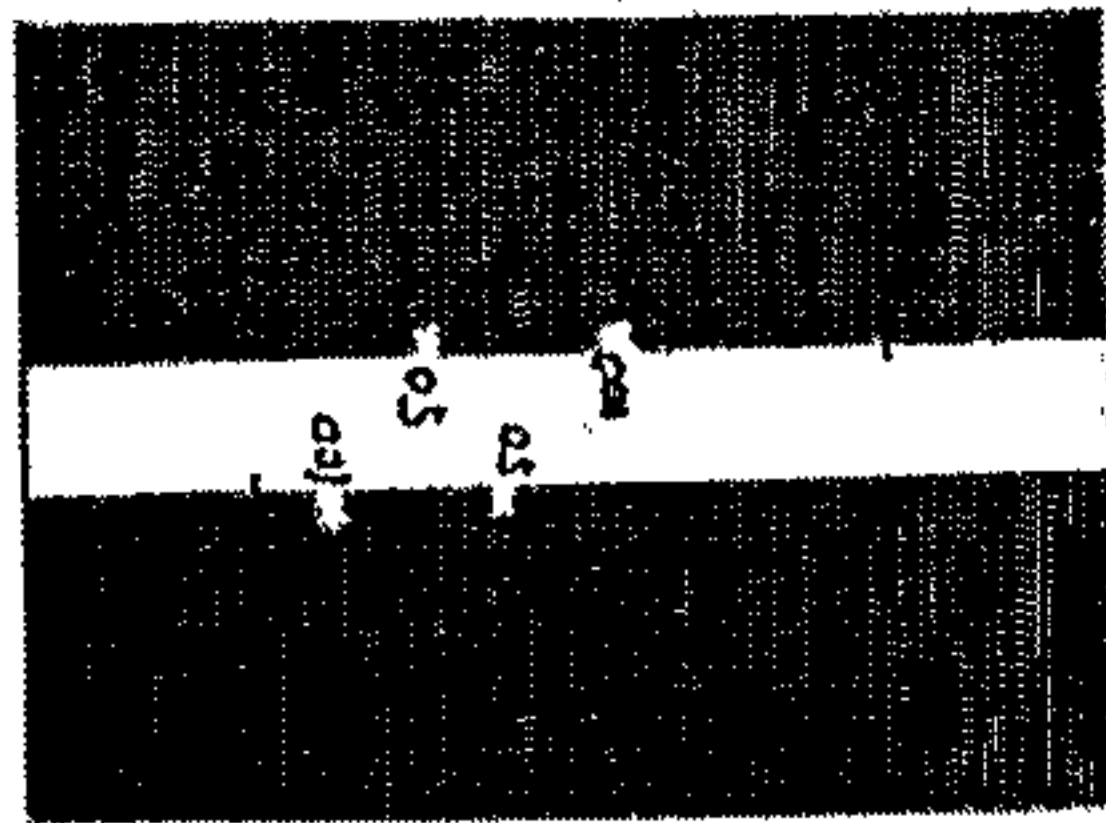
Cat oil

Microcut

Silicone



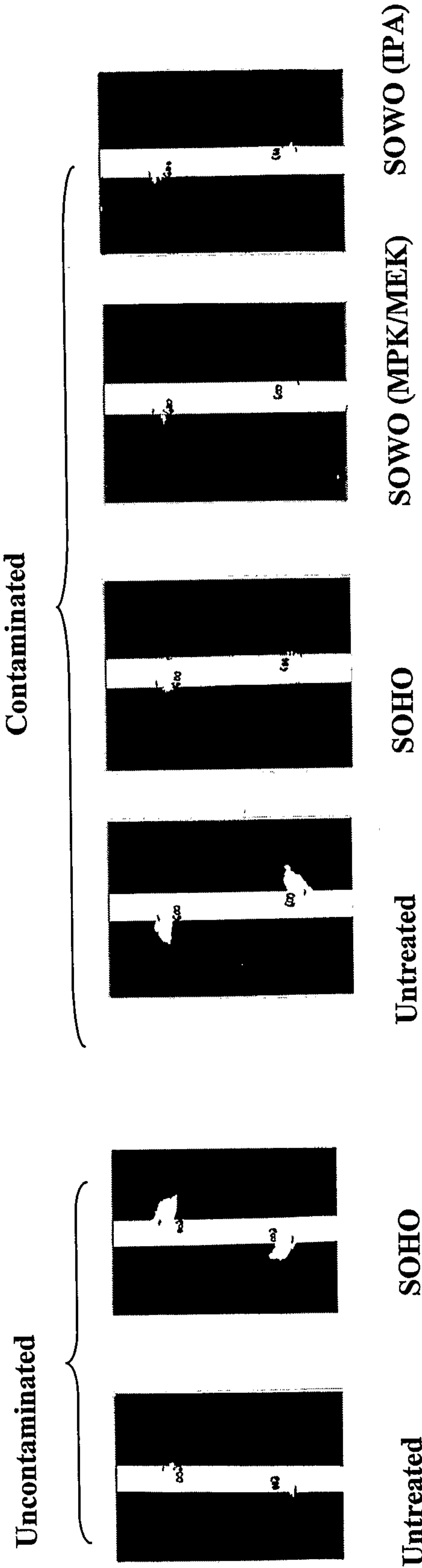
Not
Reactivated



Reactivated
1.0%
LiBH₄

Untreated		SOHO		Untreated		SOHO	
Untaminated		SOHO		Untreated		SOHO	

b) Aeroshell 33

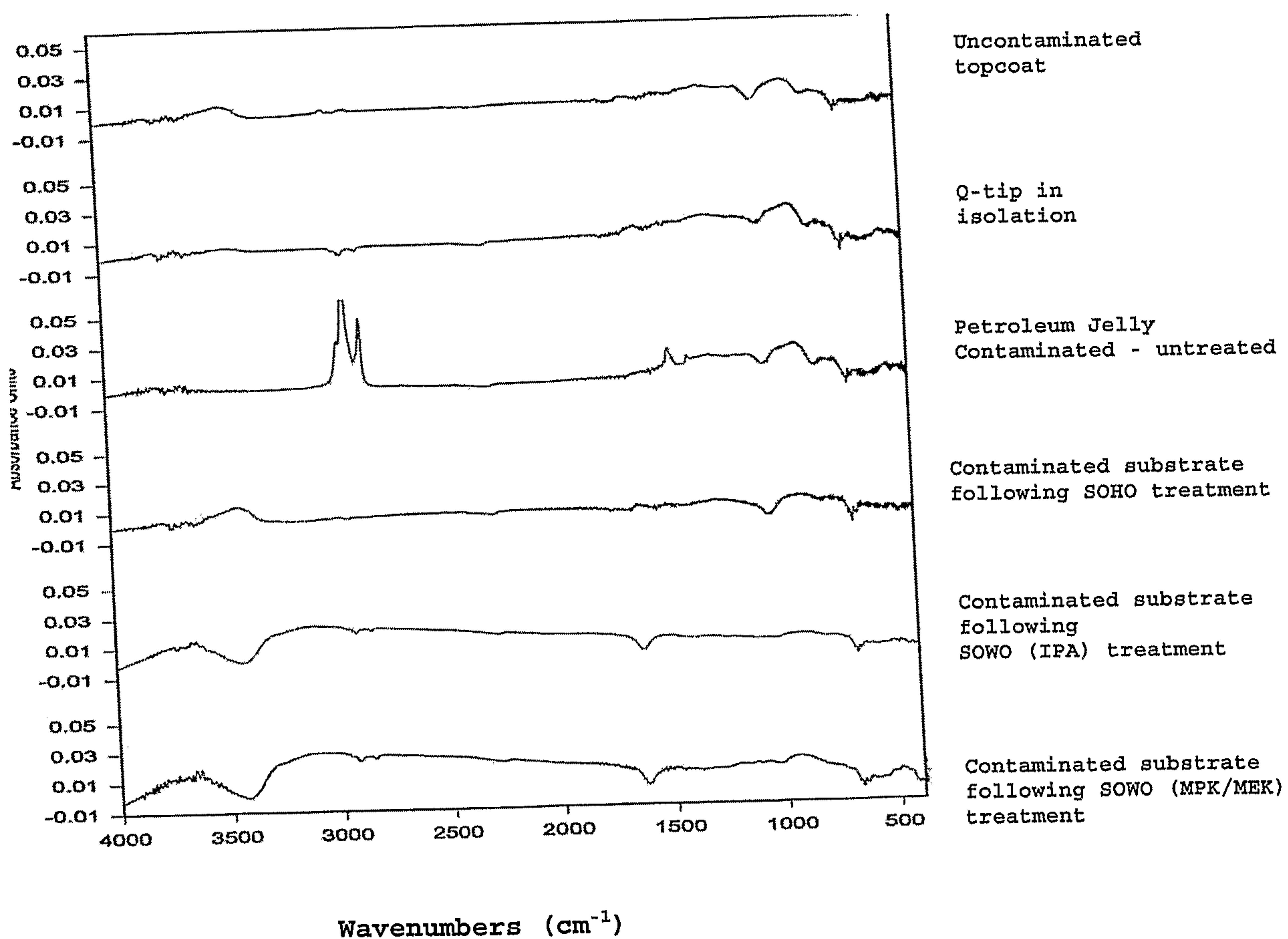


The above example clearly demonstrates that improved inter-coat adhesion and paint appearance may be obtained when the Desothane HS coatings contaminated with common aerospace residues from manufacturing processes are reactivated prior to over-coating.

- 68 -

(iii) Supporting FTIR evidence for selected contaminants: Samples were swabbed with a hexane soaked "Q-tip" and the hexane containing sample absorbed onto NaCl. Following compression molding of the NaCl into Plaques, FTIR spectra was obtained.

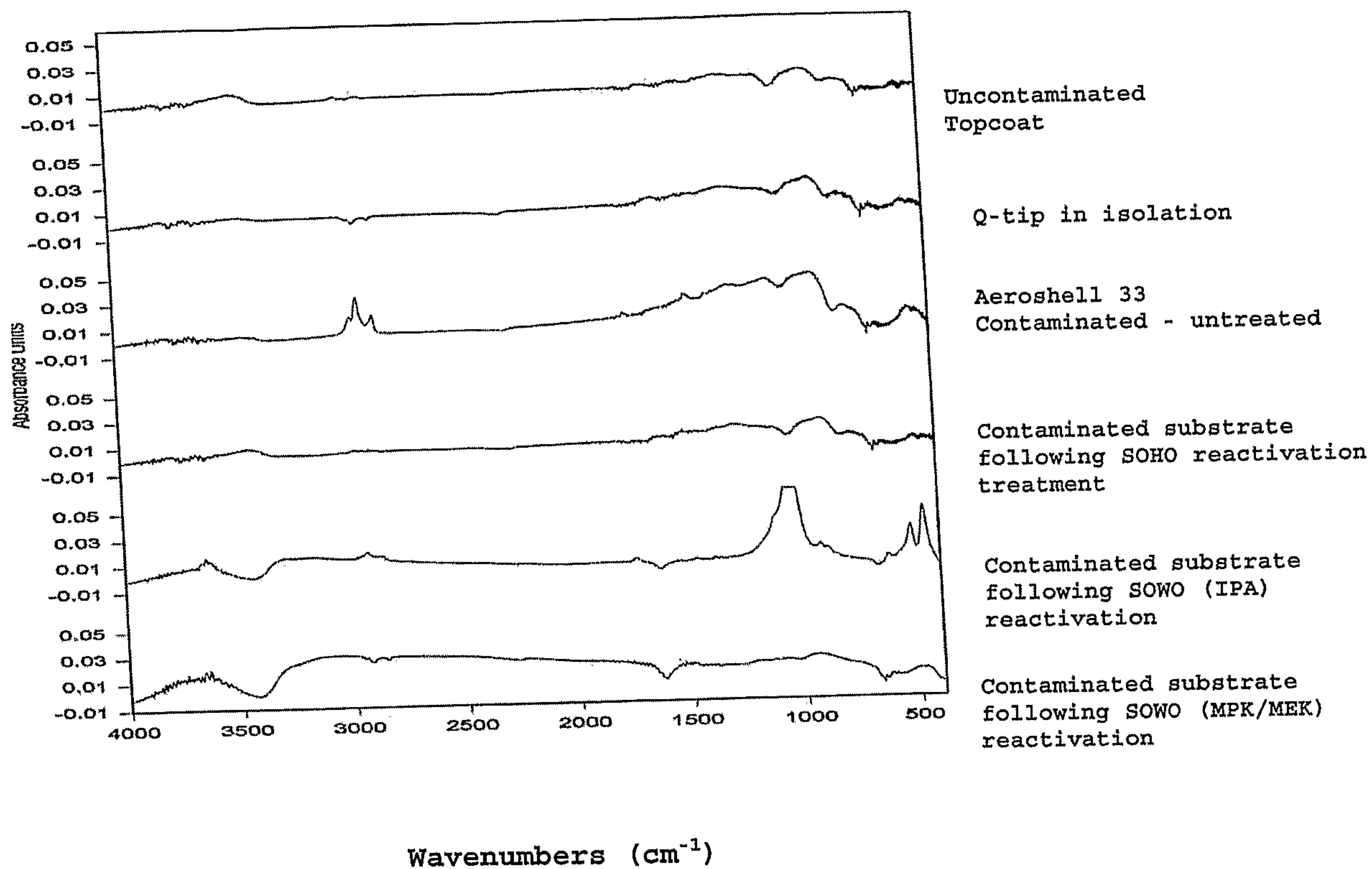
(a) Petroleum Jelly Contaminant



NOTE: typical absorptions around 3000 cm⁻¹ for the contaminant was removed or reduced following reactivation under the conditions listed.

- 69 -

(b) Aeroshell 33 Contaminant



NOTE: typical absorptions around 3000 cm⁻¹ for the contaminant was removed or reduced following reactivation under the conditions listed.

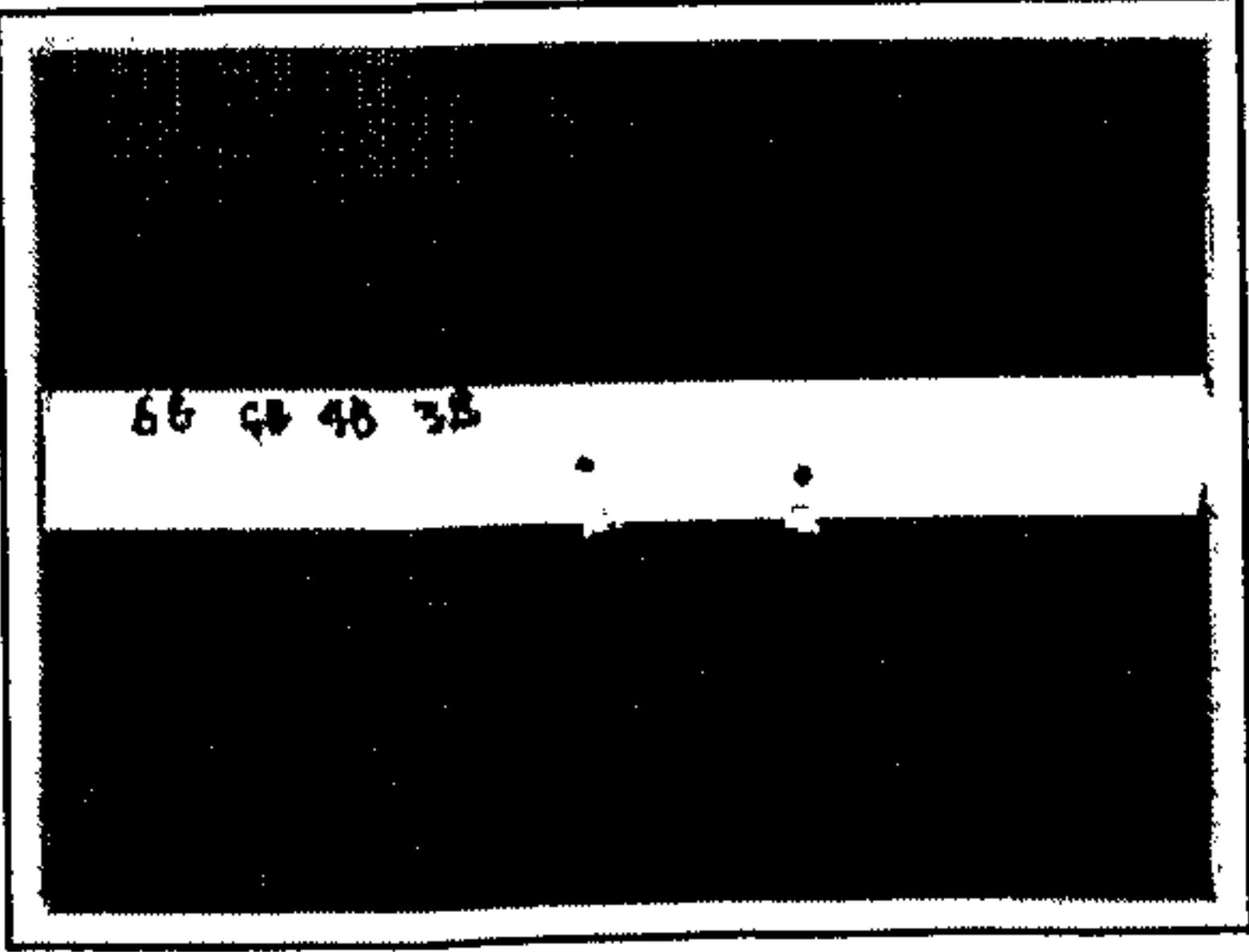
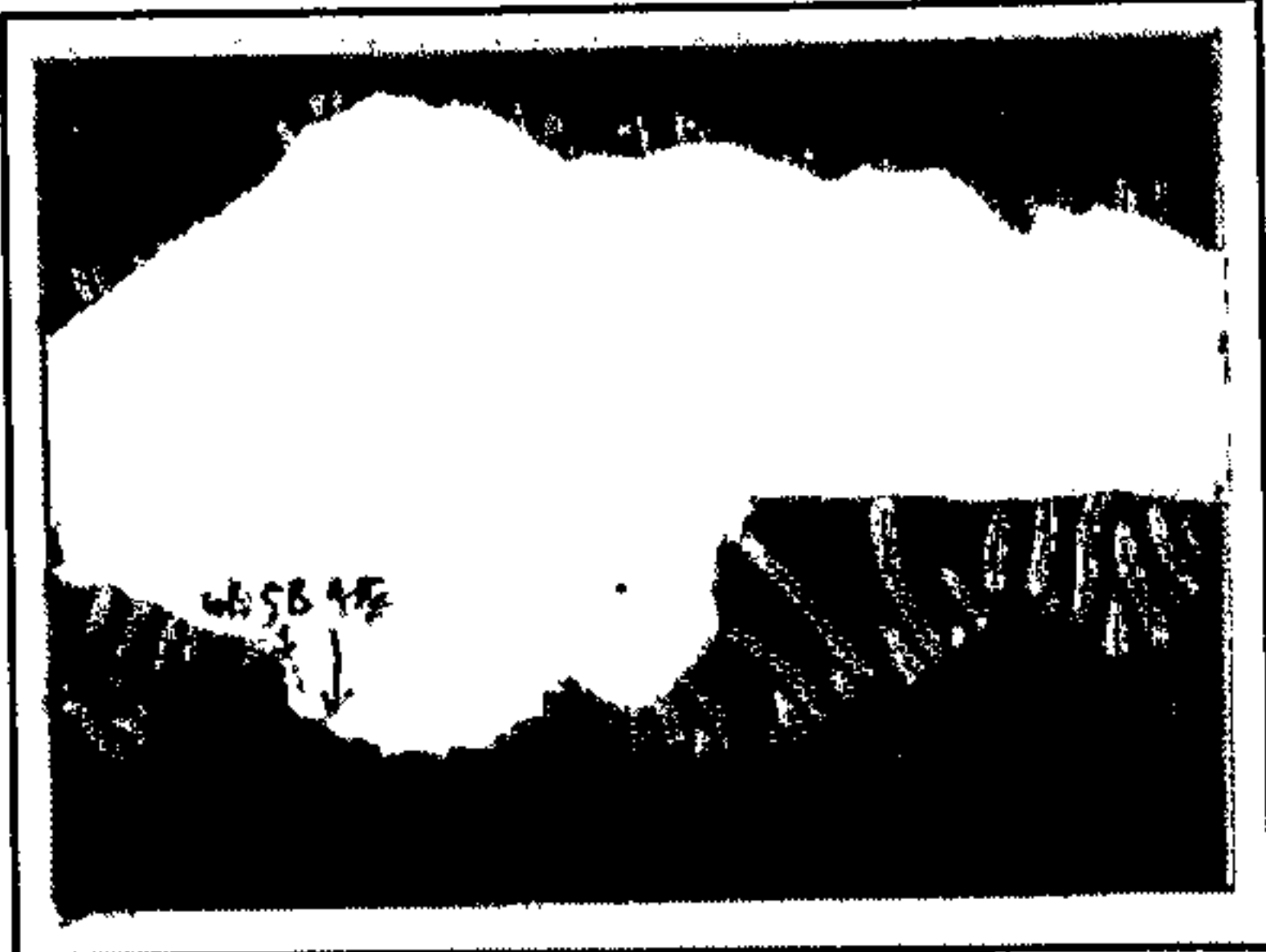
Examples illustrate that the level of contaminate is clearly reduced or removed following the reactivation treatment.

(iv) Supporting surface energy results for selected contaminants following no treatment, solvent wipe only and reactivation treatments of the contaminated aged Desothane HS 70846X white topcoat under the conditions specified.

Contamination		Surface Energy (mJ/m ²)					
		No Treatment		MEK/MPK Wipe Only		0.1% LiBH ₄ (Proglyde, 2% tBAC) MEK/MPK Wipe	
		Dispersive	Specific	Dispersive	Specific	Dispersive	Specific
None		45	4.2	43	3.9	45	8.6
Microcut		48	3.2	45	4.2	45	6.9
Catoil		47	2.0	44	2.9	45	6.0
Boelube		37	6.0	46	3.5	46	5.9
Aeroshell33		43	2.2	44	2.8	46	8.0
Petroleum Jelly		49	3.0	41	3.9	43	6.5

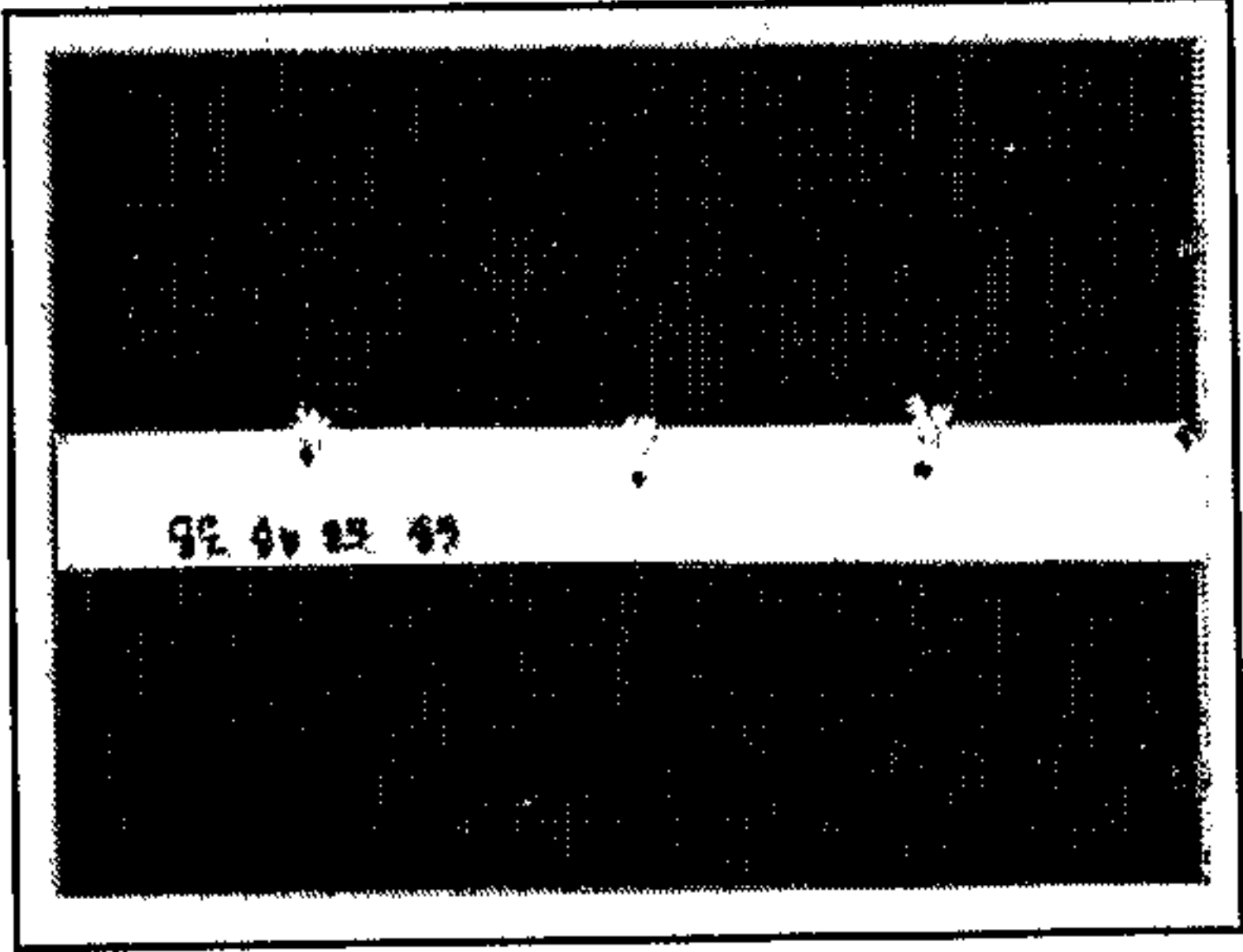
The specific surface energy component of total surface energy is significantly reduced after contaminants are applied to the surface of the aged Desothane HS 70846X substrate. Wiping the surface with just solvent only marginally improved the specific contribution to surface energy (not back to untreated, non-contaminated) whilst specimens reactivated with LiBH₄ under the conditions listed provided a significant improvement in the specific contribution to surface energy above that for non-contaminated substrates indicating simultaneous cleaning and reactivation has occurred.

Example 25. Example 25. (i) SIJA inter-coat adhesion of aged Desothane HS 70846X white (C2) reactivated under the conditions specified - one (thinapplication) or two (thicker application) applications followed by water hose-off after the 30 minute treatment time (SOHO) and over-coated with Desothane S400X. Following cure of the over-coating the samples were immersed in Skydrol aviation fluid for a period of 30 days under ambient conditions prior to adhesion testing.

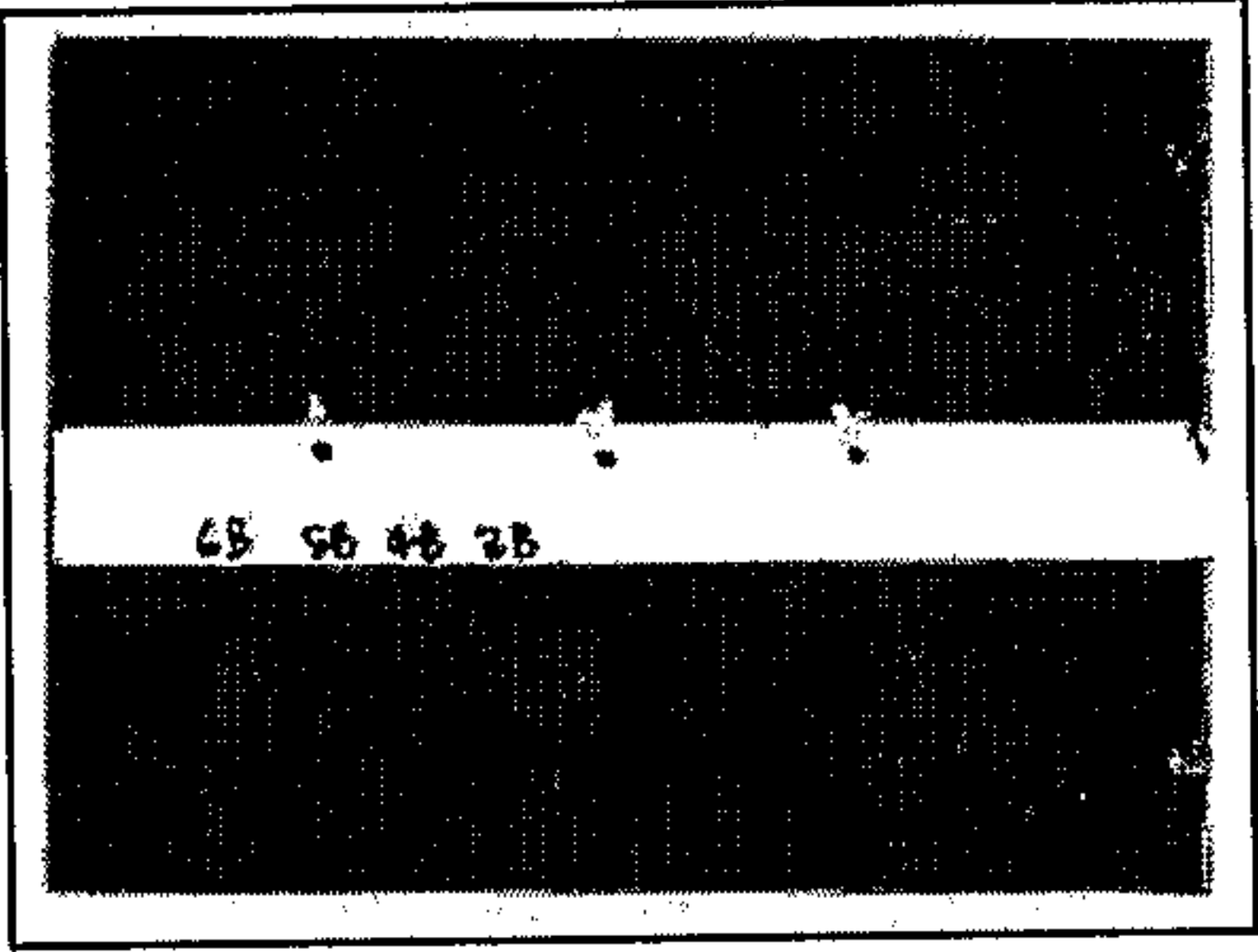


Untreated /
Sanded

1 x 30 min treatment



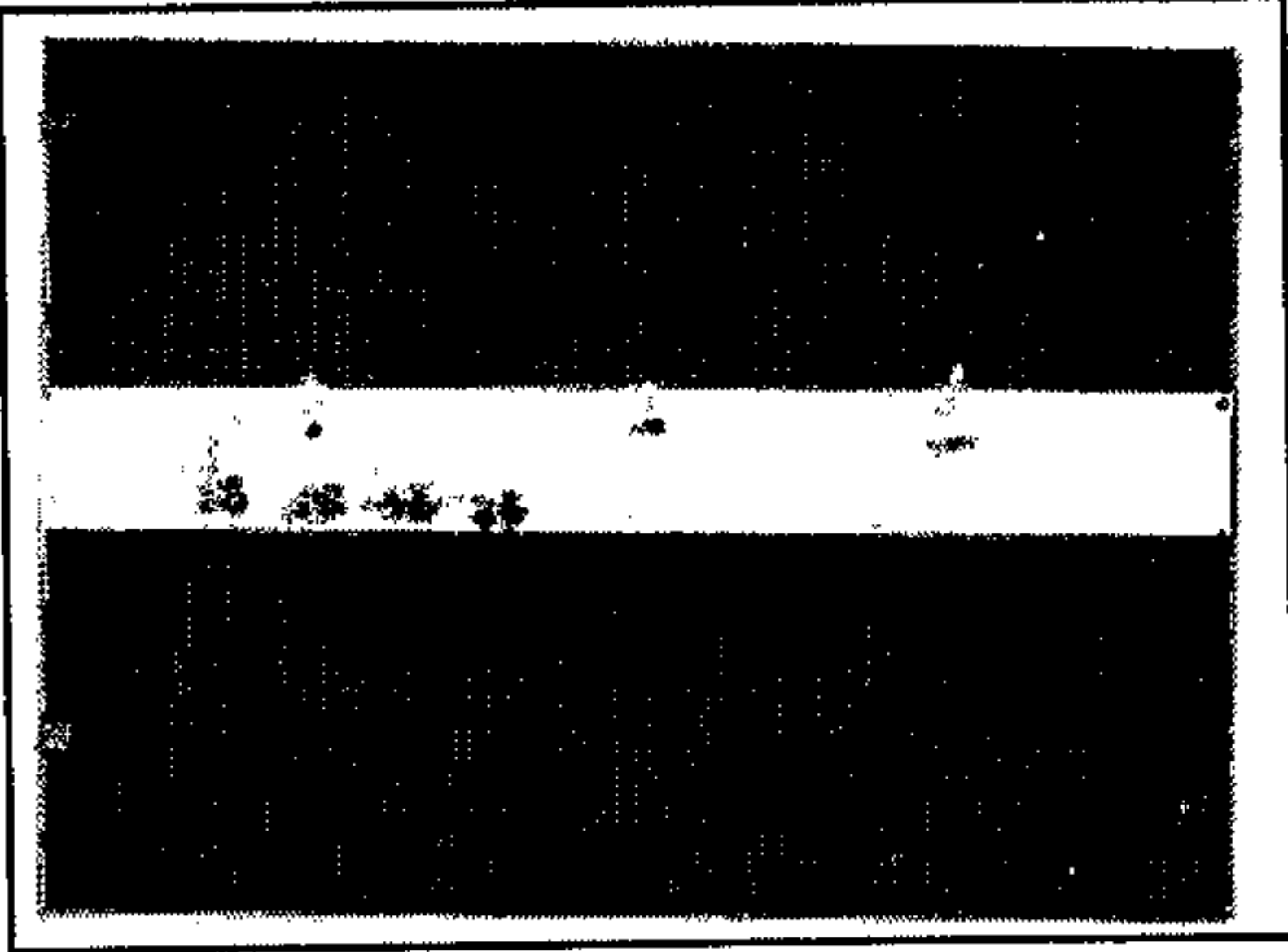
0.1% LiBH4



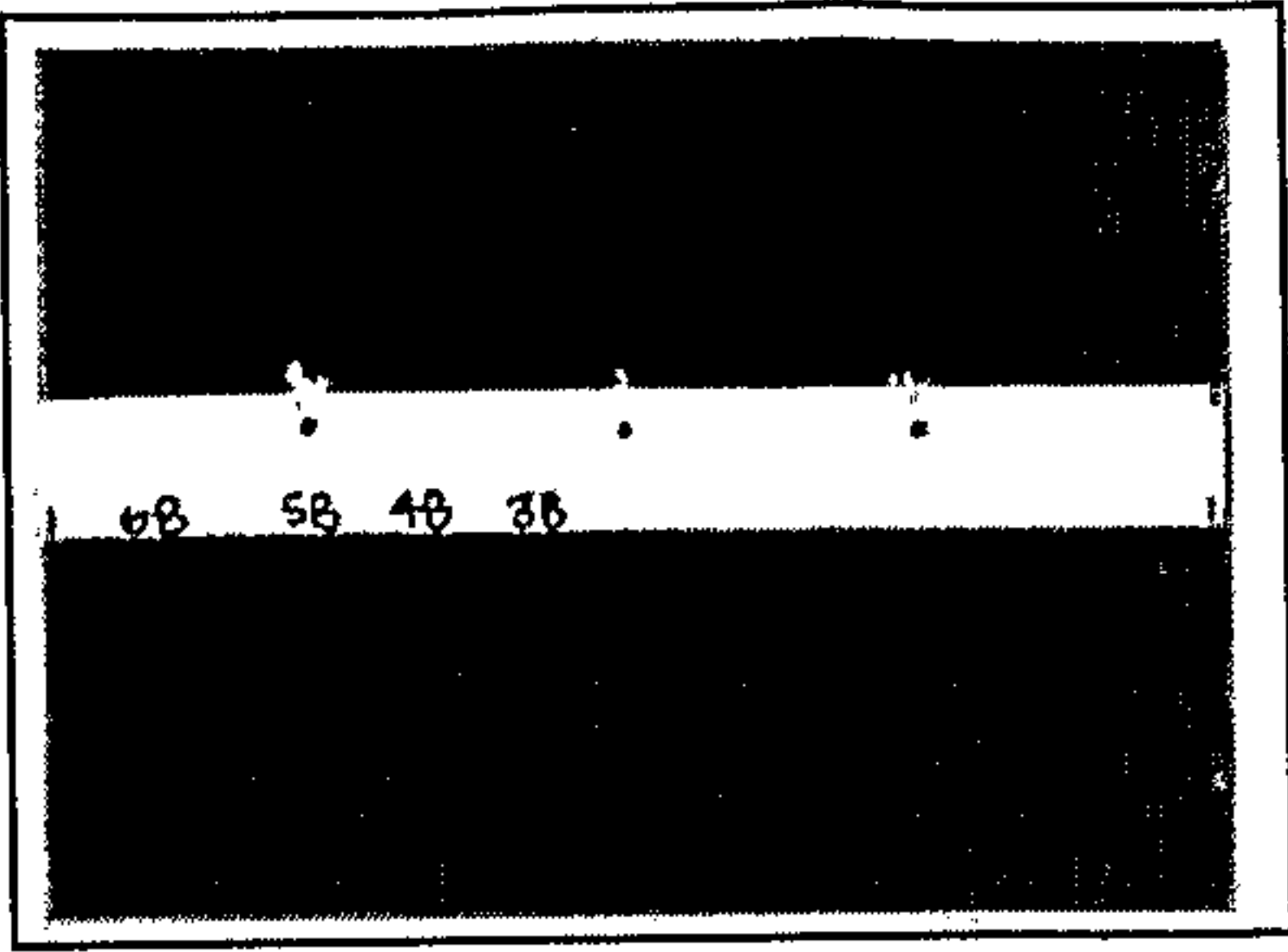
0.25%LiBH4

In Propylene DMM

2 x 30 min treatment



0.1% LiBH4



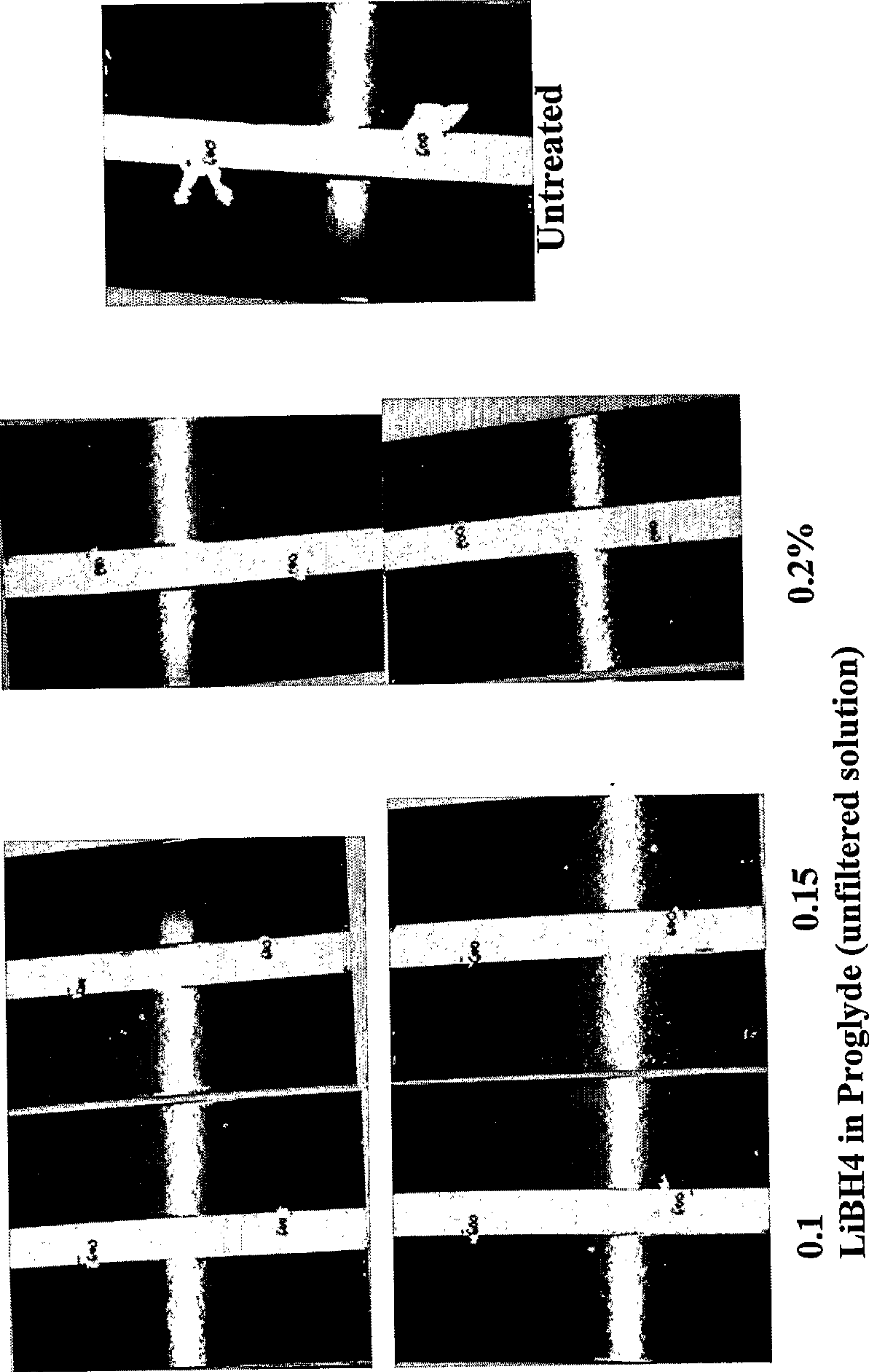
0.25%LiBH4

The example illustrates that the inter-coat adhesion between topcoat layers is resistant to hydraulic fluids.

(ii) SIJA inter-coat adhesion of aged Desothane HS 70846X white reactivated under the conditions specified (SOLO, 180 min) and over-coated with Desothane HS S601X blue. Following cure of the over-coating the samples were immersed in water under ambient conditions or placed in a condensing humidity chamber at 120F / 98% RH for a period of 30 days prior to adhesion testing and visual appearance assessment.

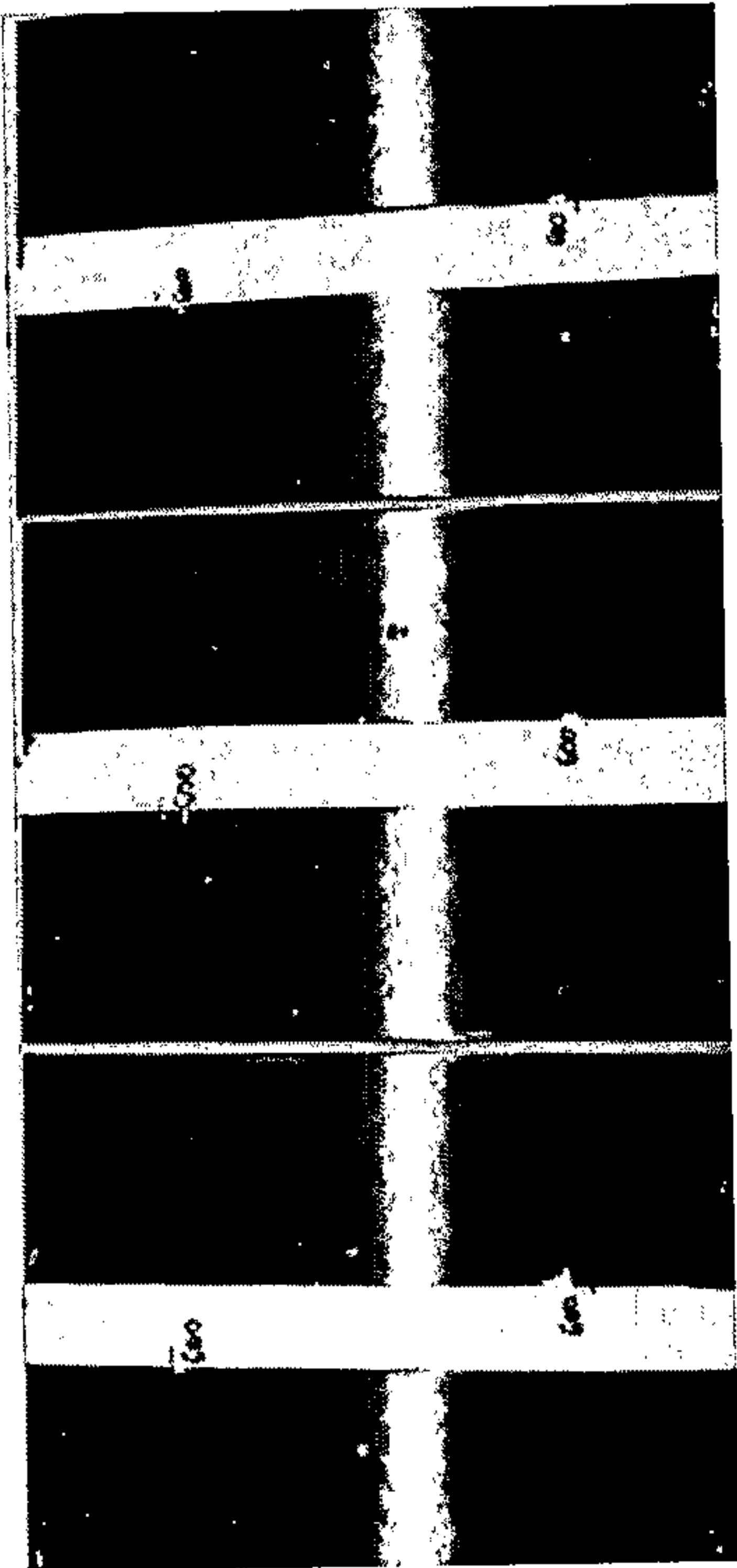
Condensing
Humidity

Water
Soak

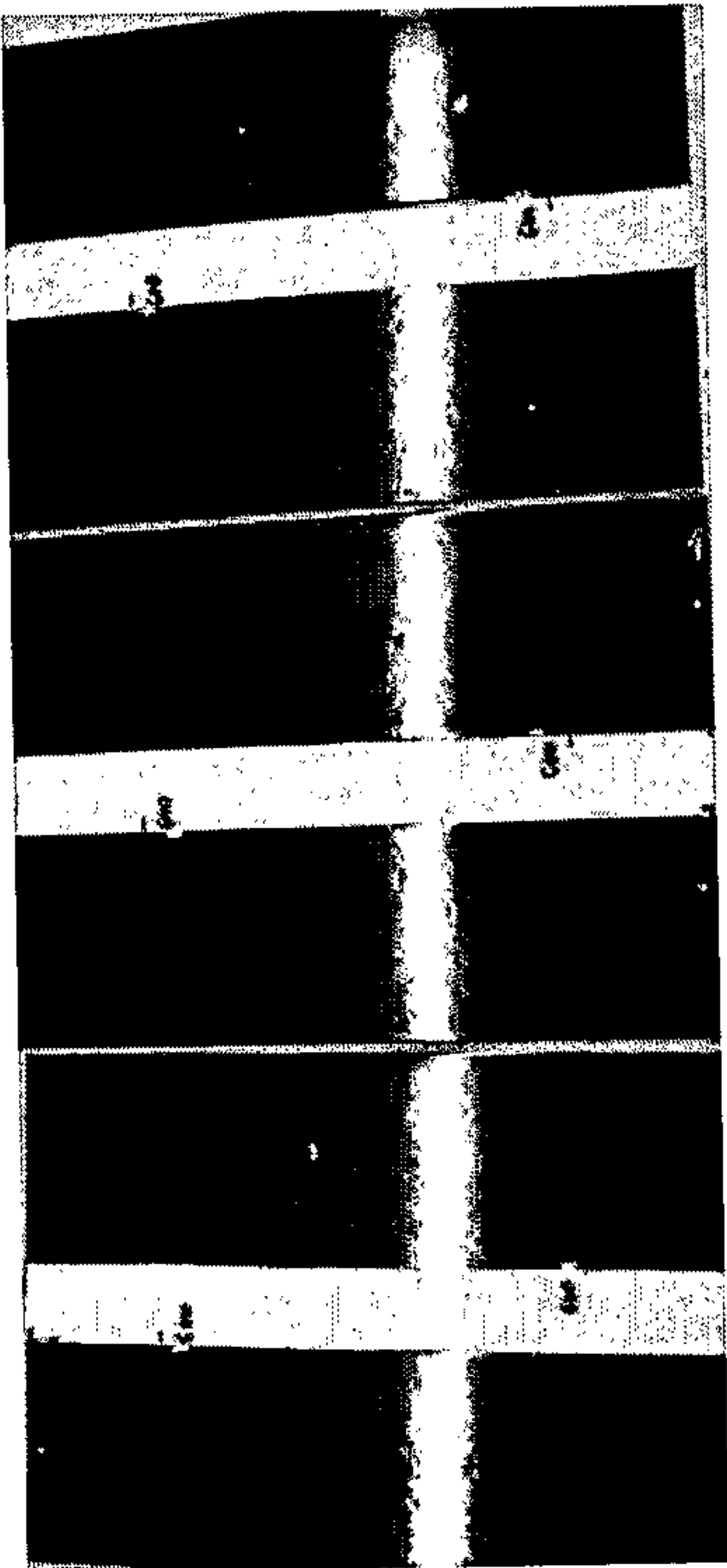


Condensing
Humidity

Water
Soak

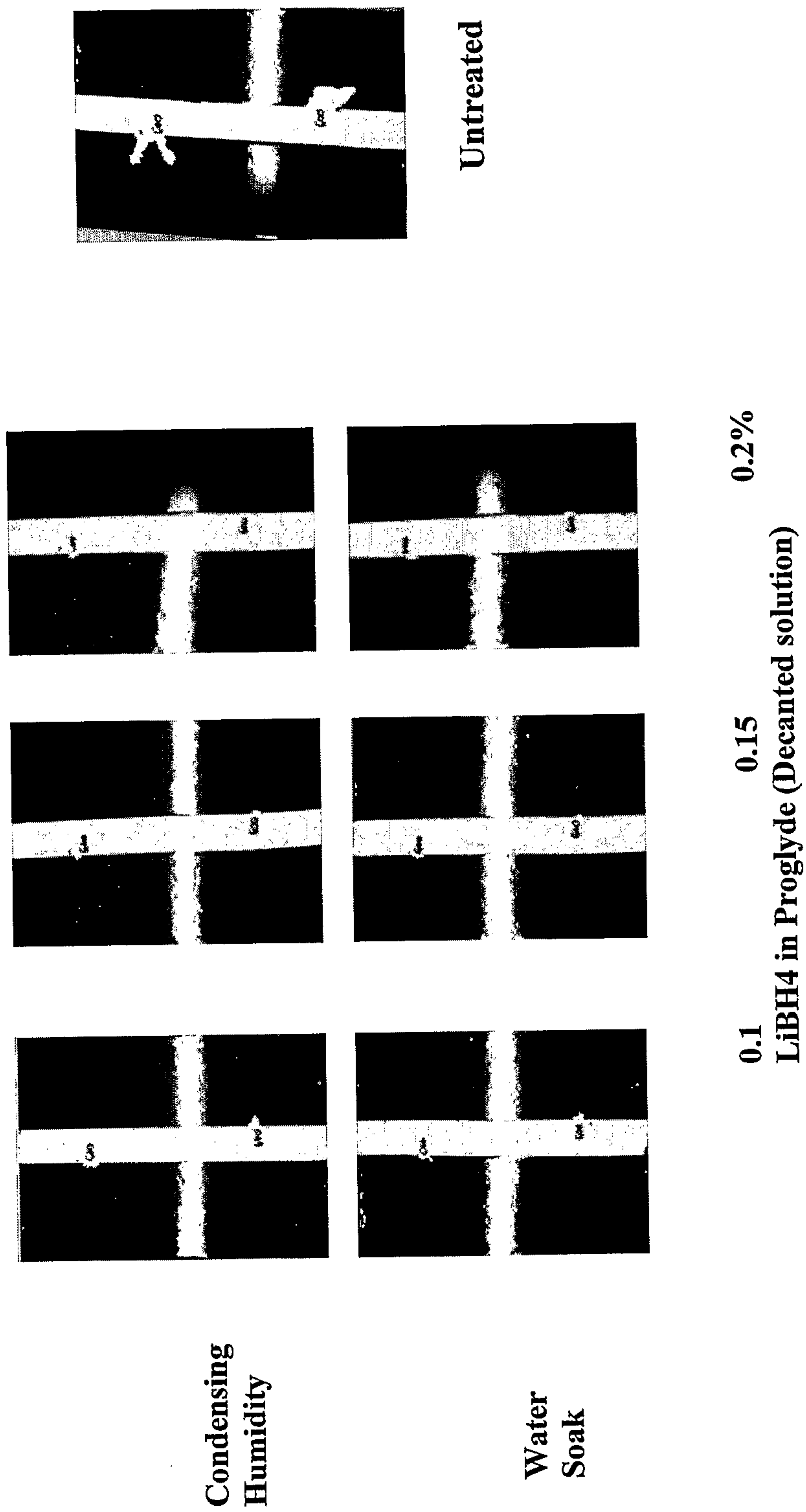


Untreated

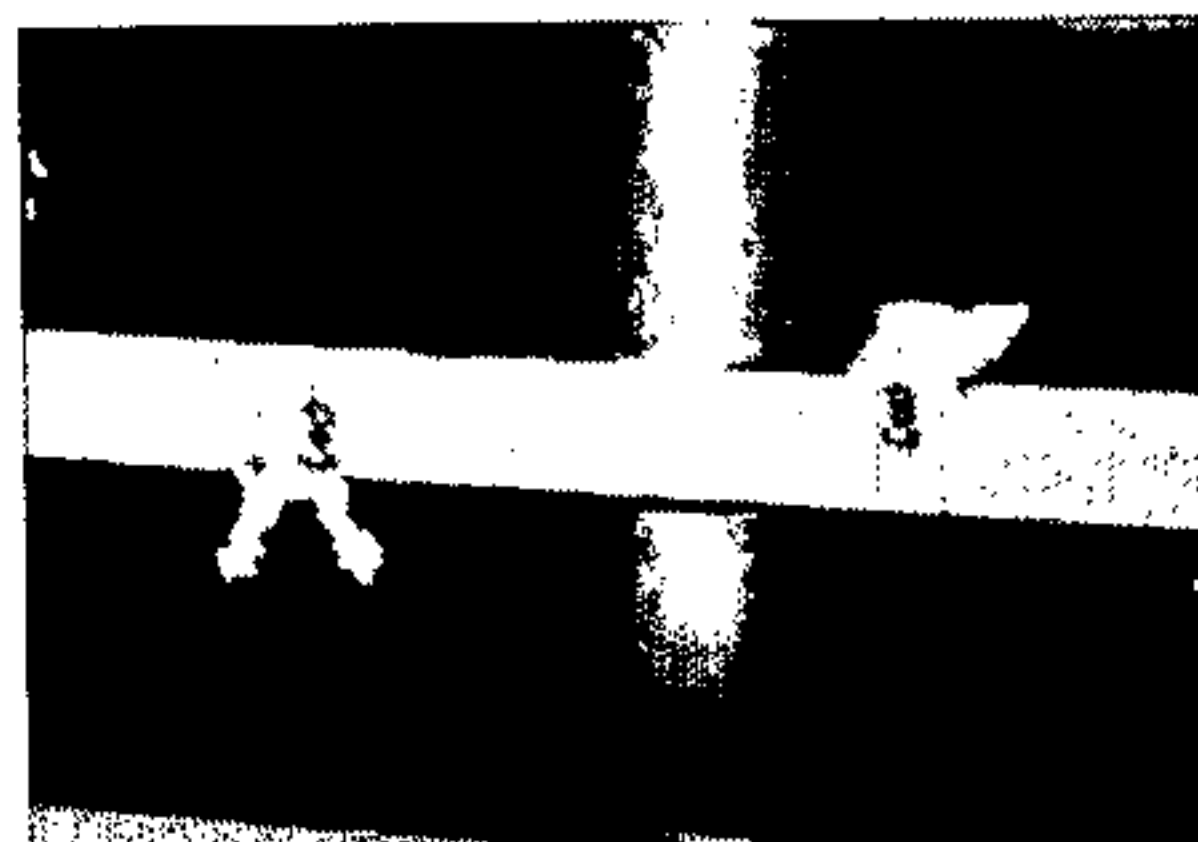


0.1 0.15 0.2%
LiBH4 in Proglyde (unfiltered solution, tack rag following application time)

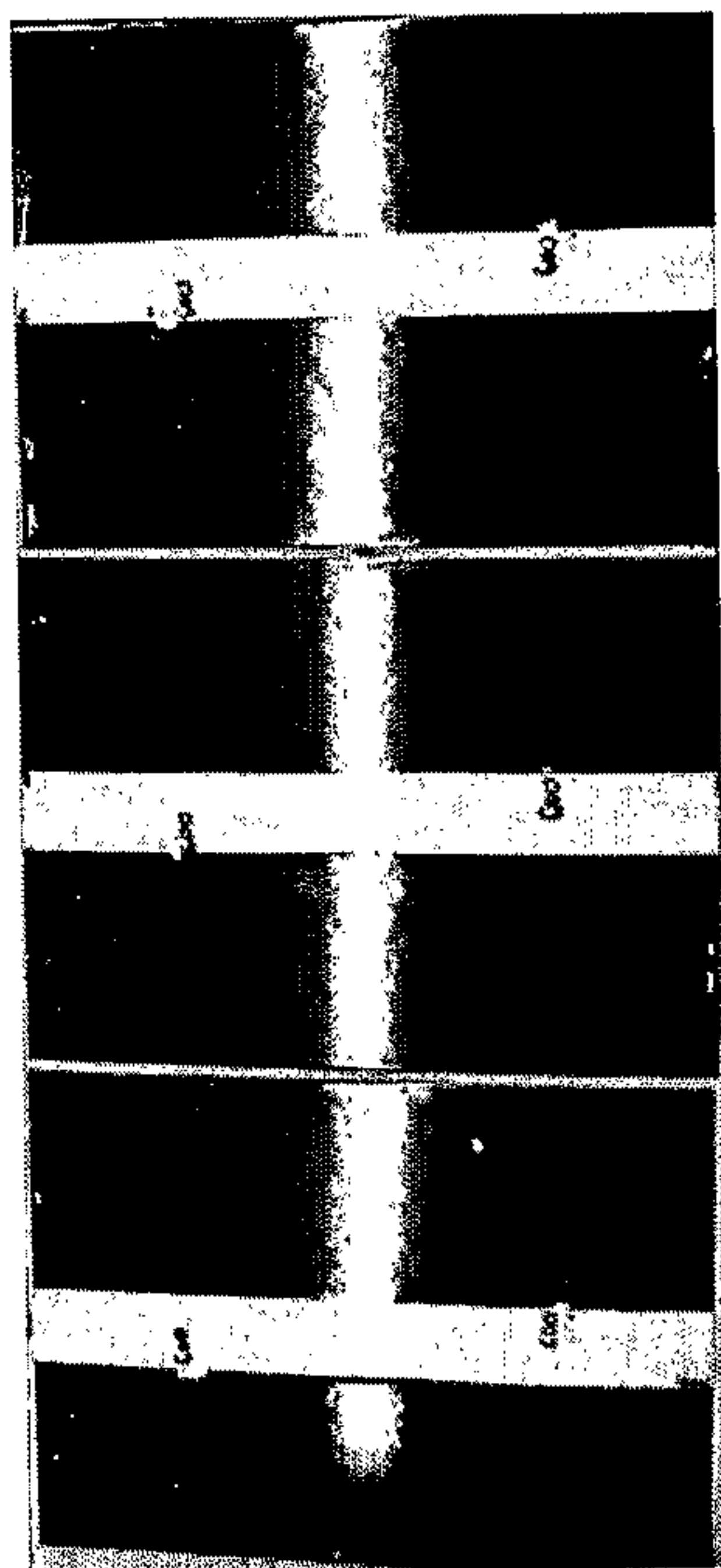
- 74 -



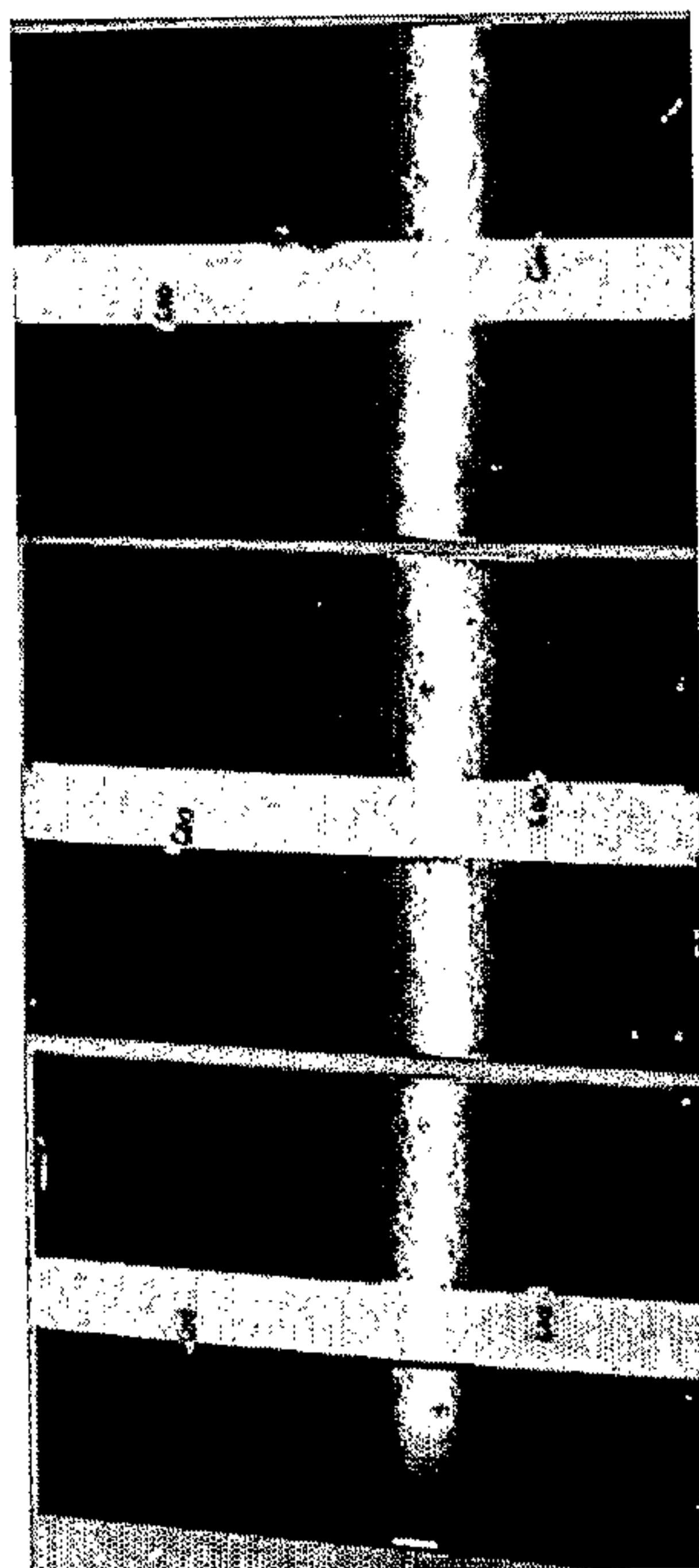
- 75 -



Untreated



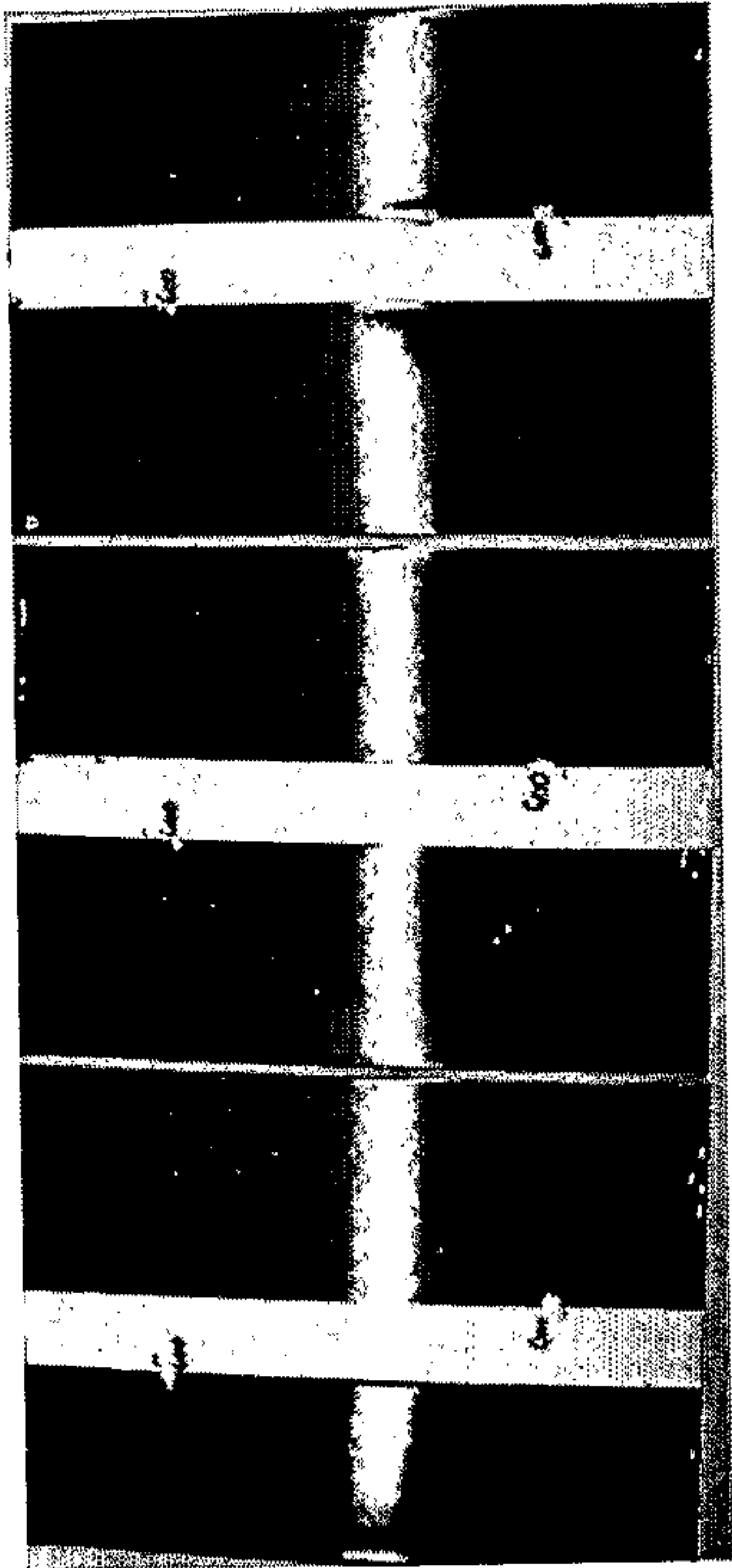
Condensing
Humidity



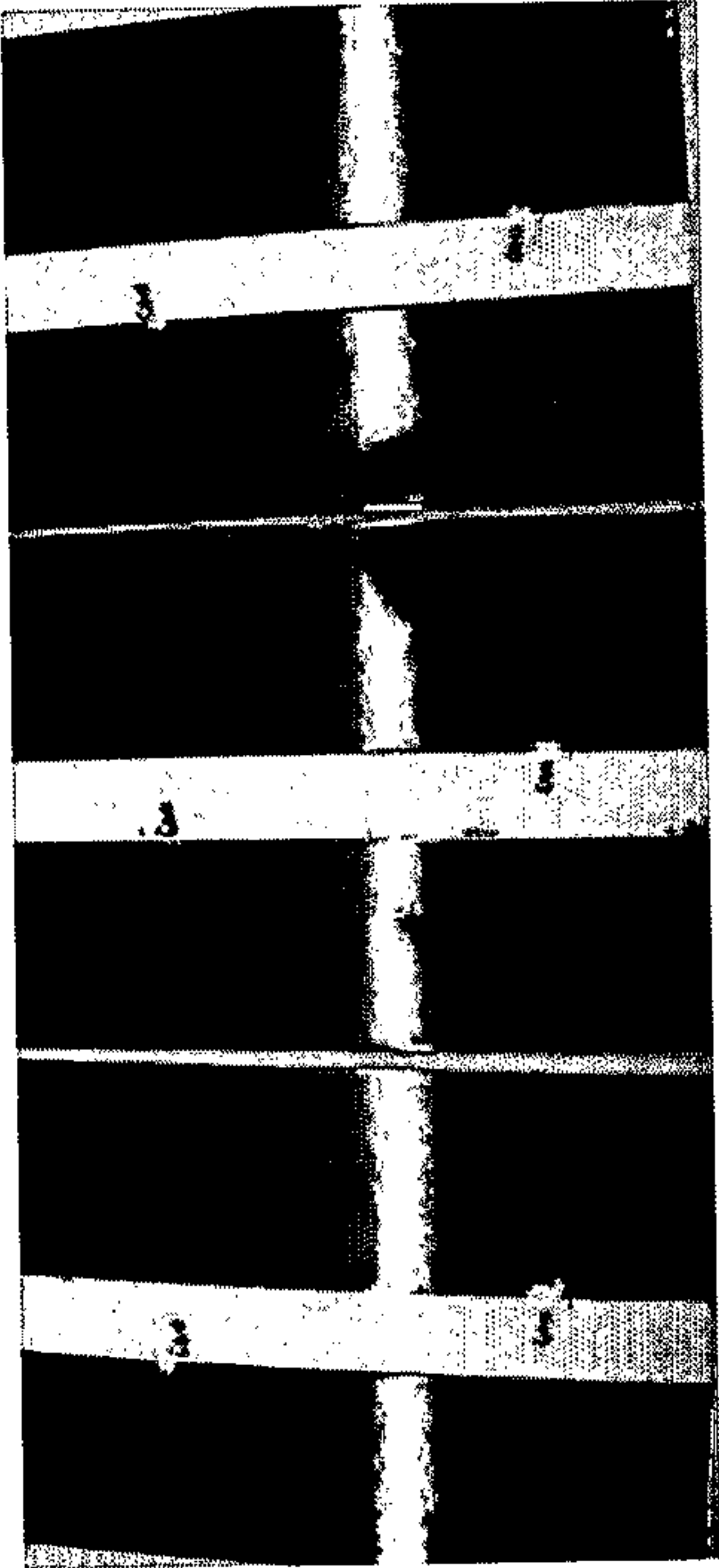
Water
Soak

0.1 0.15 0.2%
LiBH₄ in Proglyde (filtered solution)

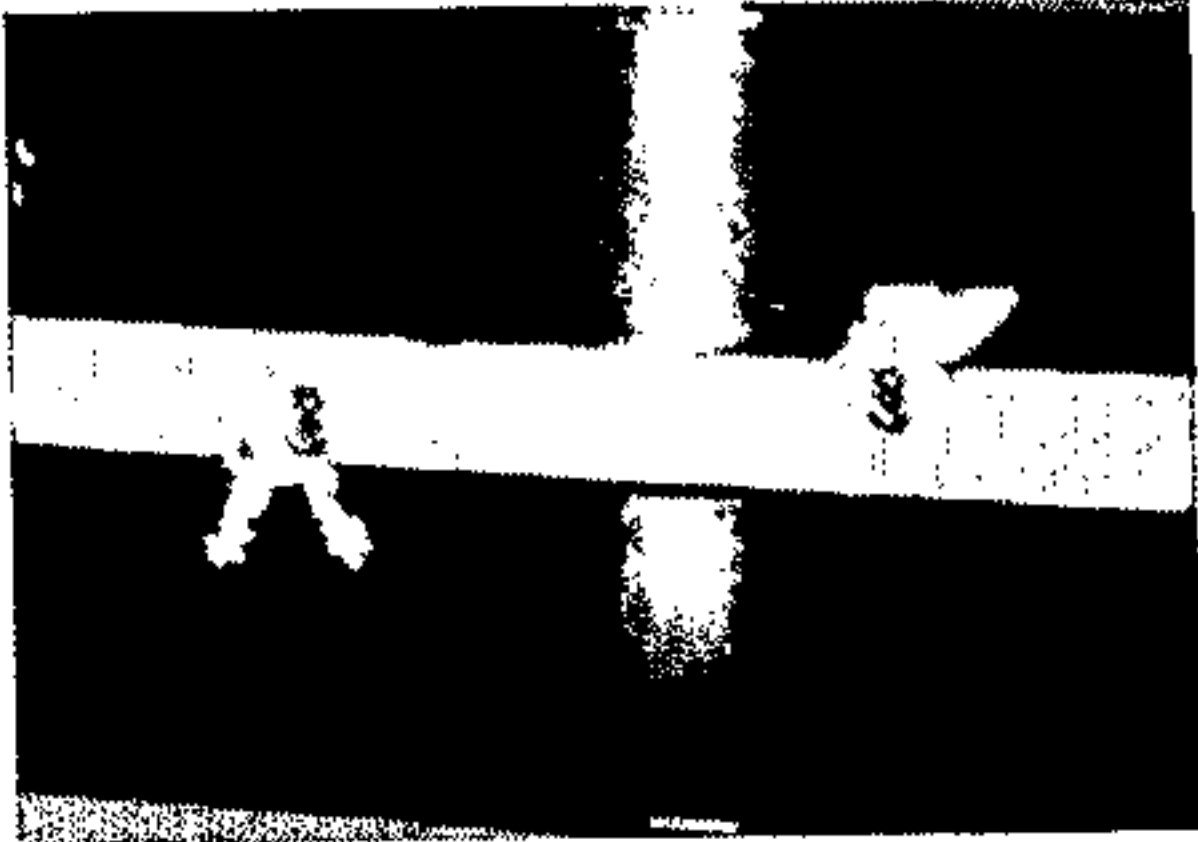
Condensing
Humidity



Water
Soak



Untreated

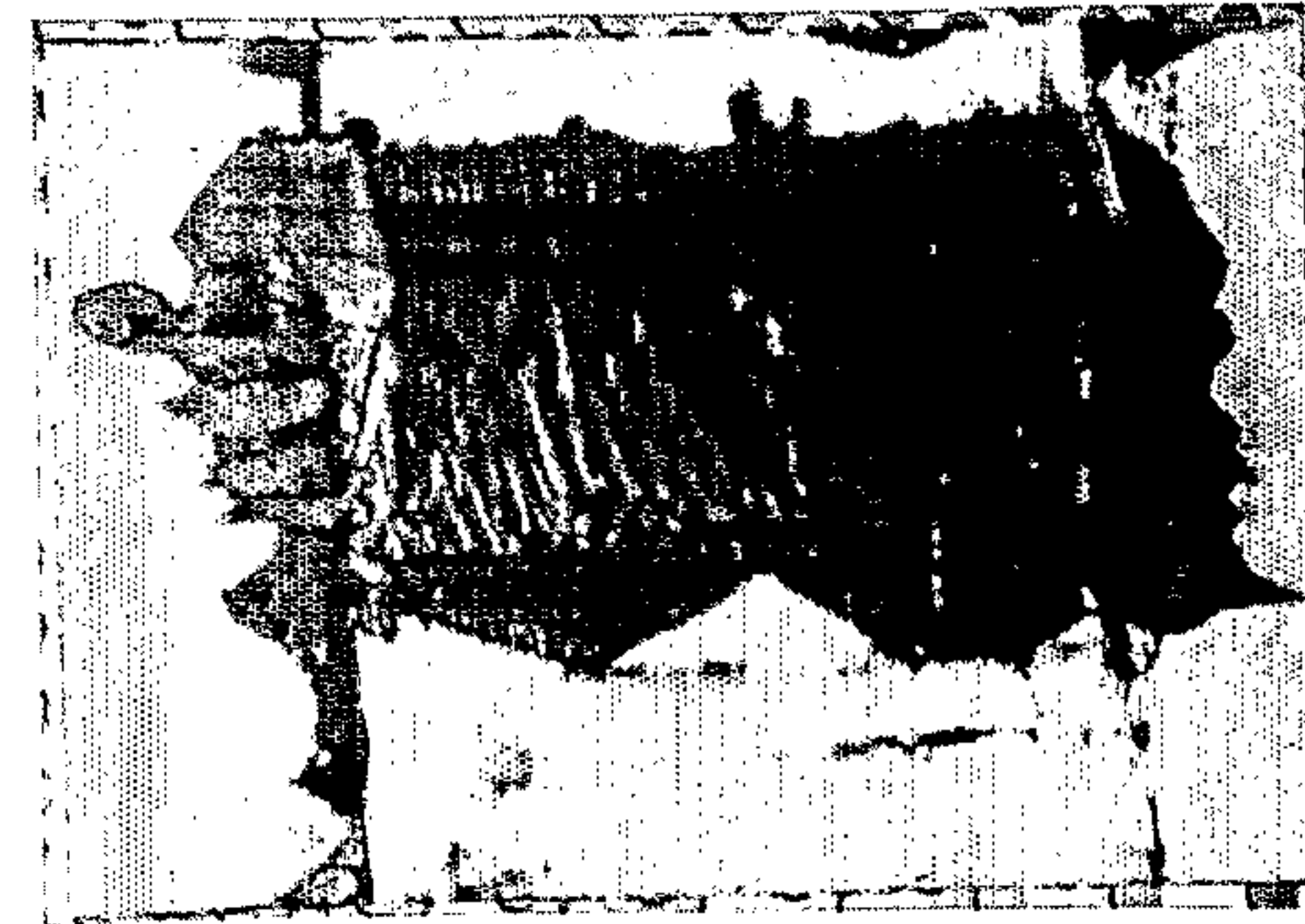


0.1 0.15 0.2%
LiBH4 in Progylde (SOHO, water))

Results indicate that excellent inter-coat adhesion was obtained after 30 days water soak under ambient conditions or 30 days conditioning at 120F and 95% RH. Paint appearance is also acceptable and further improved by either using sediment (precipitate free) treatment solutions obtained from filtering, or post treatment protocols such as a tack rag wipe, wash (SOHO) or wipe (SOWO) processes.

- 77 -

Example 26. (i) The following example illustrates effects of spray application of 0.1% LiBH_4 - Progylde DMM reactivation solution onto bare polysulfide based sealant (PRC-Desoto PR 1772) that has been applied over primed carbon fiber reinforced epoxy.

**Prior Application****On Application****Post Application**

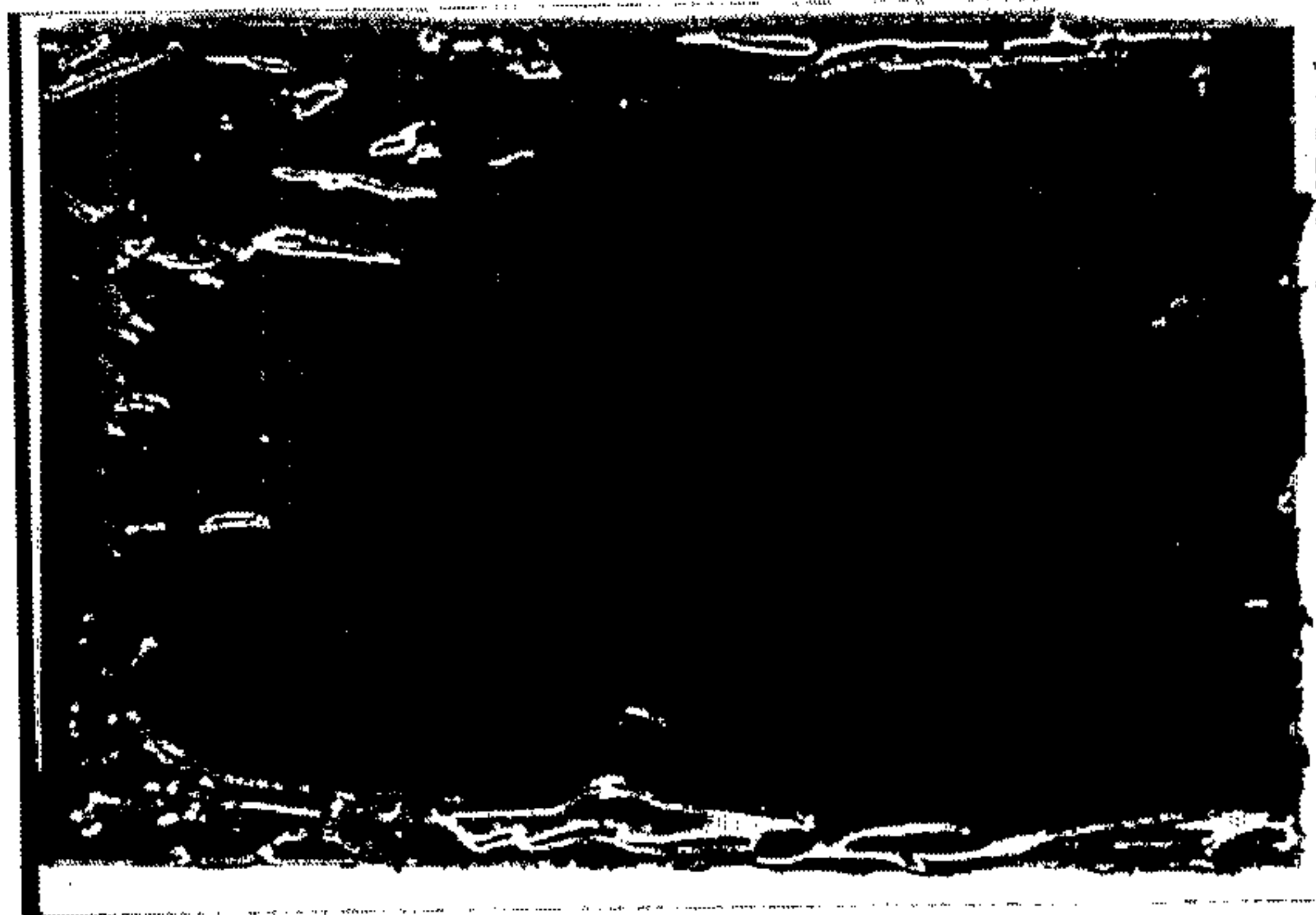
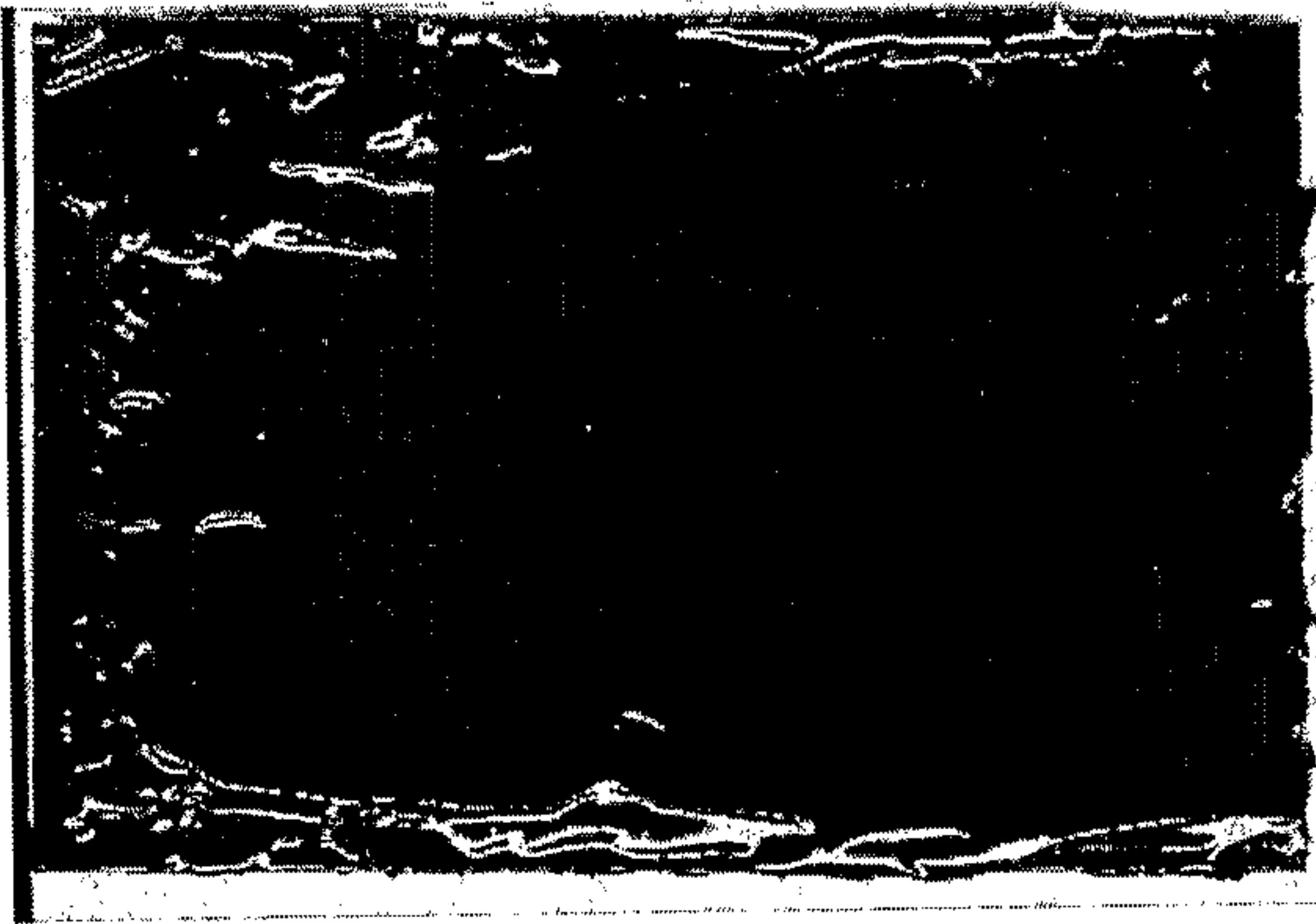
Example illustrates that no lifting, bubbling of the sealant occurs even at thin sealant thicknesses.

Adhesion of the sealant to the substrate is maintained even through application of rubbing.



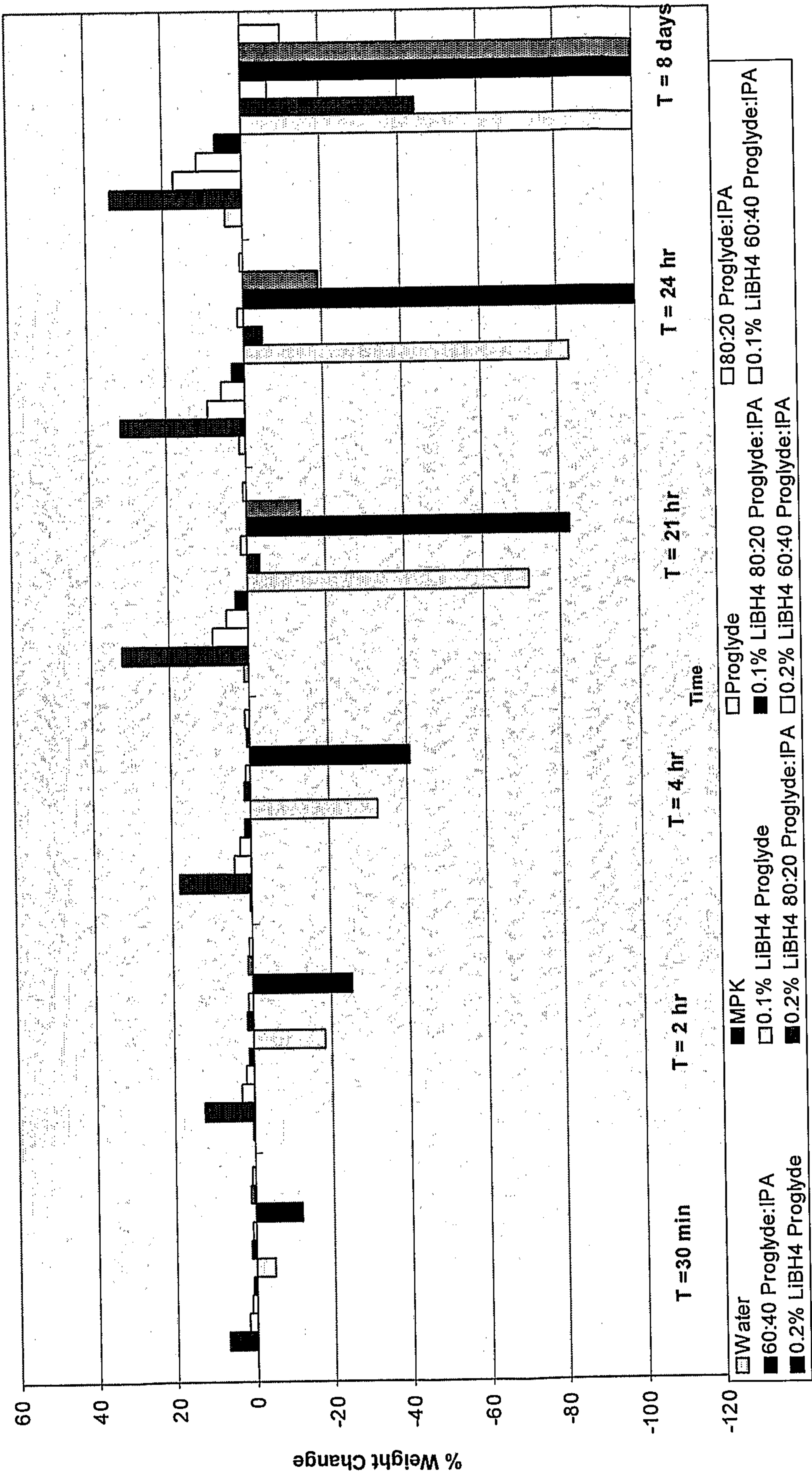
- 78 -

(ii) The following example illustrates scribe adhesion results from polysulfide sealant (PRC-Desoto PR 1772) cured for 4h before treatment with a reactivation treatment solution comprised of 0.1% LiBH_4 in propylene glycol for the time specified before overcoating with Desothane HS S601X Blue and curing for 16h under ambient conditions.

**Untreated****3h Prior to over-coating****24h Prior to over-coating**

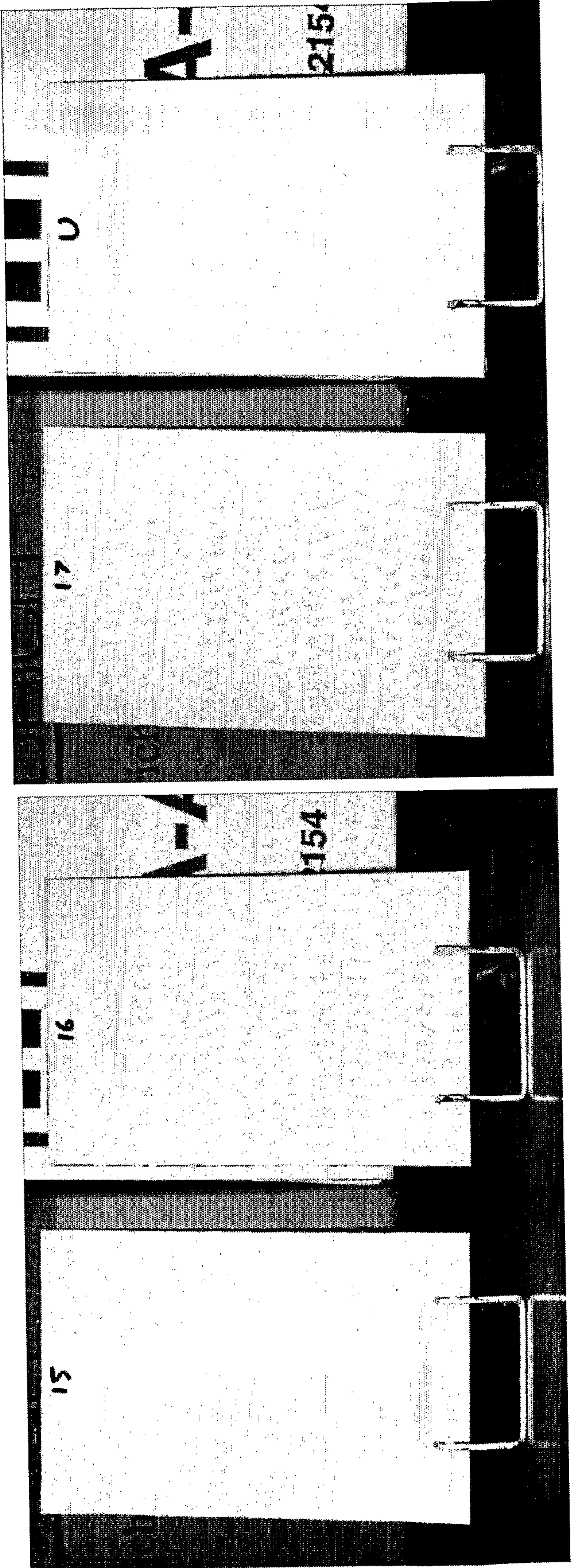
The example illustrates that no deleterious effects occur following application of the treatment solution onto the sealant prior to over-coating even when the treatment solution is applied onto only moderately cured (young) sealants.

((iii)) The following example provide weight change data for polysulfide sealant (PRC-Desoto PR 1772) when immersed into different solvents and reactivation treatment solutions.



The example illustrates that the reactivation solution may be formulated to provide only minimal weight change over periods of up to 8 days.

(iv) The following example illustrates what impact application of LiBH_4 / propylene glycol reactivation solutions has on selective stripable (intermediate) coating layers applied over primed composite panels.



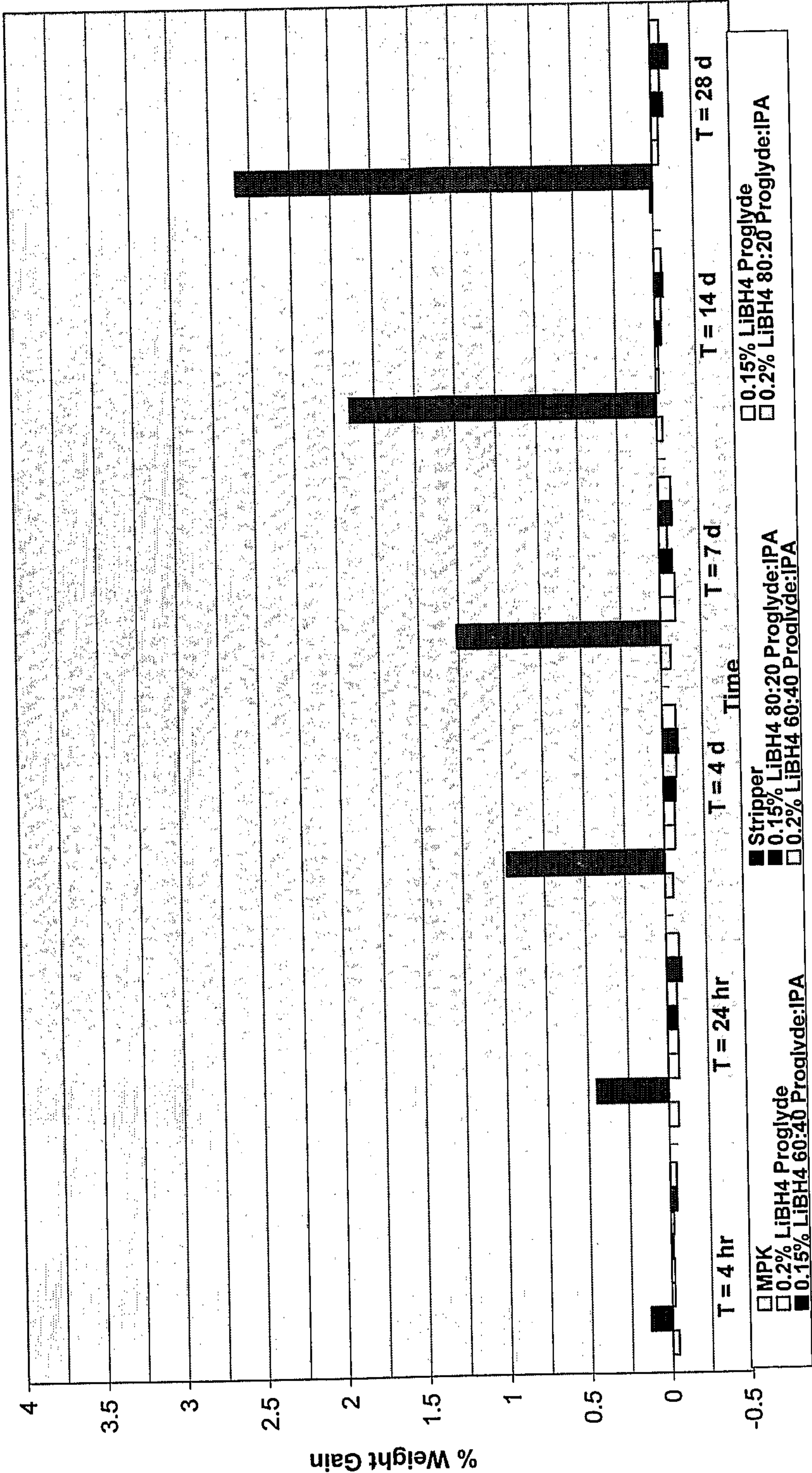
0.55% LiBH_4 in Propylene DMM	1.1% LiBH_4	2.2% LiBH_4	Untreated
---	----------------------	----------------------	-----------

The example demonstrates that no lifting or dissolution of the intermediate coating layer occurs through interaction of the reactivation treatment solution.

(v) The following examples provide immersion weight change data up to 28 days of various aerospace substrate materials in various solvents, typical aerospace paint stripper, and reactivation treatment solutions. (a) BMS8-256 - carbon fiber reinforced epoxy (b) BMS8-79 - glass fiber reinforced epoxy (c) BMS8-276 - carbon fiber reinforced epoxy with Metlbond 1515 adhesive film (d) BMS 8-276 with Surface Master 905 adhesive film (e) Various metals, Al - aluminum, Ti - titanium, SS - stainless steel, HSS - high strength steel.

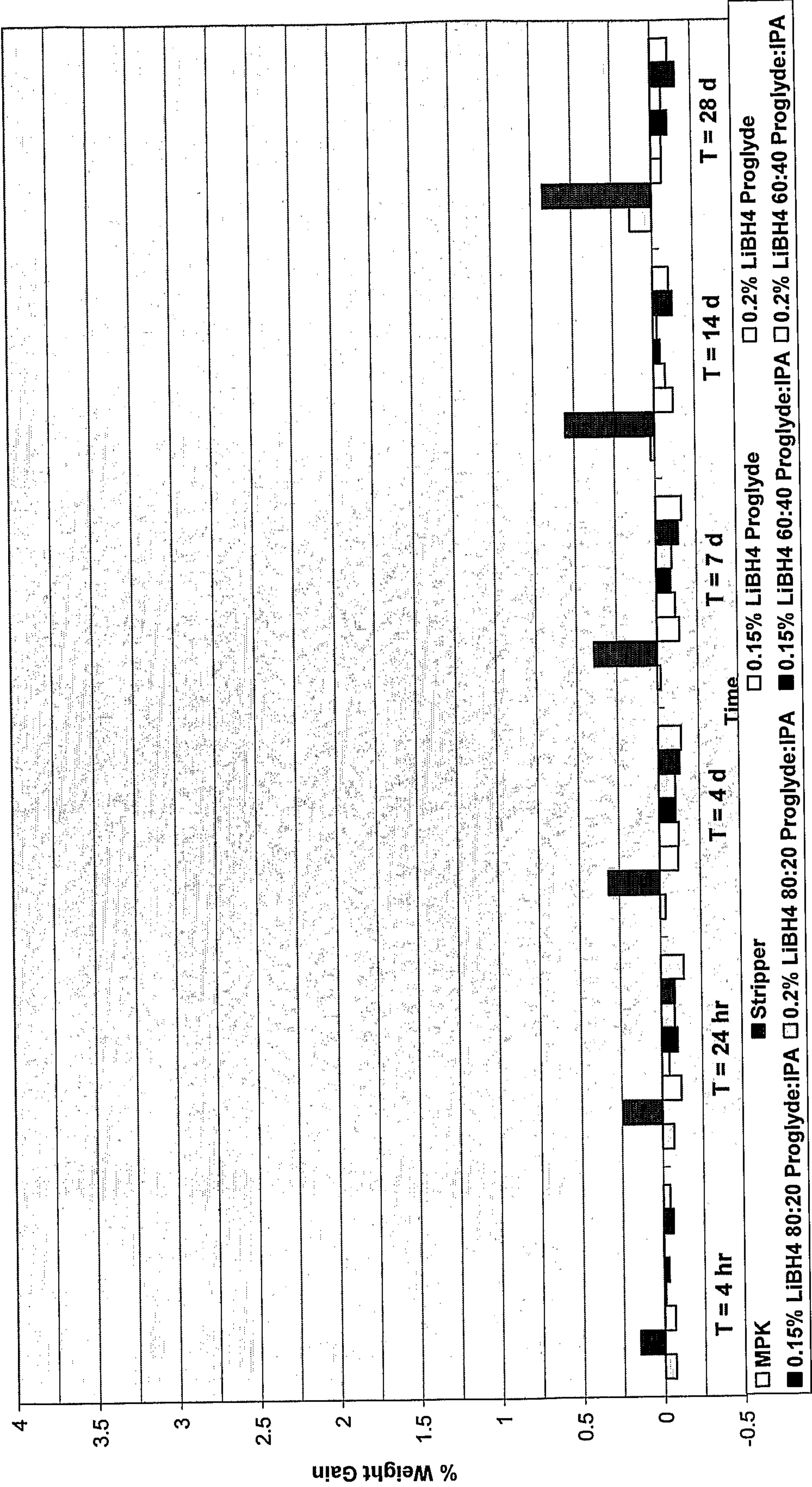
BMS8-256

a.



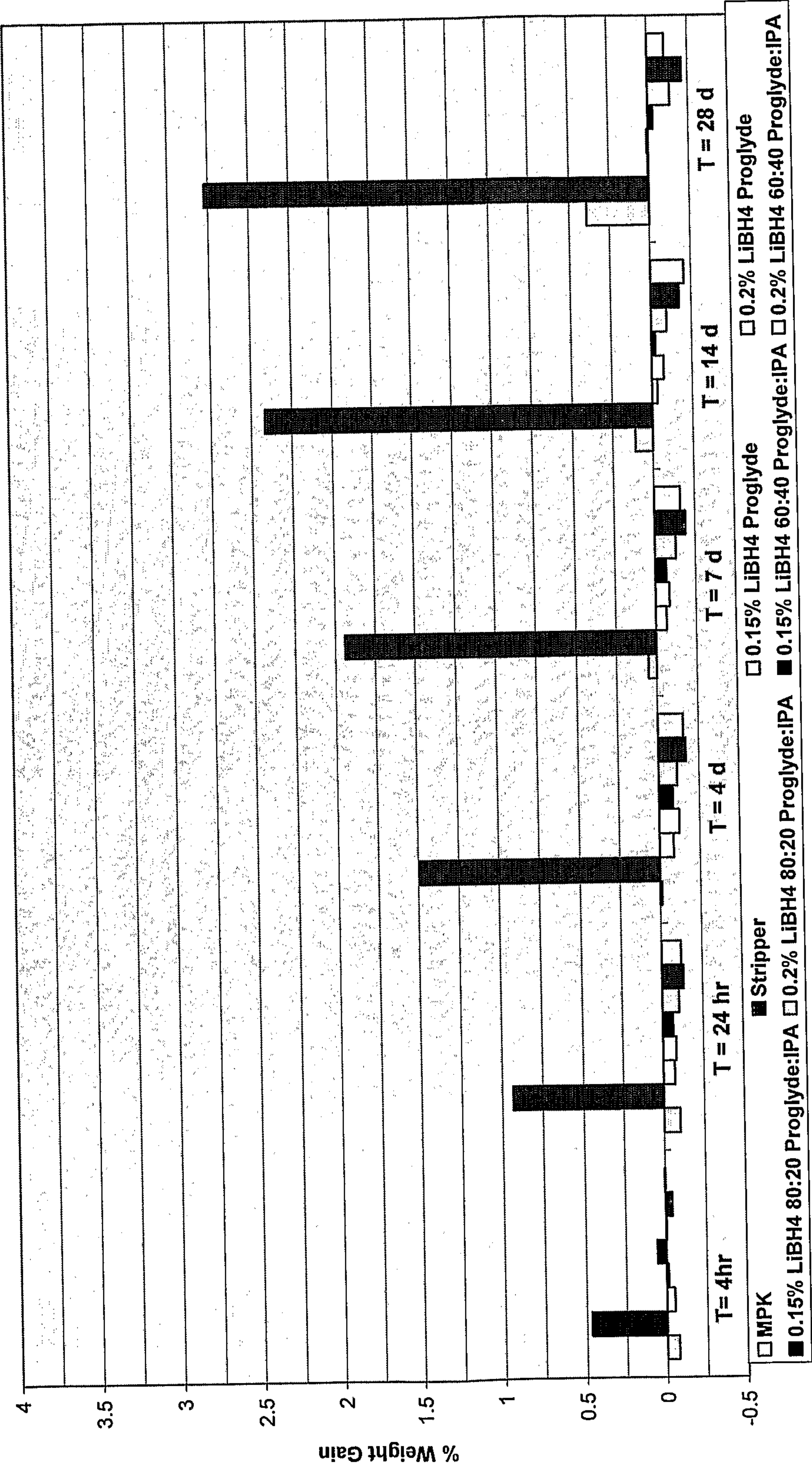
b.

BMS8-79



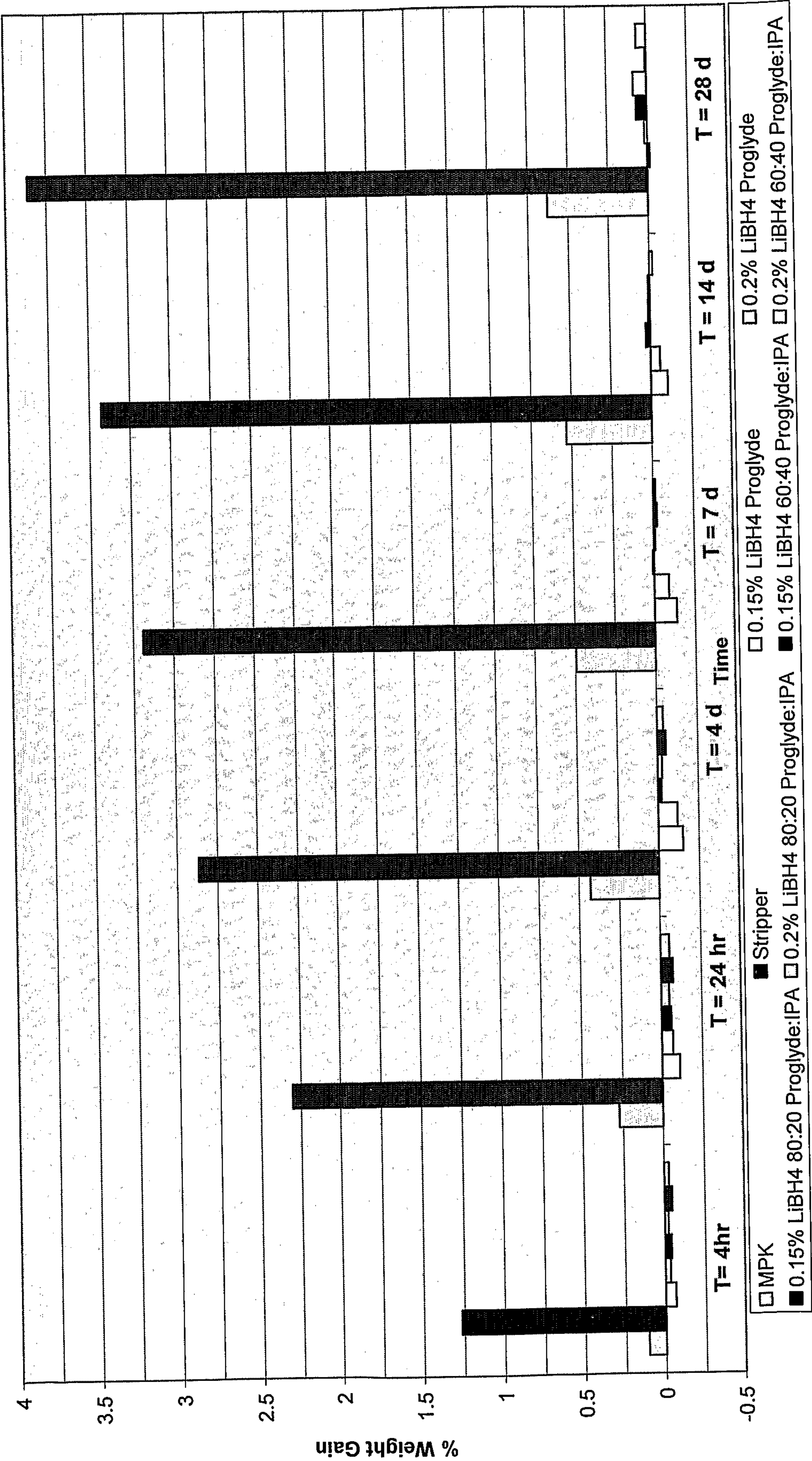
C.

BMS8-276 with Metlbond

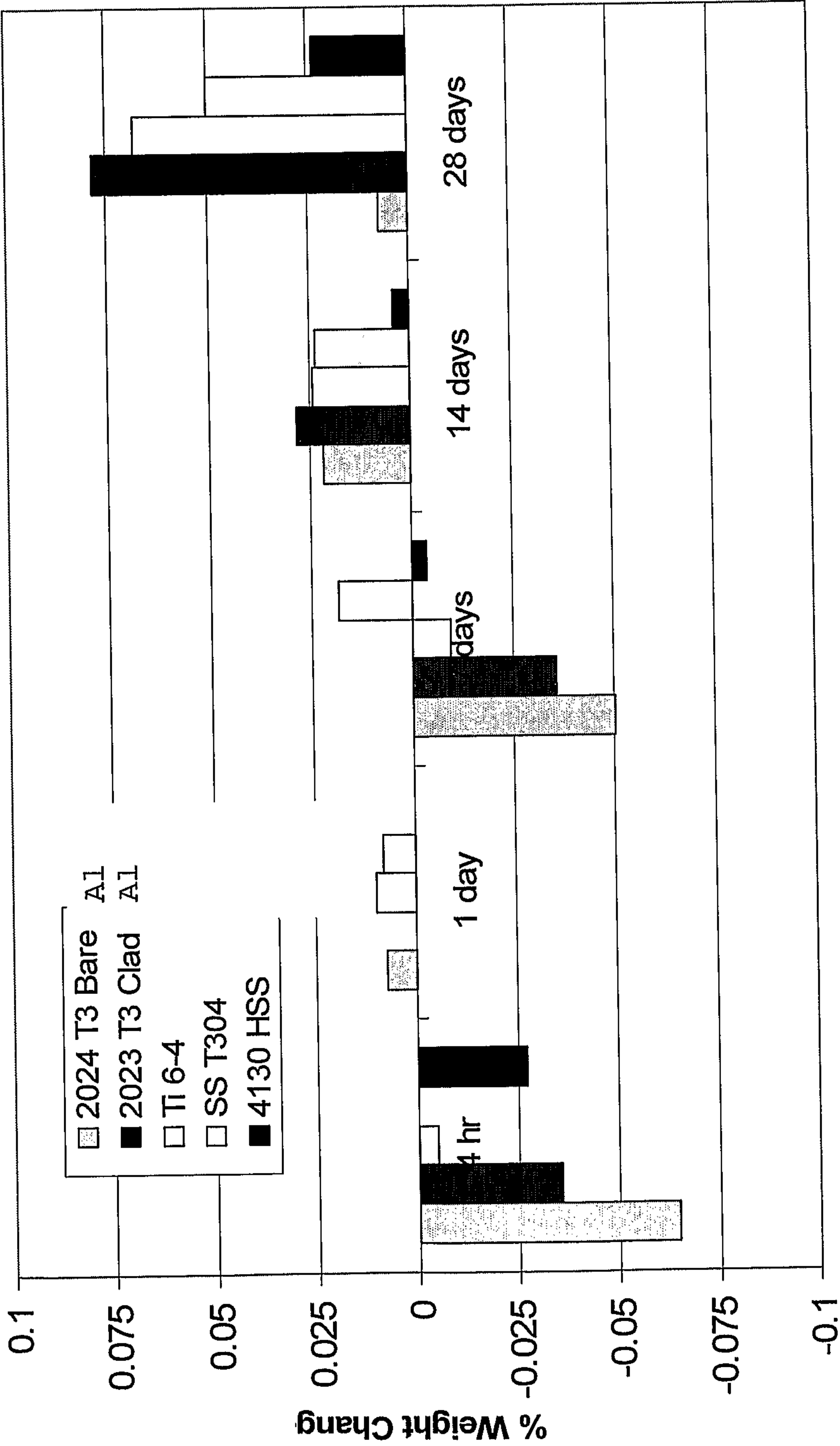


BMS8-276 with SM905

d.



e. LiBH_4 (0.2%) in propylene glycol used for immersion

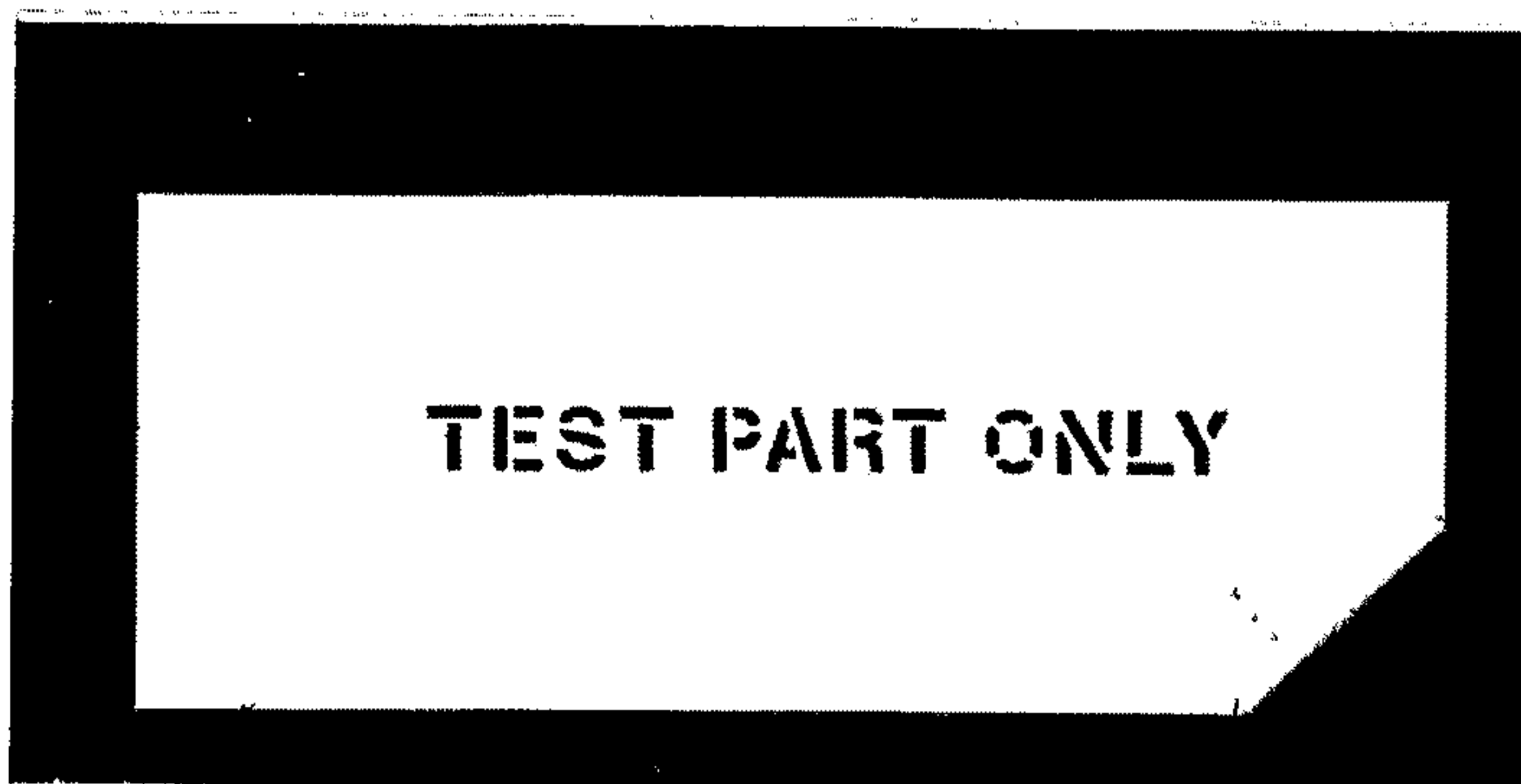


The examples demonstrate that the reactivation solutions may be formulated for minimal negative interaction with a range of materials from plastics, composites, elastomers, and metals relative to common solvents or chemical formulations often used in industries such as the aerospace sector. In the case of metals, weight loss is within measurement uncertainty.

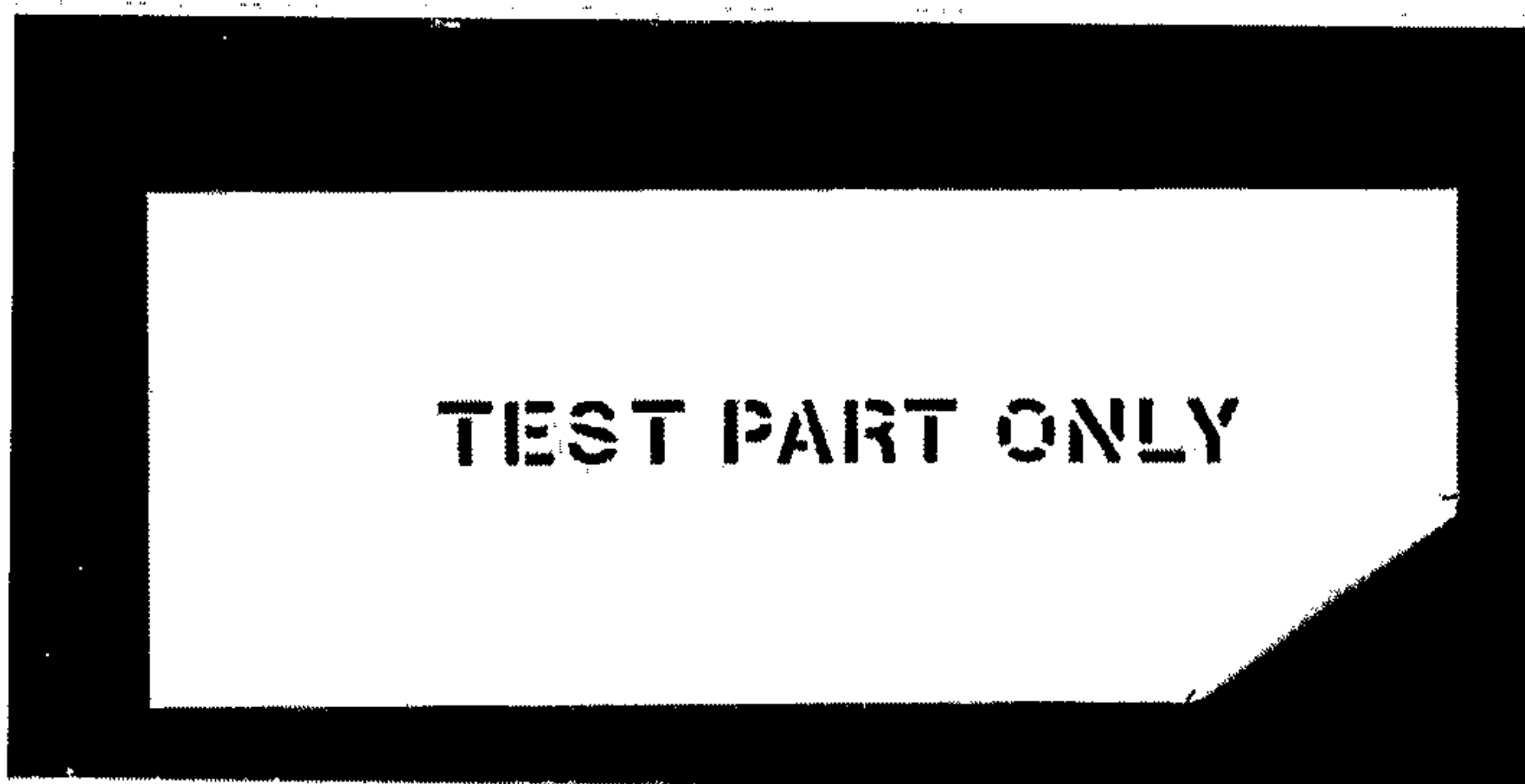
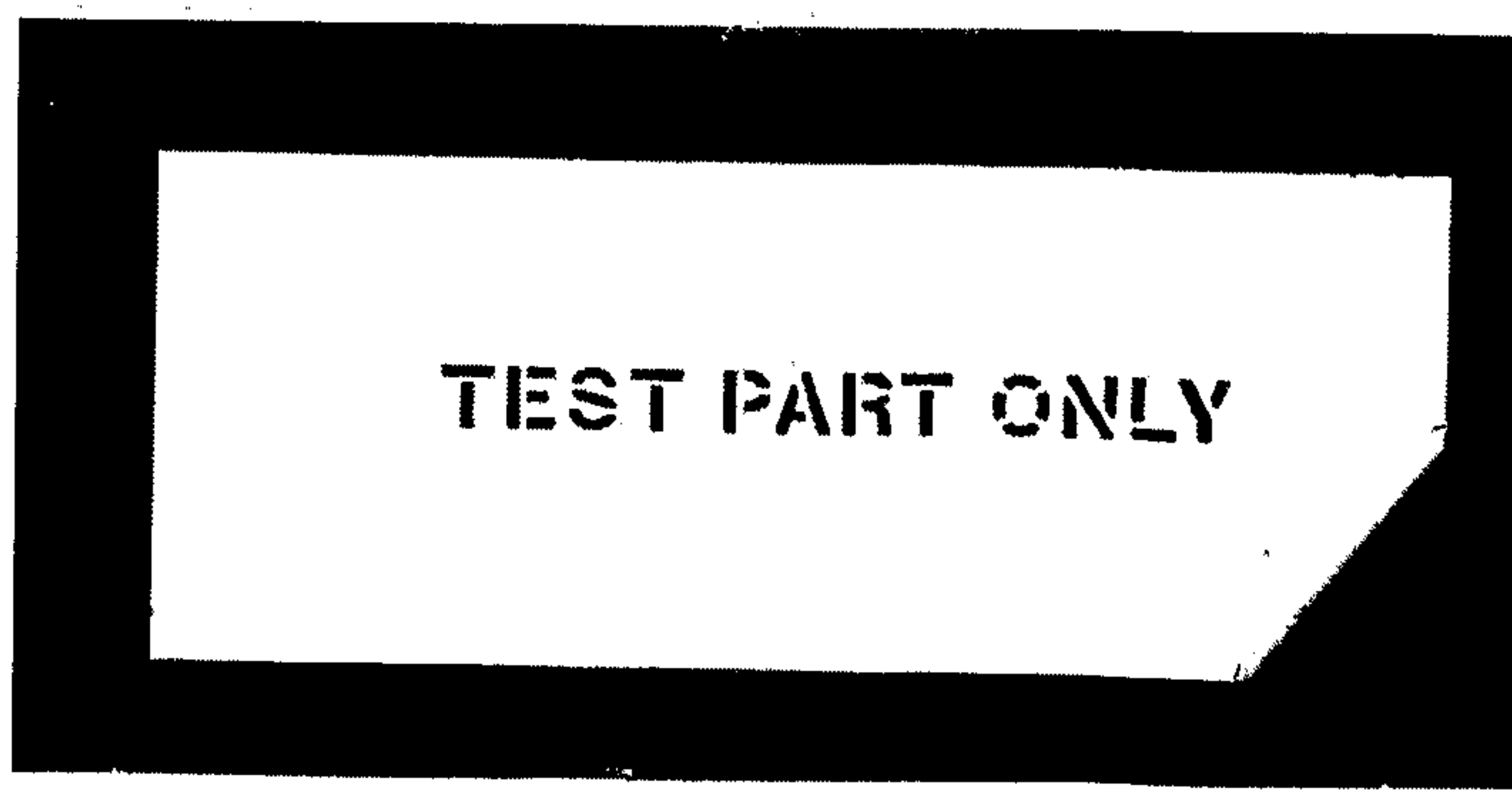
- 87 -

Example 27. The following examples demonstrate the reactivation solution may be used in conjunction with materials such as stencils and design masks and tapes for the production of decorative painted finishes.

(i) Reactivation (LiBH_4 in propylene glycol:IPA 40:60 SOLO application 30min) applied onto aged Desothane HS white 70846X topcoat (16h, 120F, 8%RH) with pre-applied vinyl based stencil prior to painting with Desothane HS S601X blue (C2) cured for 16h at ambient conditions.



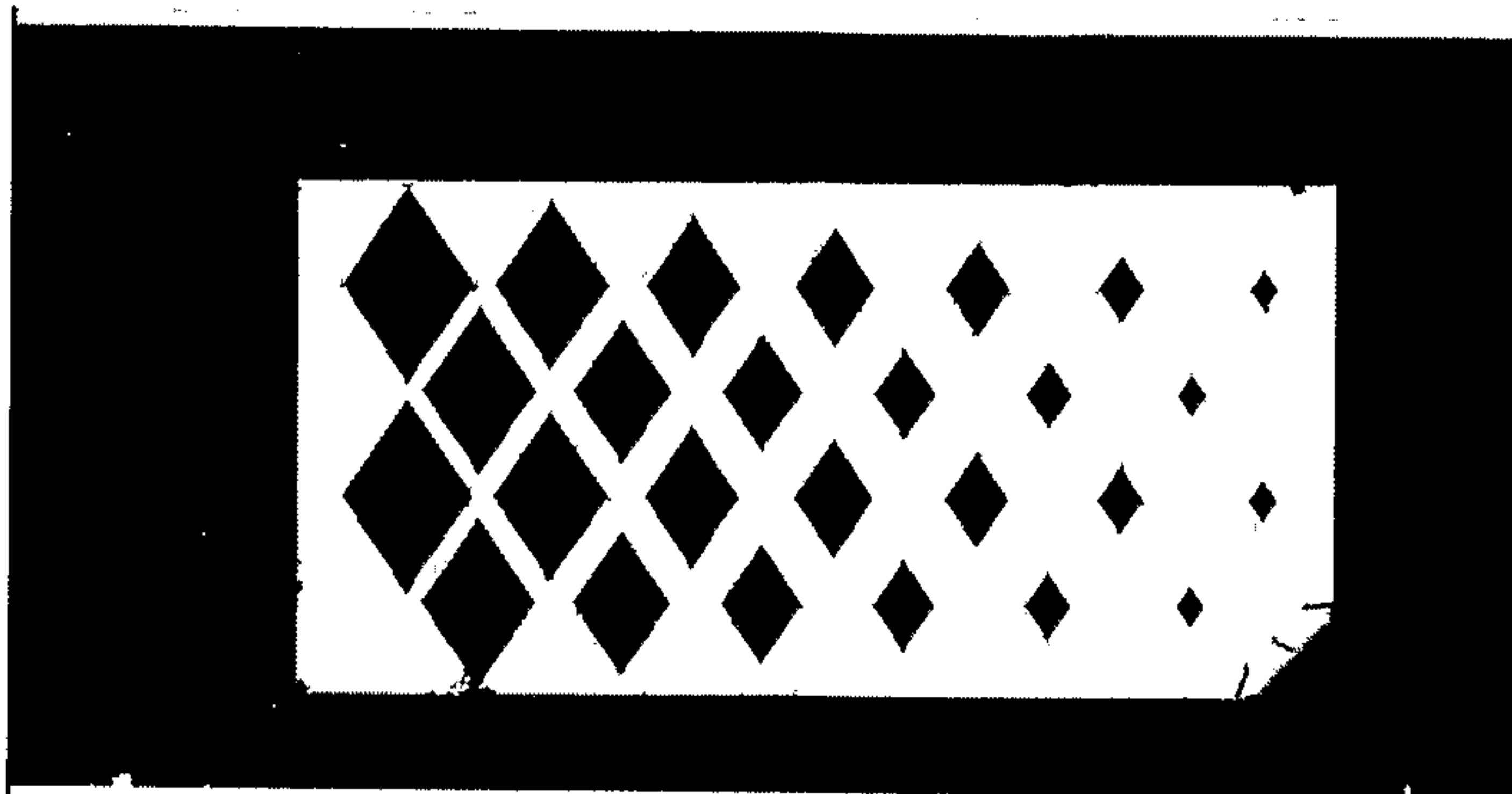
Untreated

0.05% LiBH_4 0.15% LiBH_4

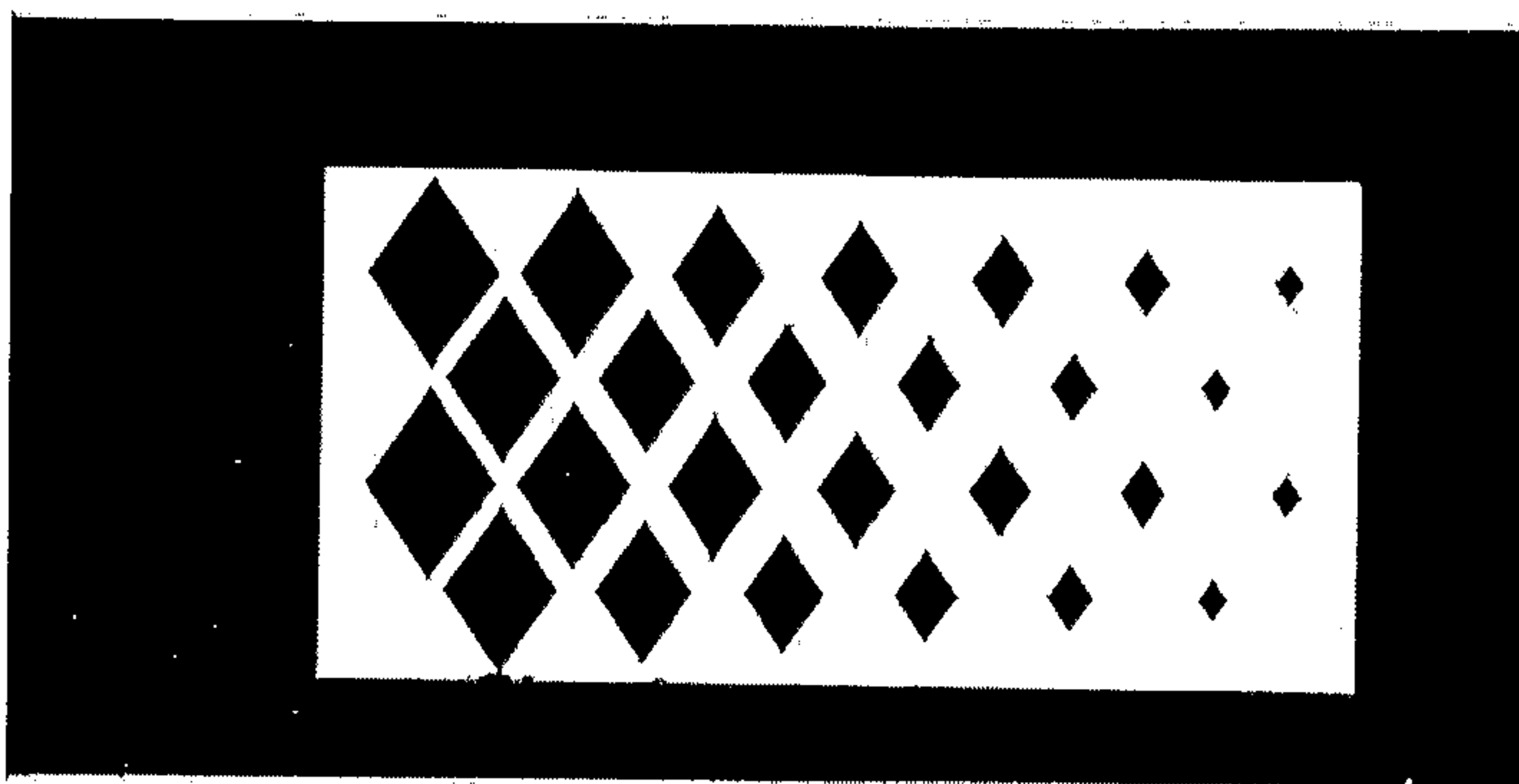
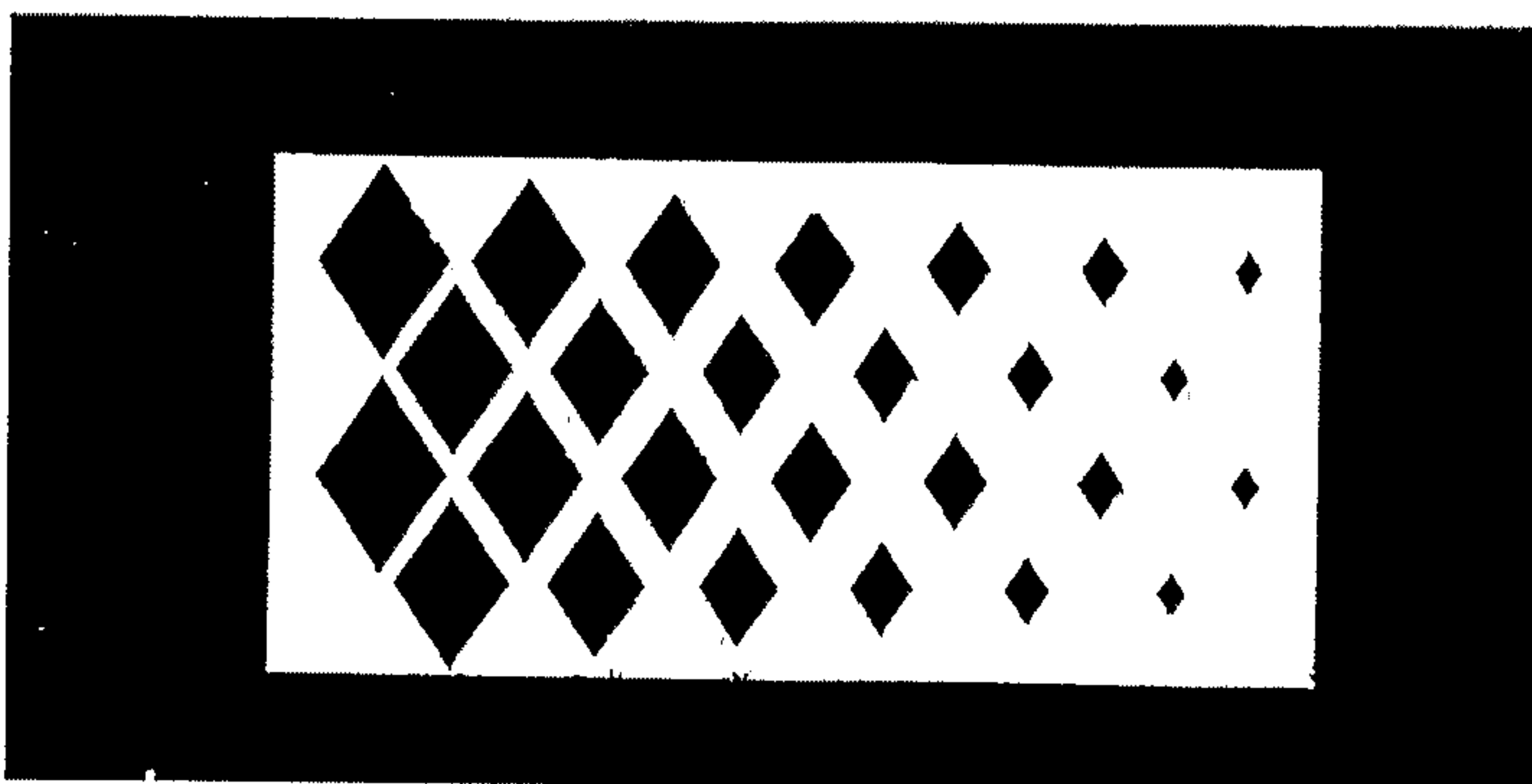
Example illustrates that crisp non-distorted letters are maintained even when the treatment solution is applied over the top of the stencil.

- 88 -

(ii) Reactivation (LiBH_4 in proglyde:IPA 40:60 SOLO application 30min) applied onto aged Desothane HS white 70846X topcoat (16h, 120F, 8%RH) with pre-applied vinyl based stencil prior to painting with Desothane HS S601X (C)blue at 120F for 16h.



untreated

0.05% LiBH_4 0.15% LiBH_4

Example illustrates that crisp non-distorted designs are maintained even when the treatment solution is applied over the top of the mask.

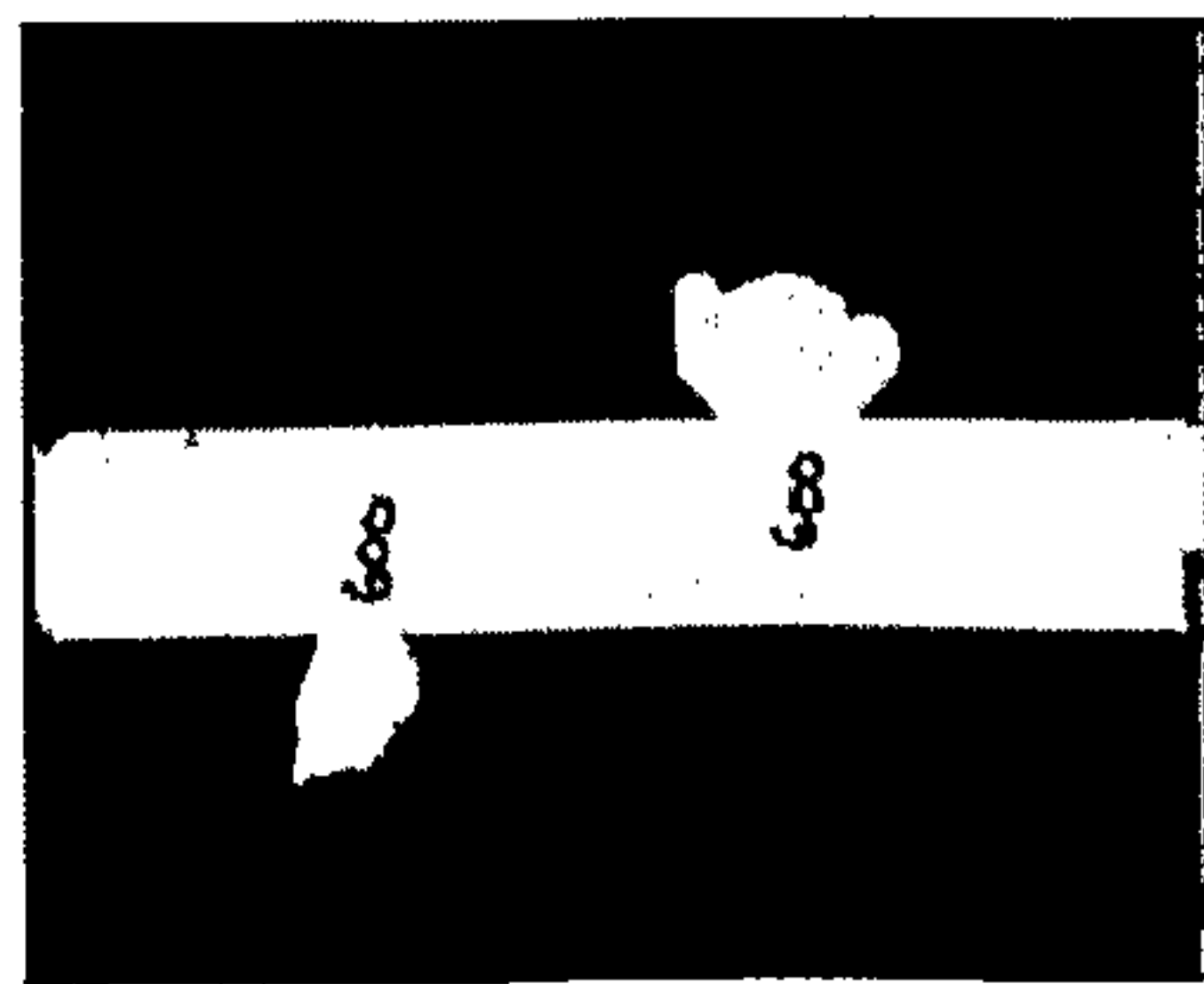
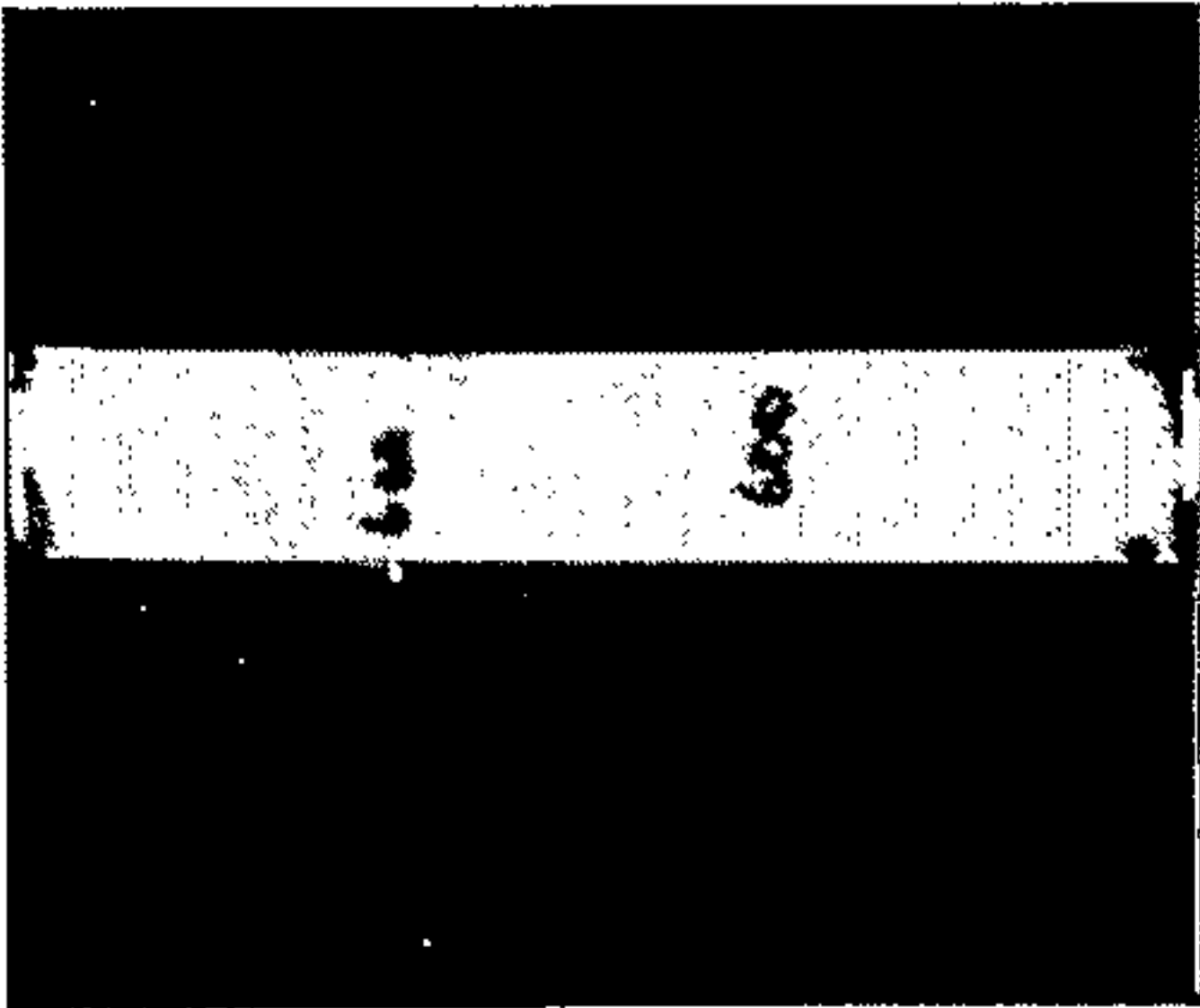
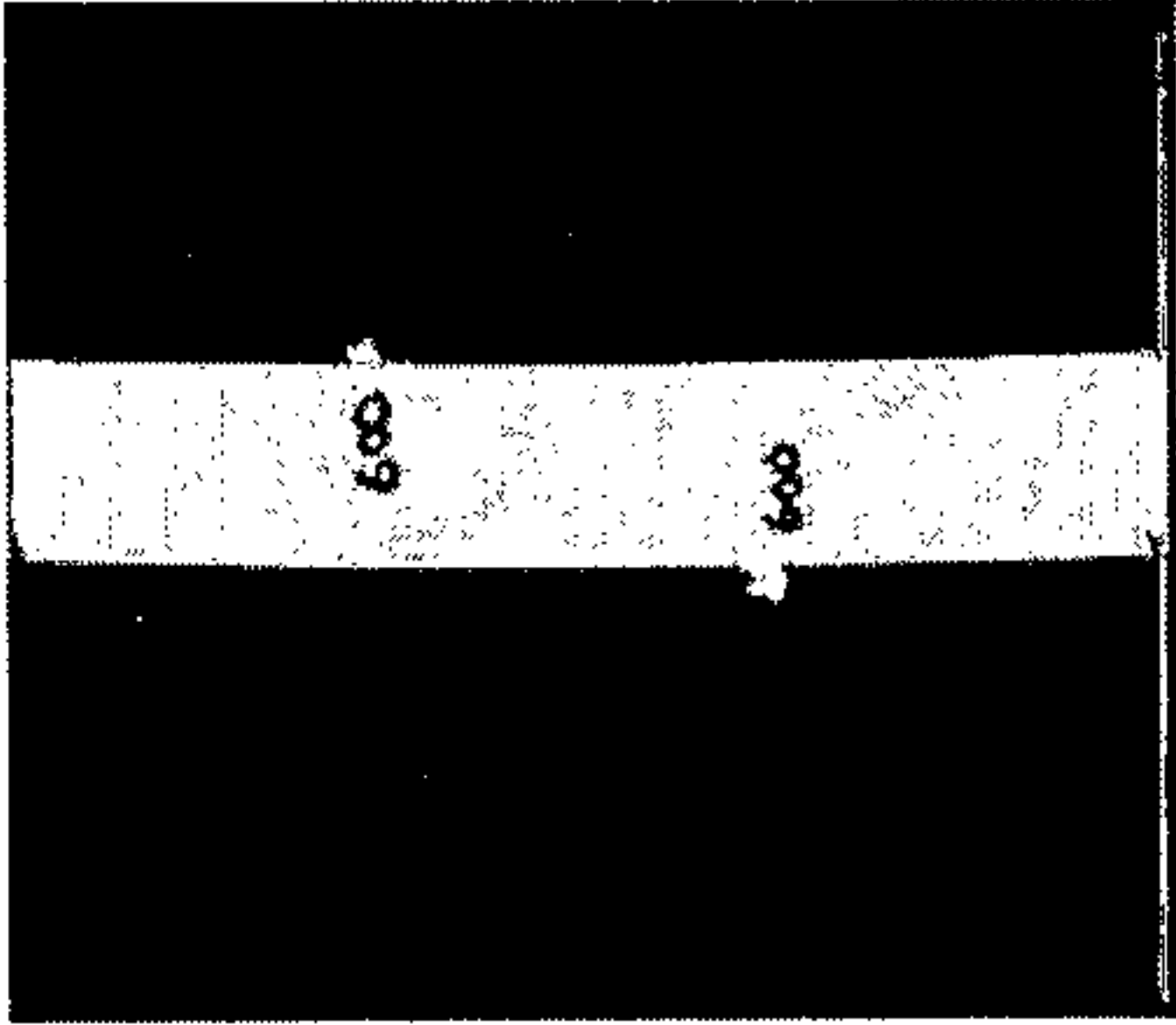
(iii) Reactivation (0.15% LiBH₄ in proglyde:IPA,30min, SOLO) applied onto aged Desothane HS white 70846X topcoat (16h, 120F) with pre-applied vinyl based stencil prior to painting with Desothane HS S601X blue (C2).

Scribe test		Stencil pull	
1	Untreated	5	20:80 Proglyde:IPA
2		30	
3		60	
4h		90min	
After blue application under abient conditions		After blue application under abient conditions	

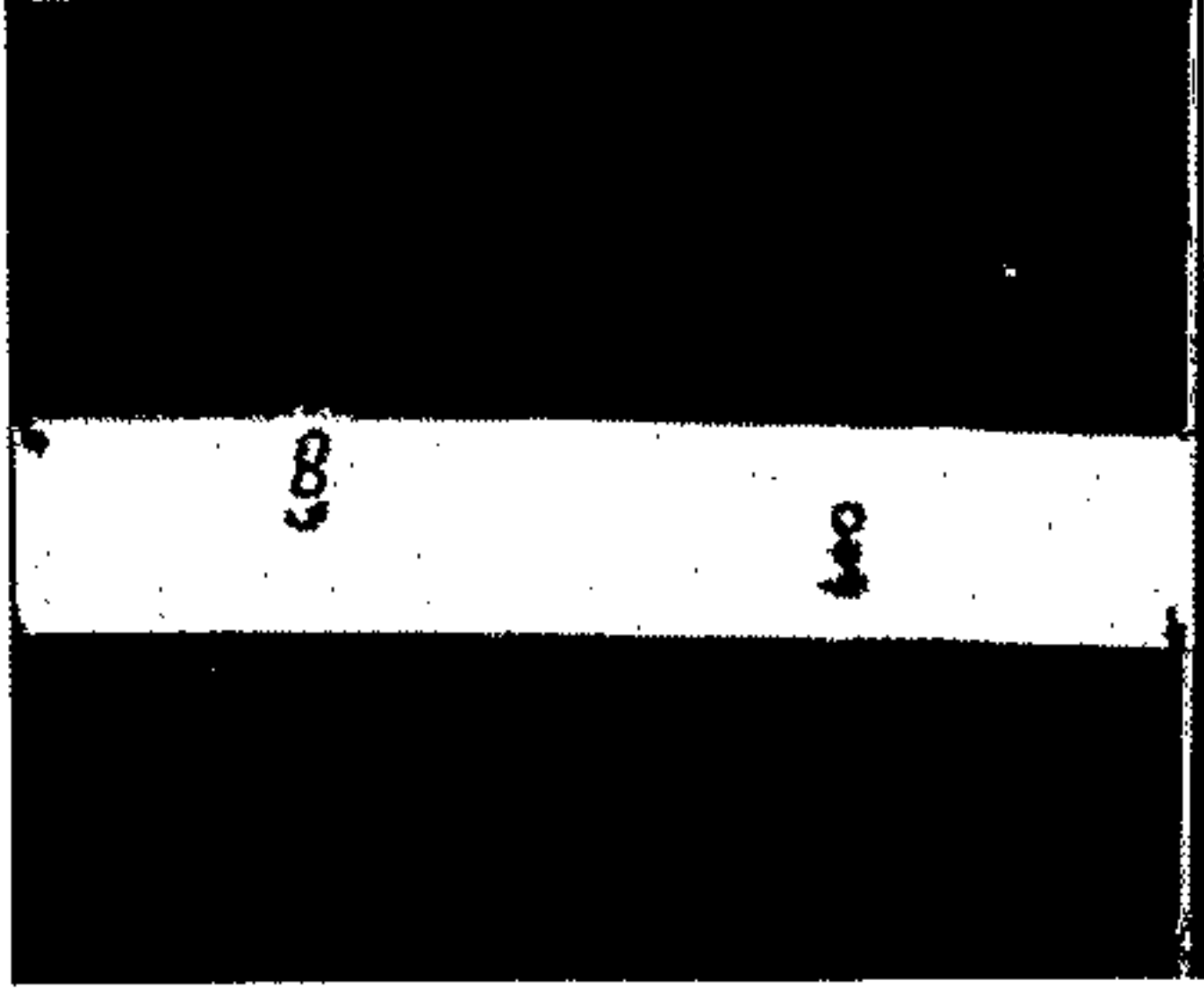
Example illustrates that excellent green adhesion, verified by scribe and stencil pull tests, is possible after 1h with reactivated samples unlike untreated and excellent letter clarity is possible across a range of stencil pull times.

- 90 -

Example 28. Desothane HS 3613X yellow or S400X red (C2) cured aged under the standard aging protocol was reactivated using the LiBH₄ concentrations indicated for 30 min SOLO prior to overcoating with Desothane HS S601X blue.

**Untreated****Sanded****0.05%**

0.1% LiBH₄
in Propylene DMM



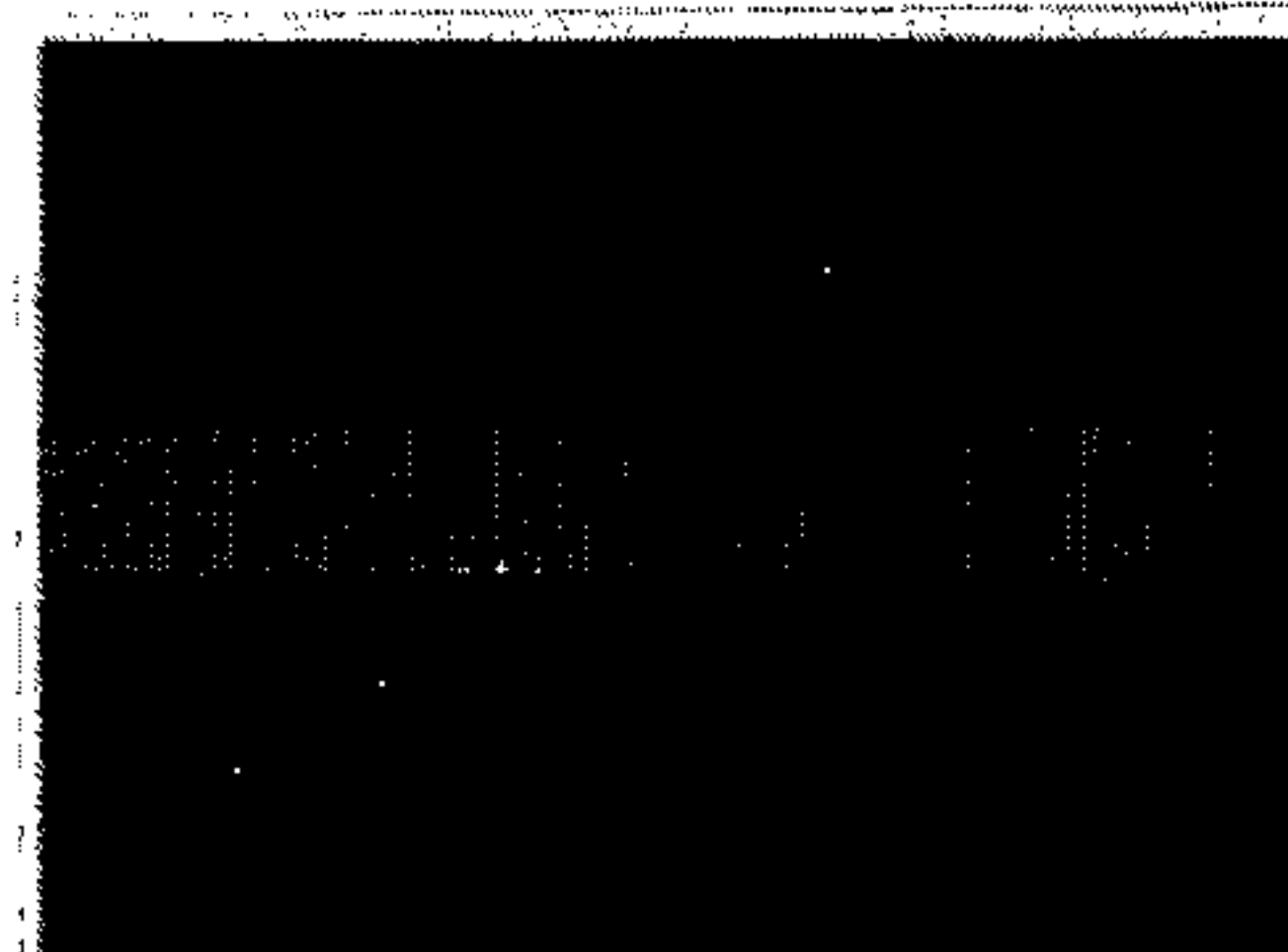


0.1% LiBH₄

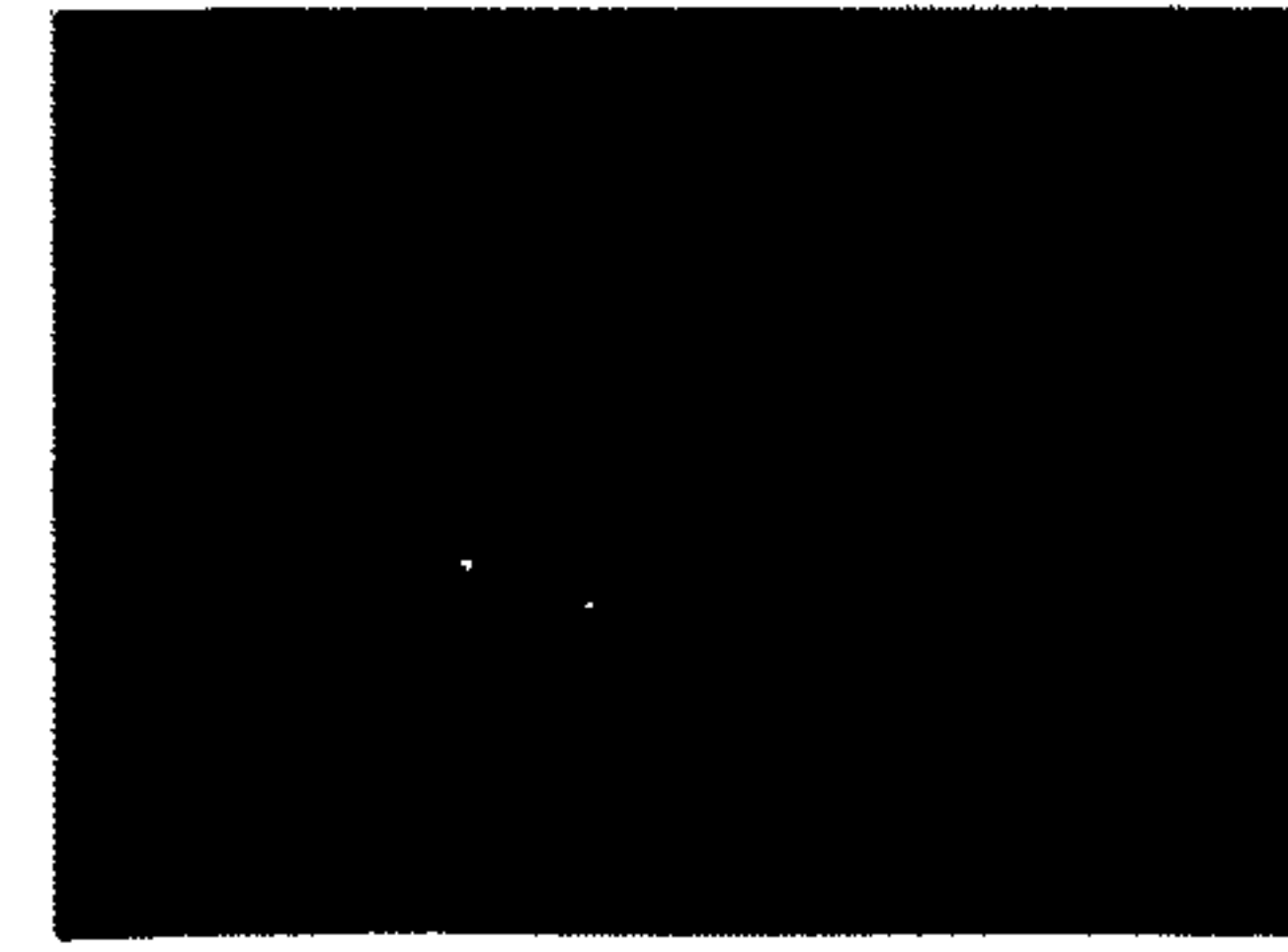


0.2%

In Proglyde : IPA, 80:20



Sanded

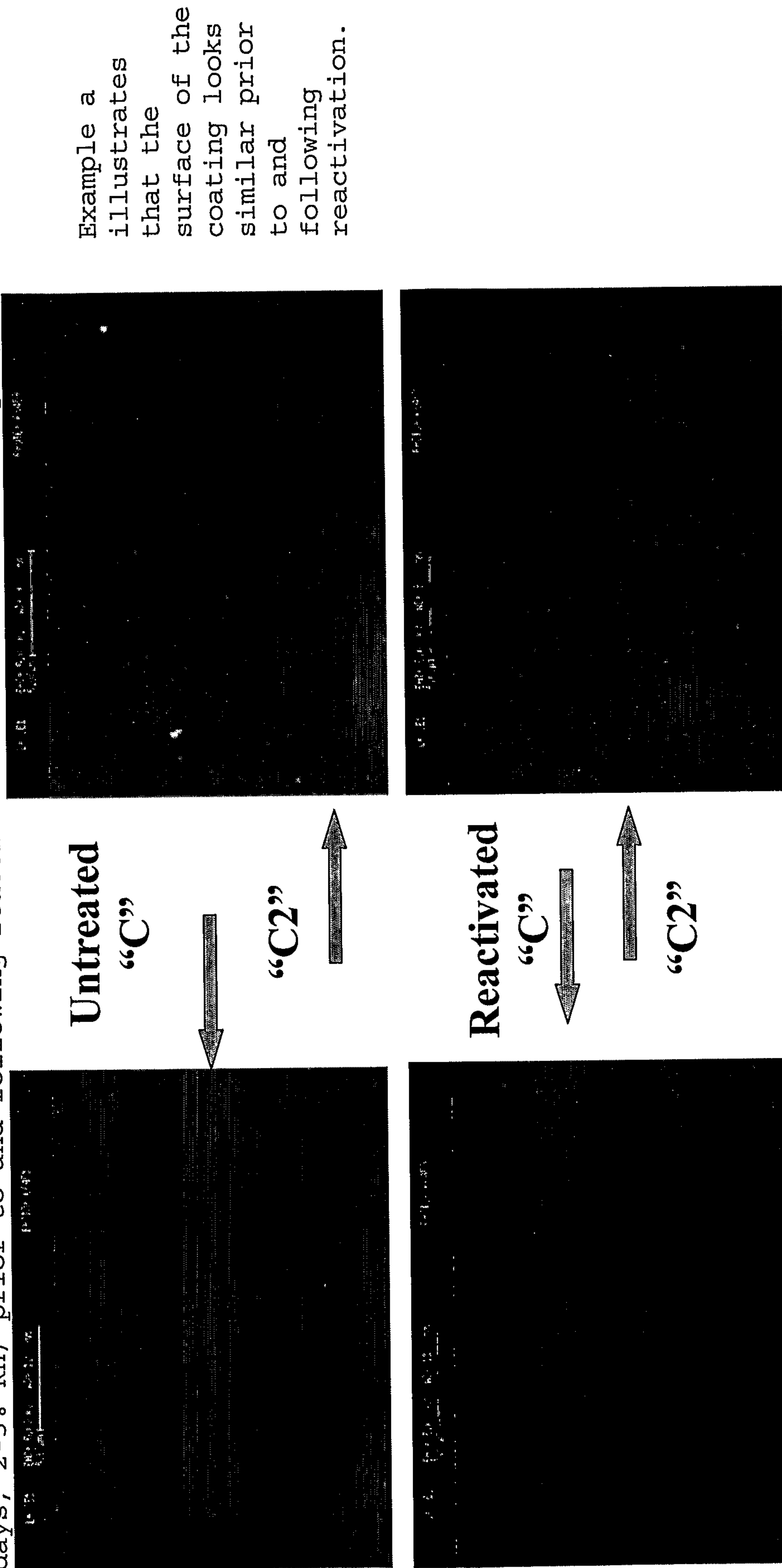


Untreated

The example illustrates that different coloured polyurethane coating may be reactivated using the reduction strategy.

Example 29

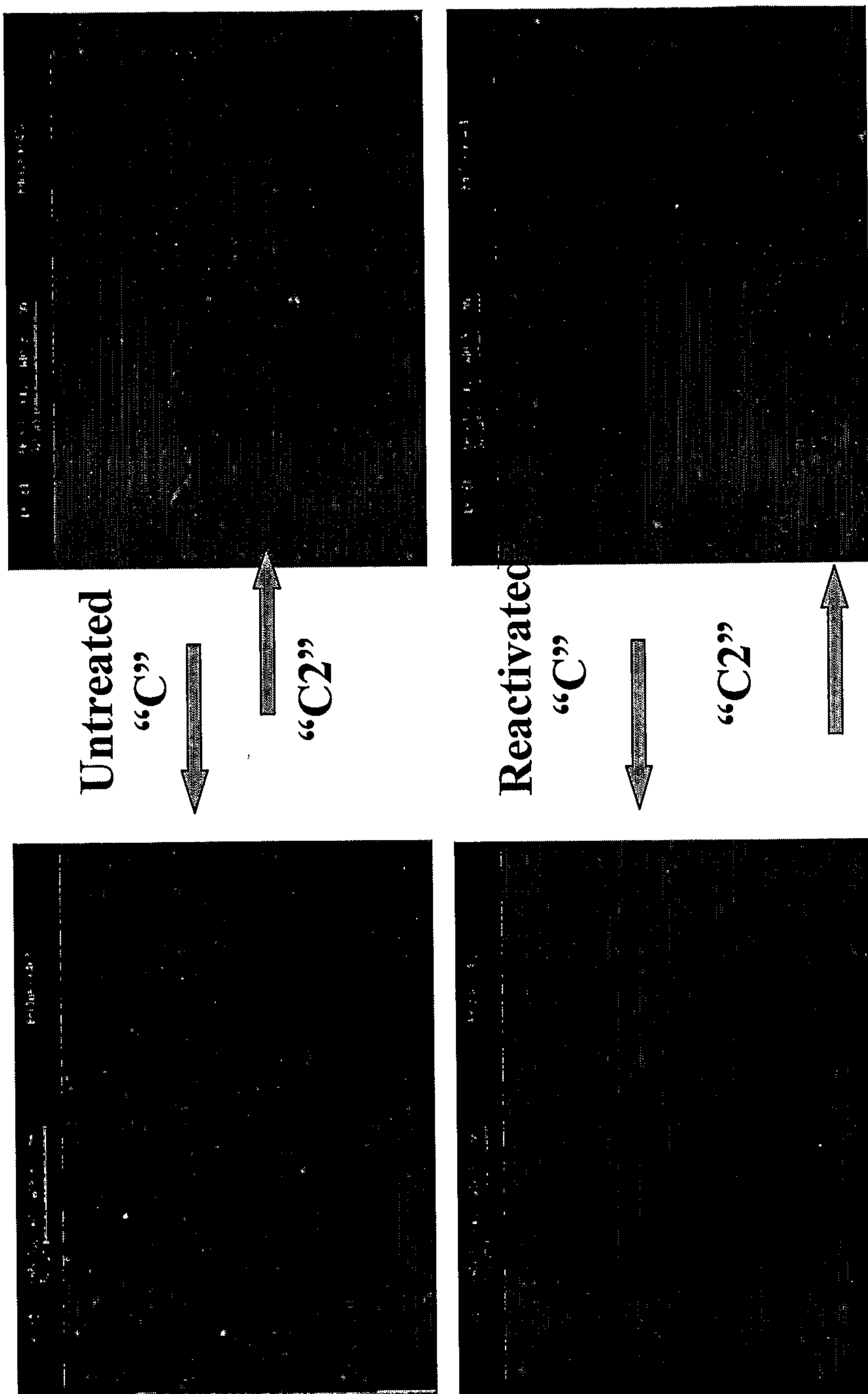
(i) SEM pictures of Desothane HS 70846X white polyurethane coatings both (C) and (C2) aged under the (a) standard cure cycle aging conditions and (b) low humidity conditions (120F, 5 days, 2-3% RH) prior to and following reactivation with 0.1% LiBH₄ in proglyde.



Example a illustrates that the surface of the coating looks similar prior to and following reactivation.

- 93 -

Example b illustrates that the surface of the coating looks similar prior to and following reactivation.



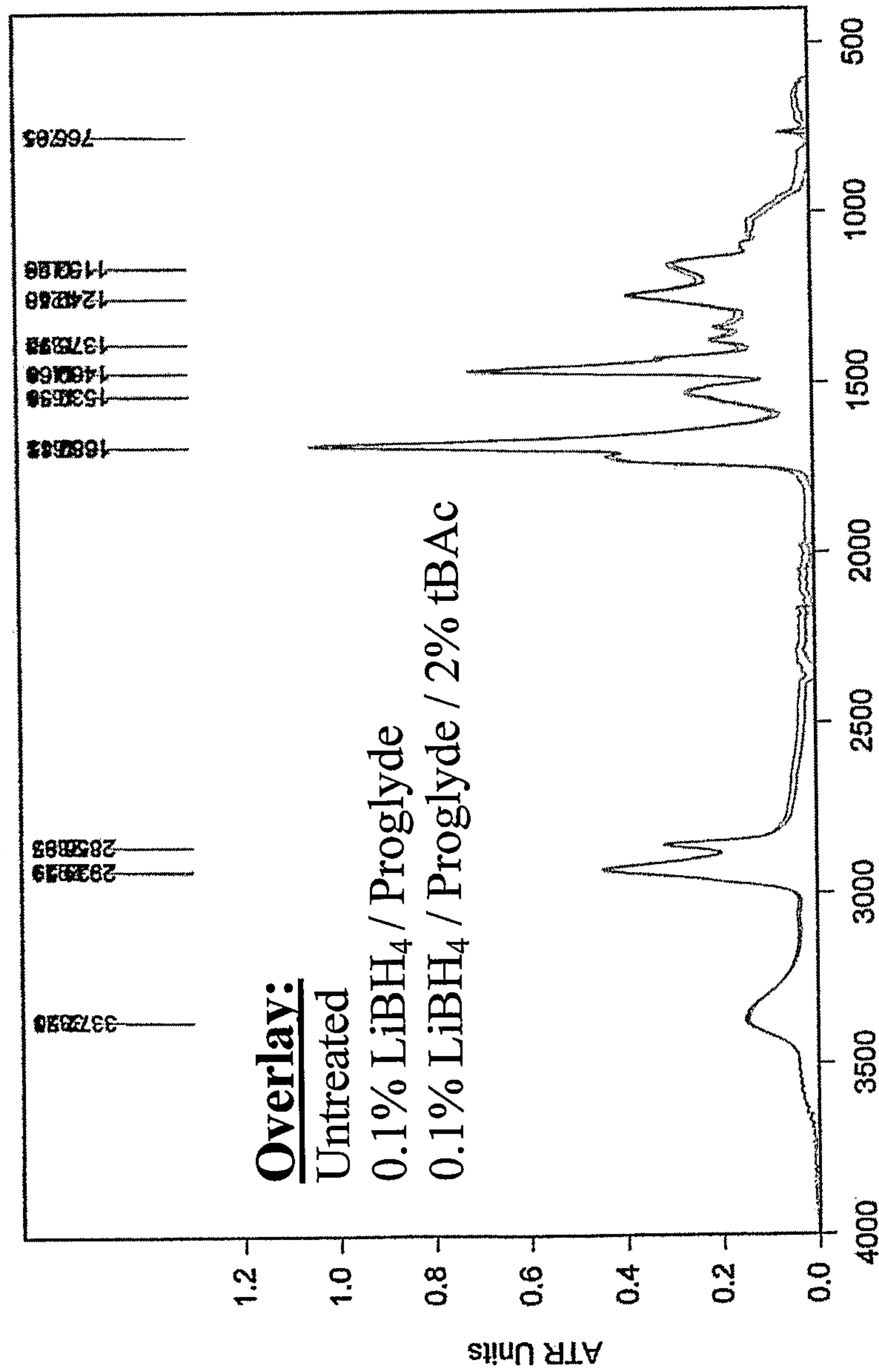
(ii) Surface energy results for Desothane HS 70846X white polyurethane coatings both (C) and (C2) aged using the (a) standard cure conditions and (b) low humidity cure conditions (120°F, 5 days, 2-3% RH) prior to and following reactivation with 0.1% LiBH₄ in proglyde

Substrate		Surface Energy (mJ/m ²)	
Cure	Treatment*	Dispersive	Specific
Low Humidity Cycle (5 days, 120°F, 2-3% RH)			
"C"	-	44.2	5.4
"C"	0.1% LiBH ₄	43.9	6.3
"C2"	-	41.5	5.5
"C2"	0.1% LiBH ₄	42.4	7.3
Ageing Cycle: 120°F, 5% RH 40 h, (ii) 120°F 50% RH 48 h, and (iii) oven cure at 160°F for 24h			
"C"	-	43.6	3.6
"C"	0.1% LiBH ₄	45.4	5.9
"C2"	-	45.2	4.2
"C2"	0.1% LiBH ₄	45.5	7.3

Example illustrates that increases in the Specific contribution to surface energy results from exposure to the reactivation treatment solution for the coatings aged under difference conditions and with catalyst levels (eg: C and C2) .

- 95 -

(iii) FTIR-ATR results from Desothane HS 70846X white polyurethane coatings (C2) aged under the standard conditions and reactivated as indicated.

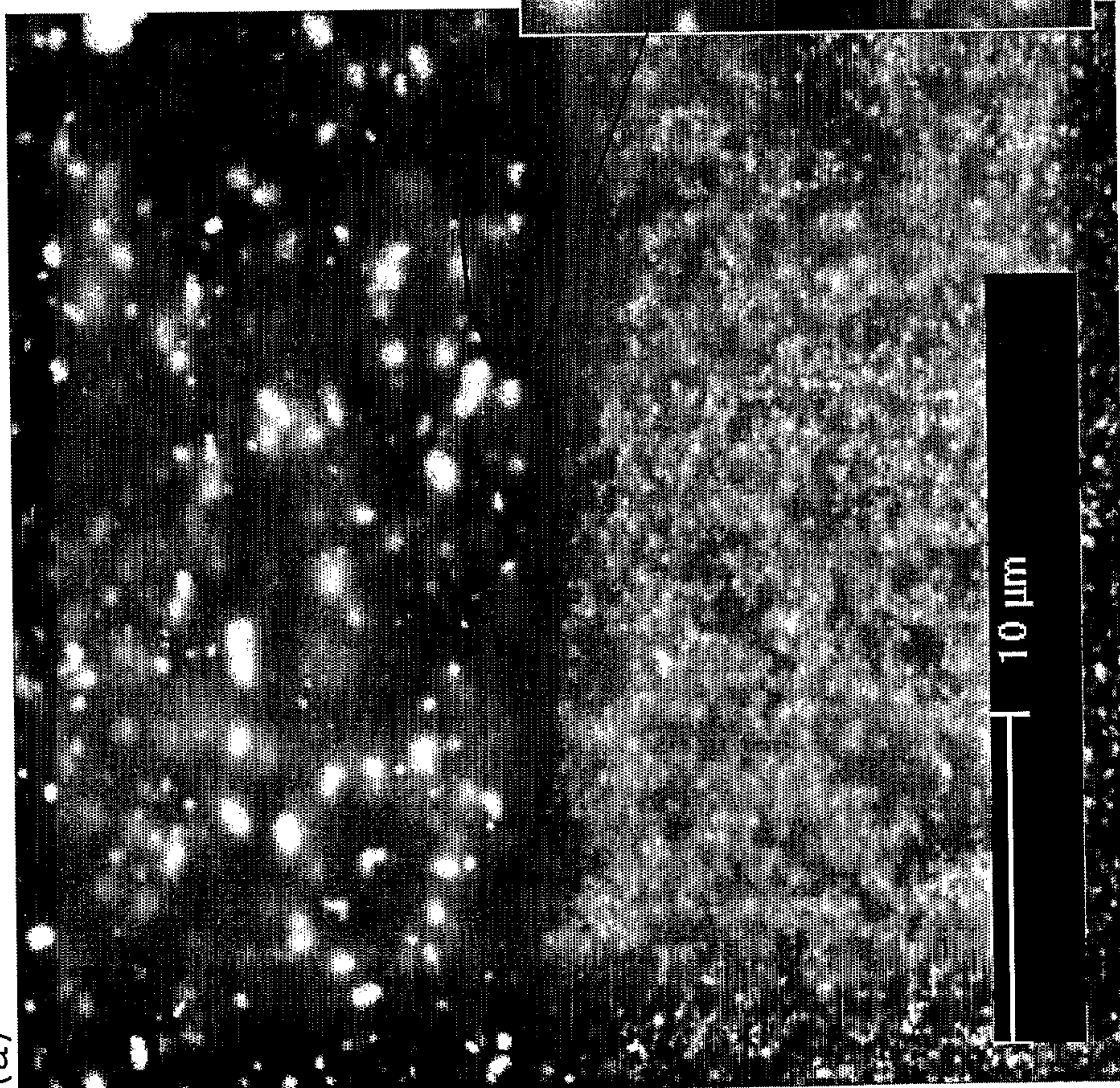


The example illustrates that similar FTIR-ATR traces result between untreated and treated samples, indicating that surface modification occurs primarily in the upper most portion of the coating combining the results from (ii) and (iii) and not deeply into the coating such that FTIR-ATR provides discernable differences in chemical structure.

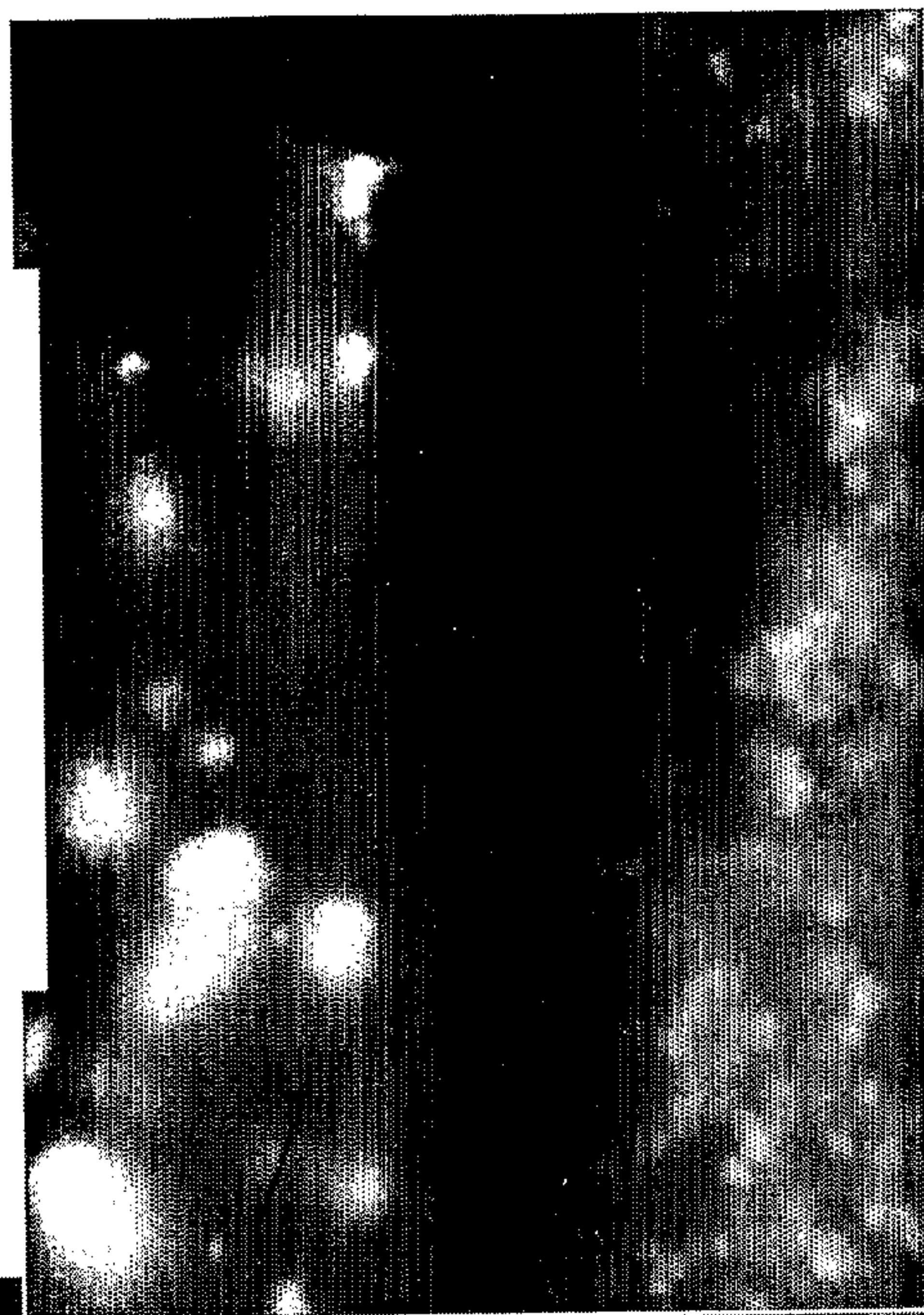
- 96 -

(iv) SEM cross section images of cured aged Desothane HS 70846X white (C2) applied over primer and aluminium substrate (a) untreated, (b) sanded and (c) reactivated using 0.1% LiBH₄ in propylene glyde 30 min SOLO prior to over-coating with Desothane HS S601X blue.

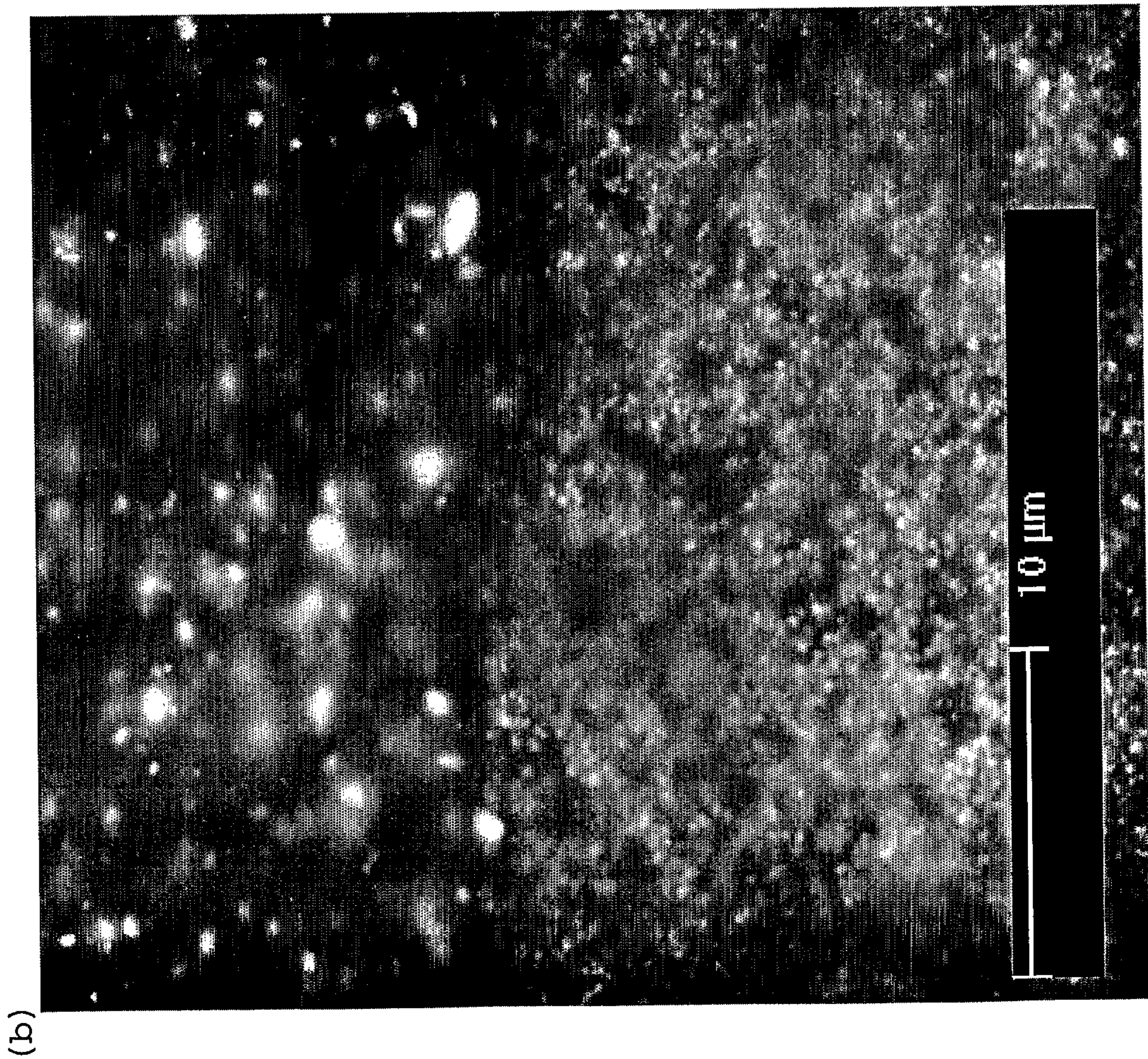
(a)



Topcoat white -
blue interface

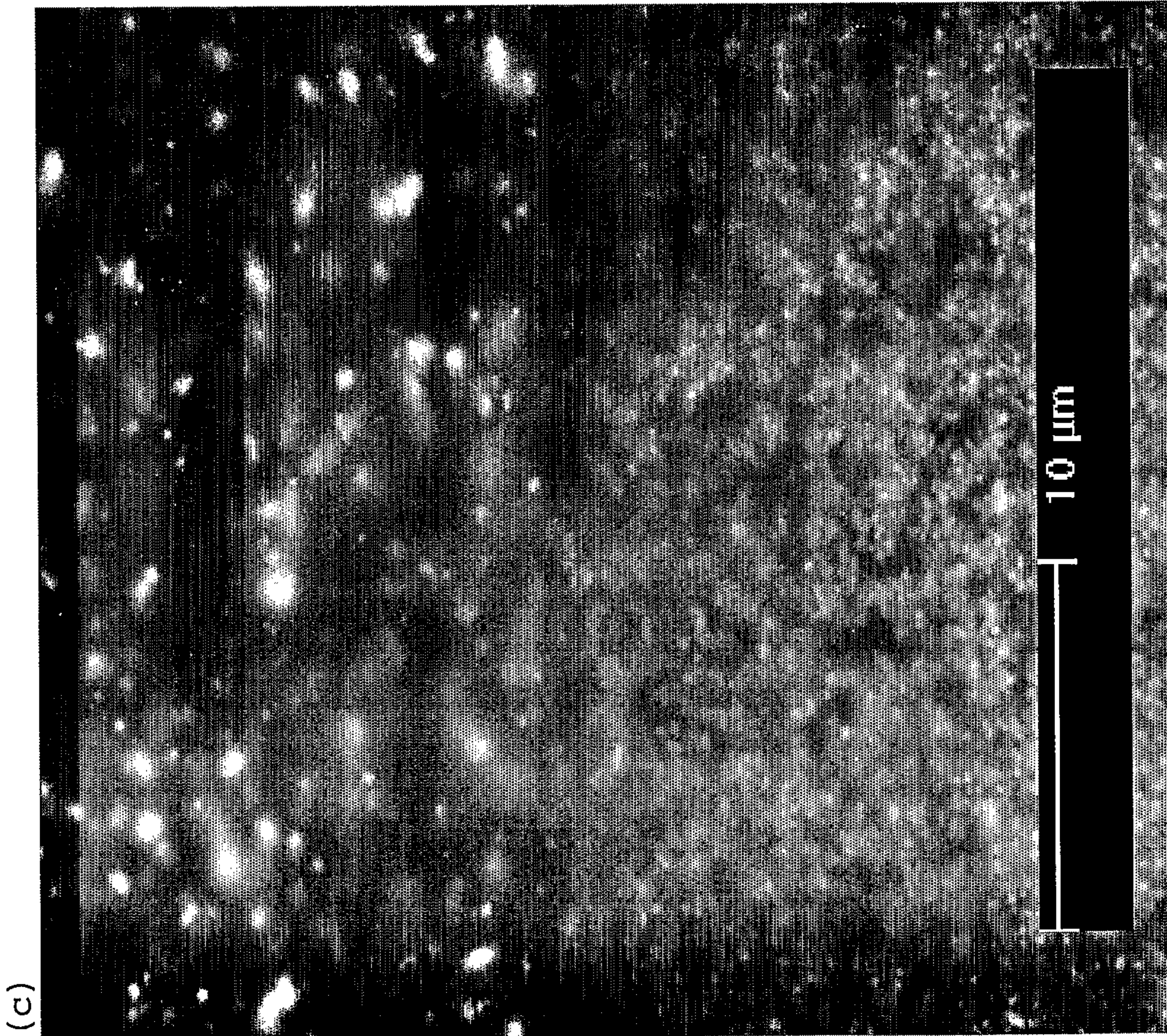


- 97 -



- 98 -

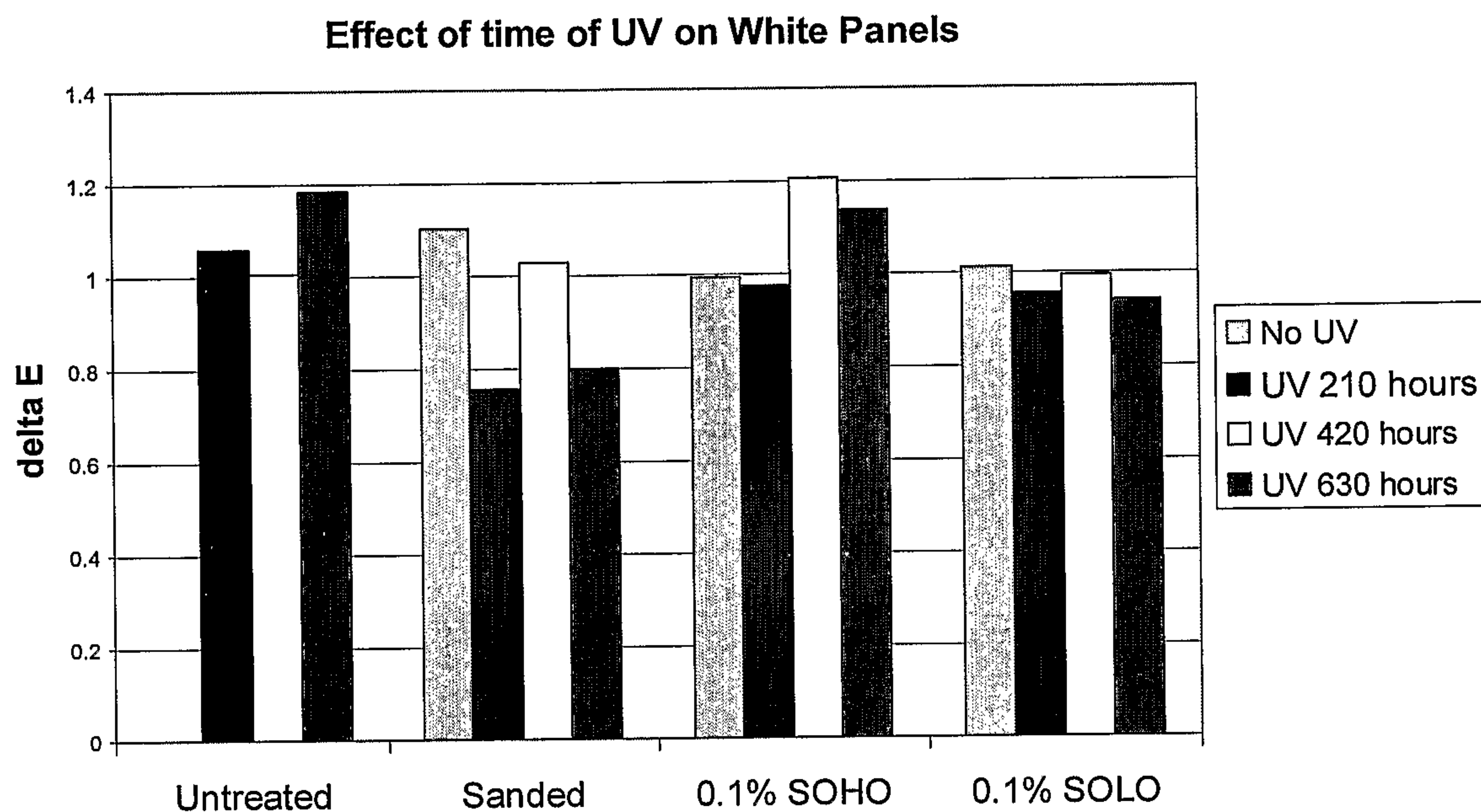
Examples illustrate that the over-coat does not wet the aged Desothane coating when untreated providing de-bonded regions. The de-bonded regions are not present in the sanded and chemically reactivated samples, providing evidence for improved interfacial interaction between the two polyurethane topcoat coating layers (white and blue).



- 99 -

Example 30. Example illustrates the impact of accelerated UV exposure on aged Desothane HS 70846X polyurethane coating relative to untreated reference for different lengths of exposure time.

(i) Change in colour for samples not over-coated.

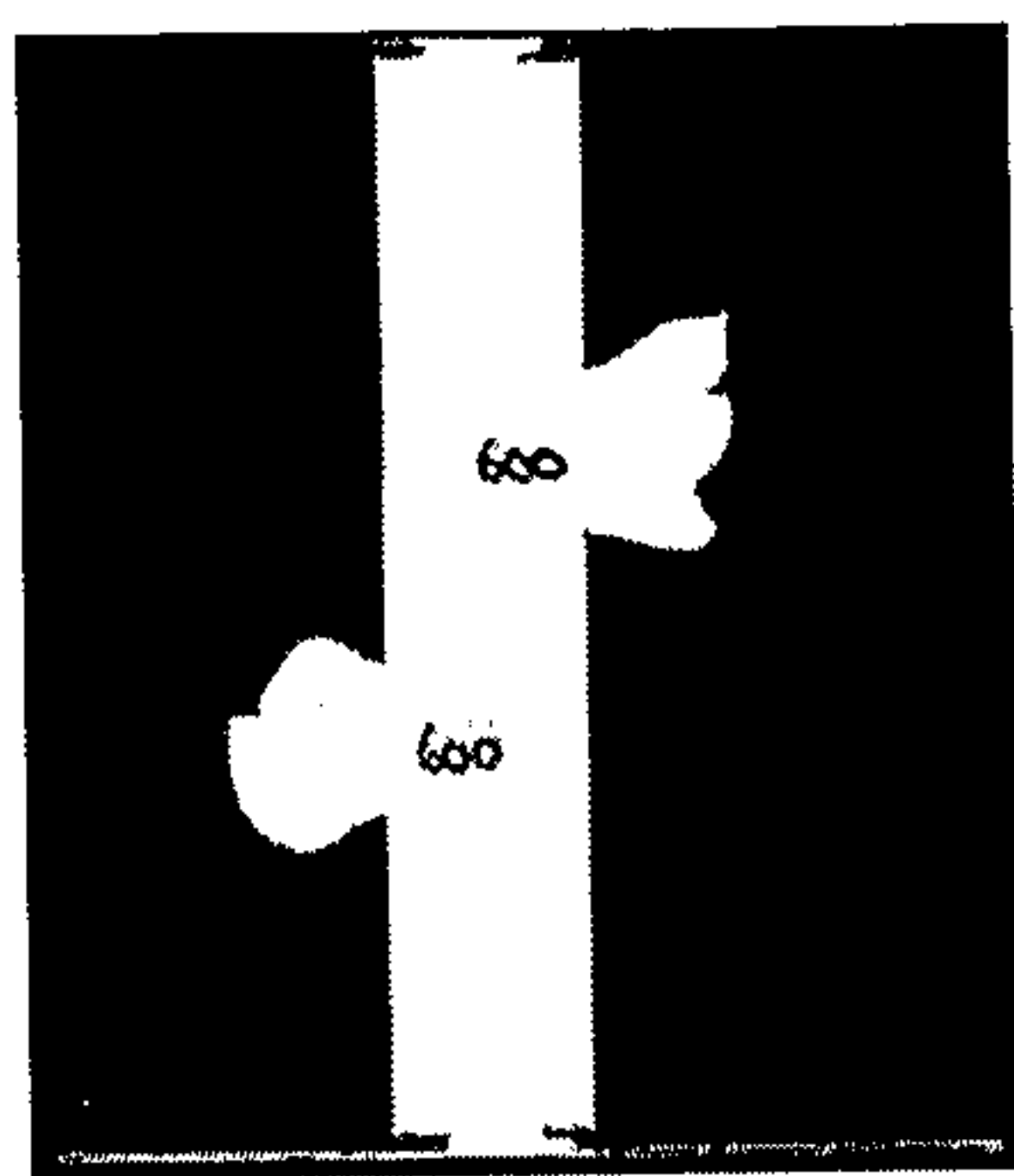


The example illustrates that the colour shift is similar for samples untreated, sanded, reactivated with 0.1% LiBH_4 in proglyde that is either removed after 30min (SOHO) or not removed (SOLO) if left not over-coated prior to various lengths of accelerated UV exposure time.

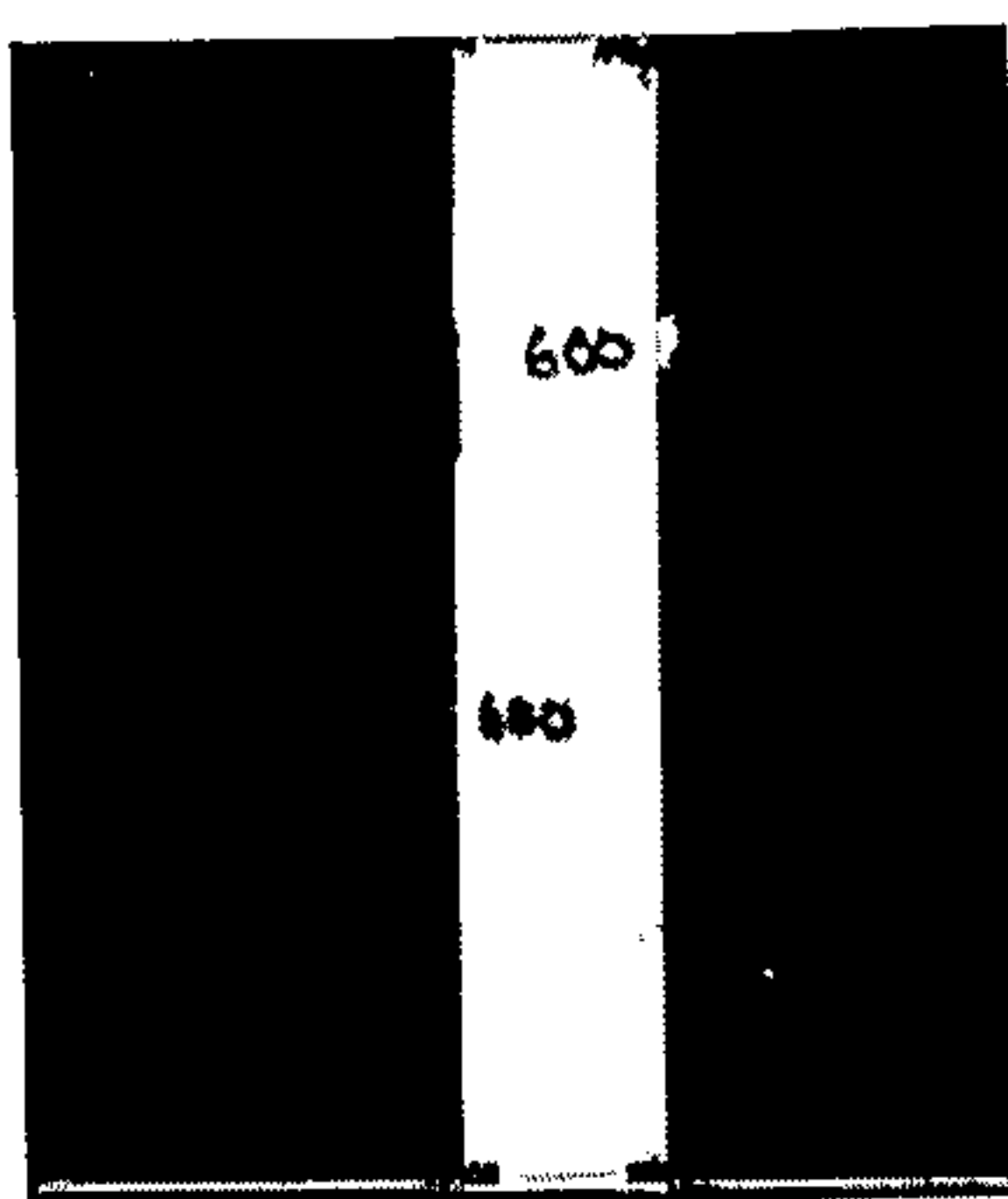
- 100 -

(ii) SIJA inter-coat adhesion results for Desothane HS 70846X white (C2) aged under the standard protocol and then accelerated UV conditions for 630h before reactivation and over-coating with Desothane S601X.

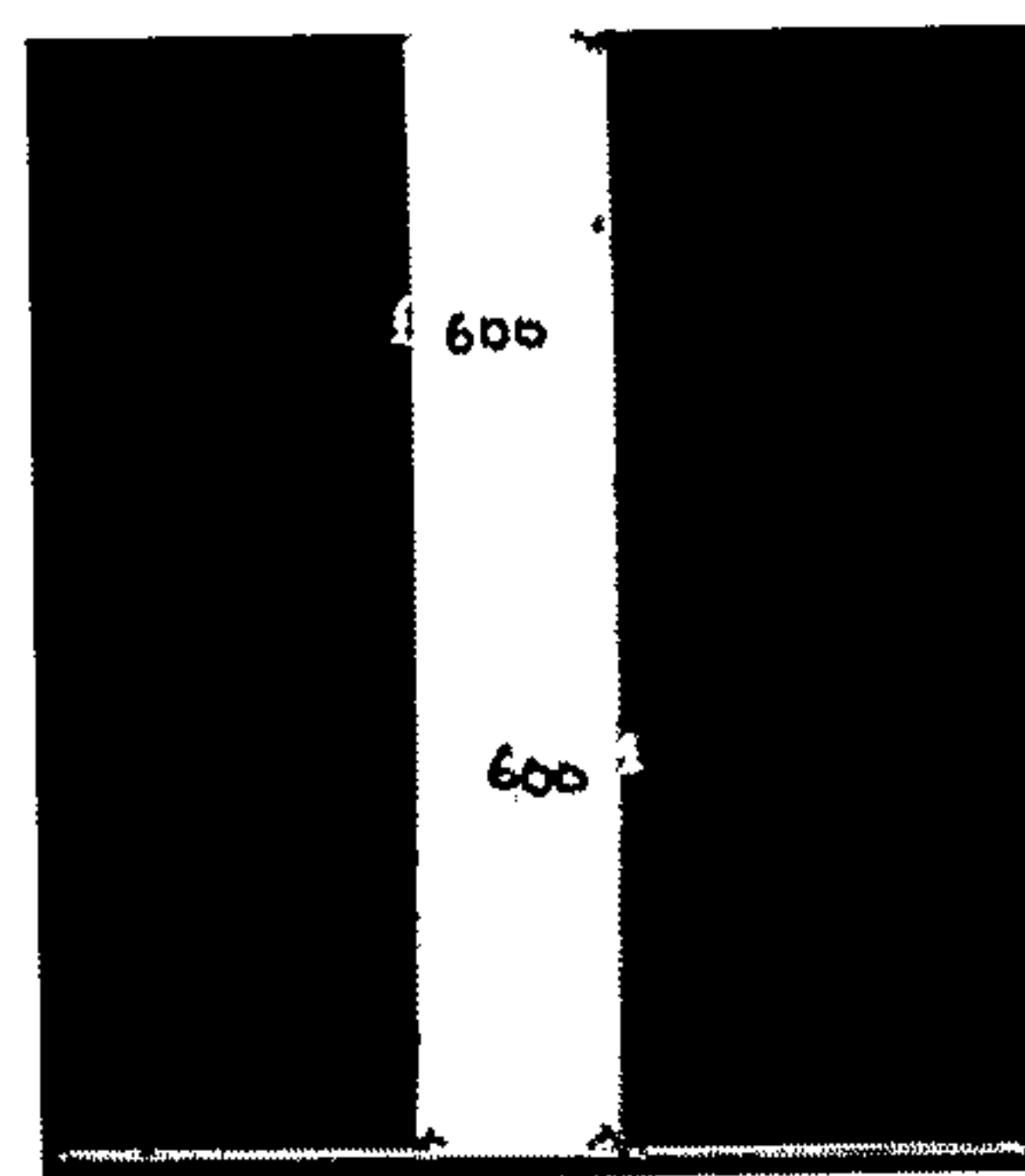
Prior UV Exposure:



Untreated

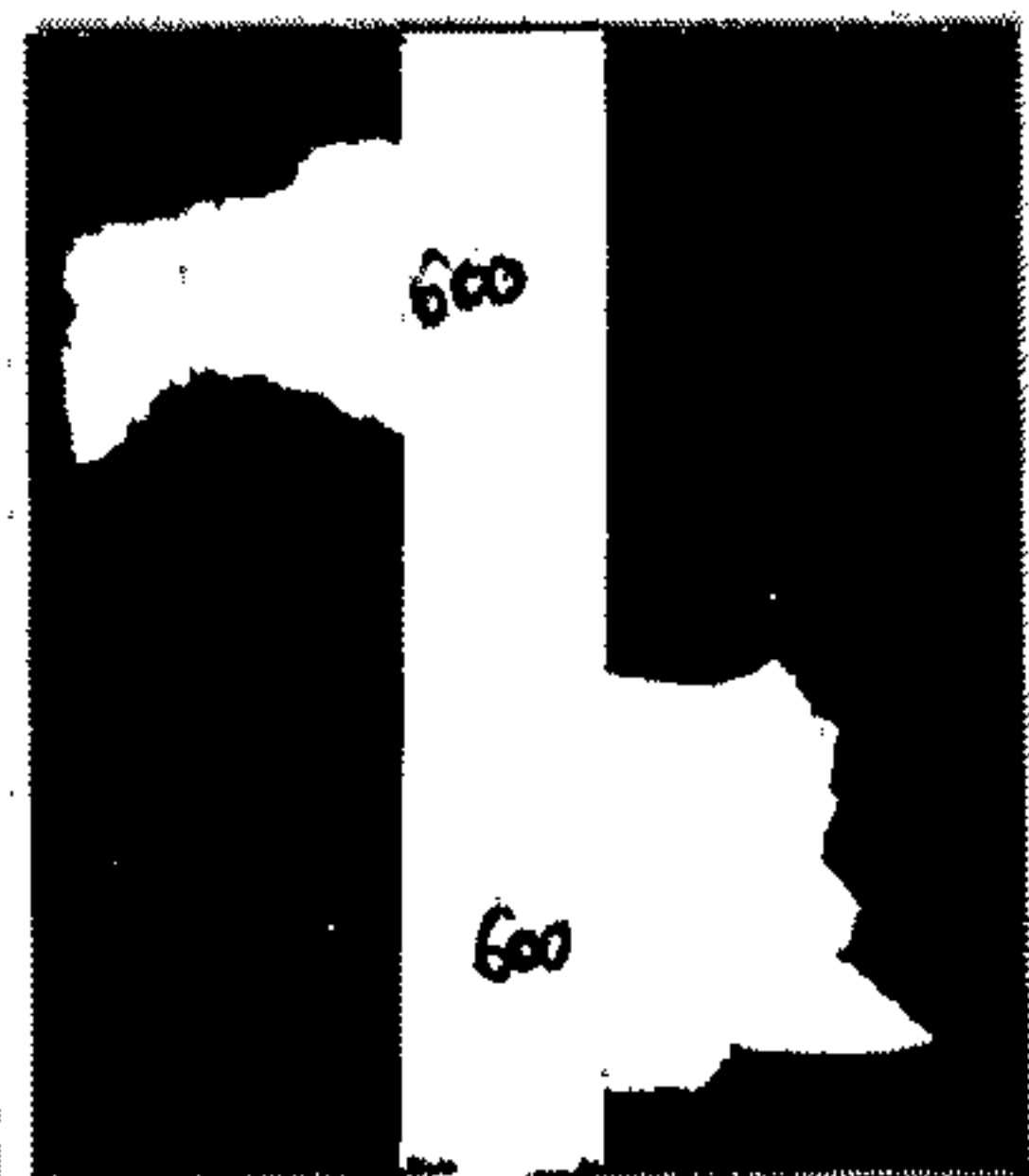


Sanded

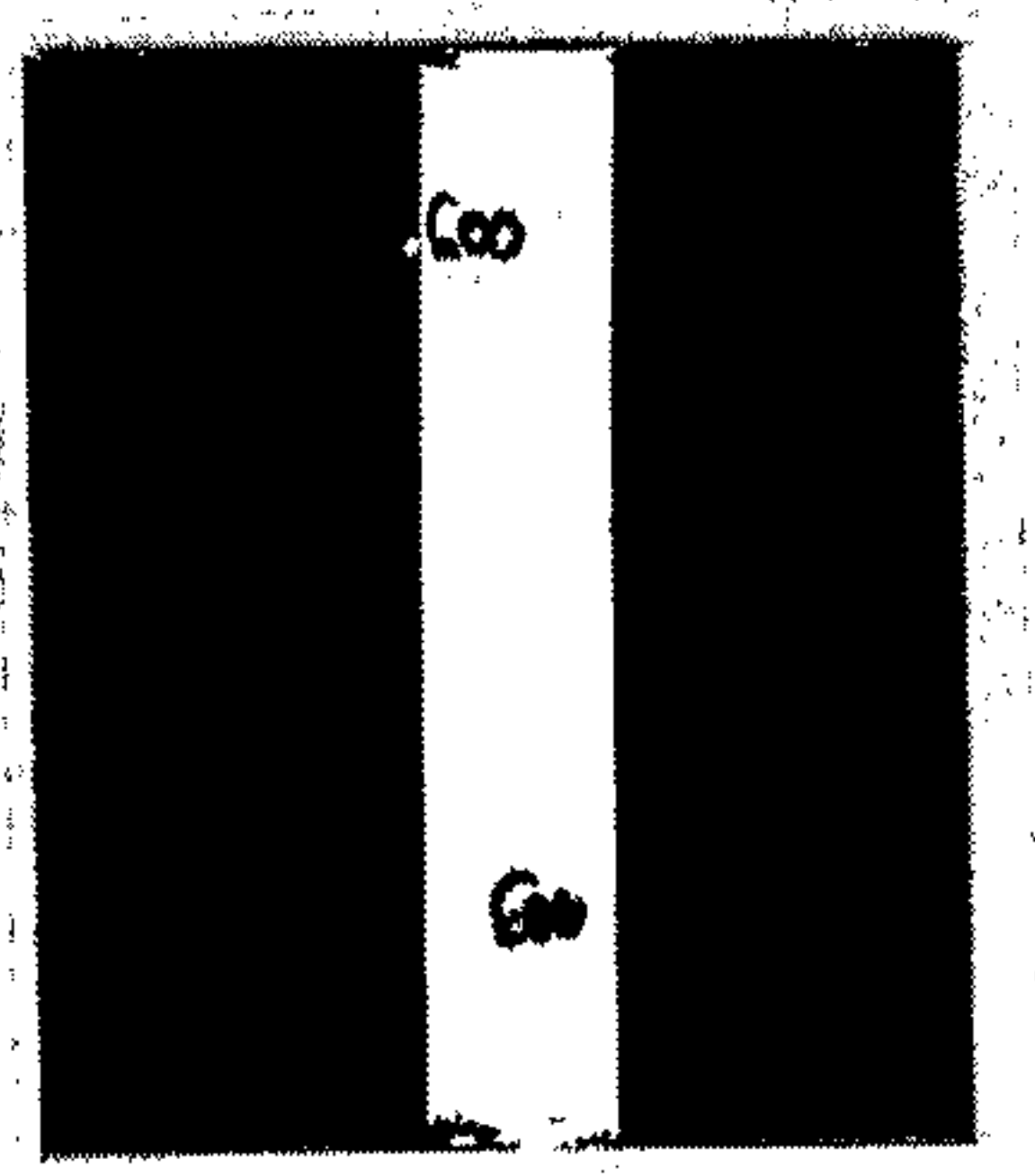


0.1% LiBH₄ (Proglyde)
SOWO (MPK/MEK), 30min

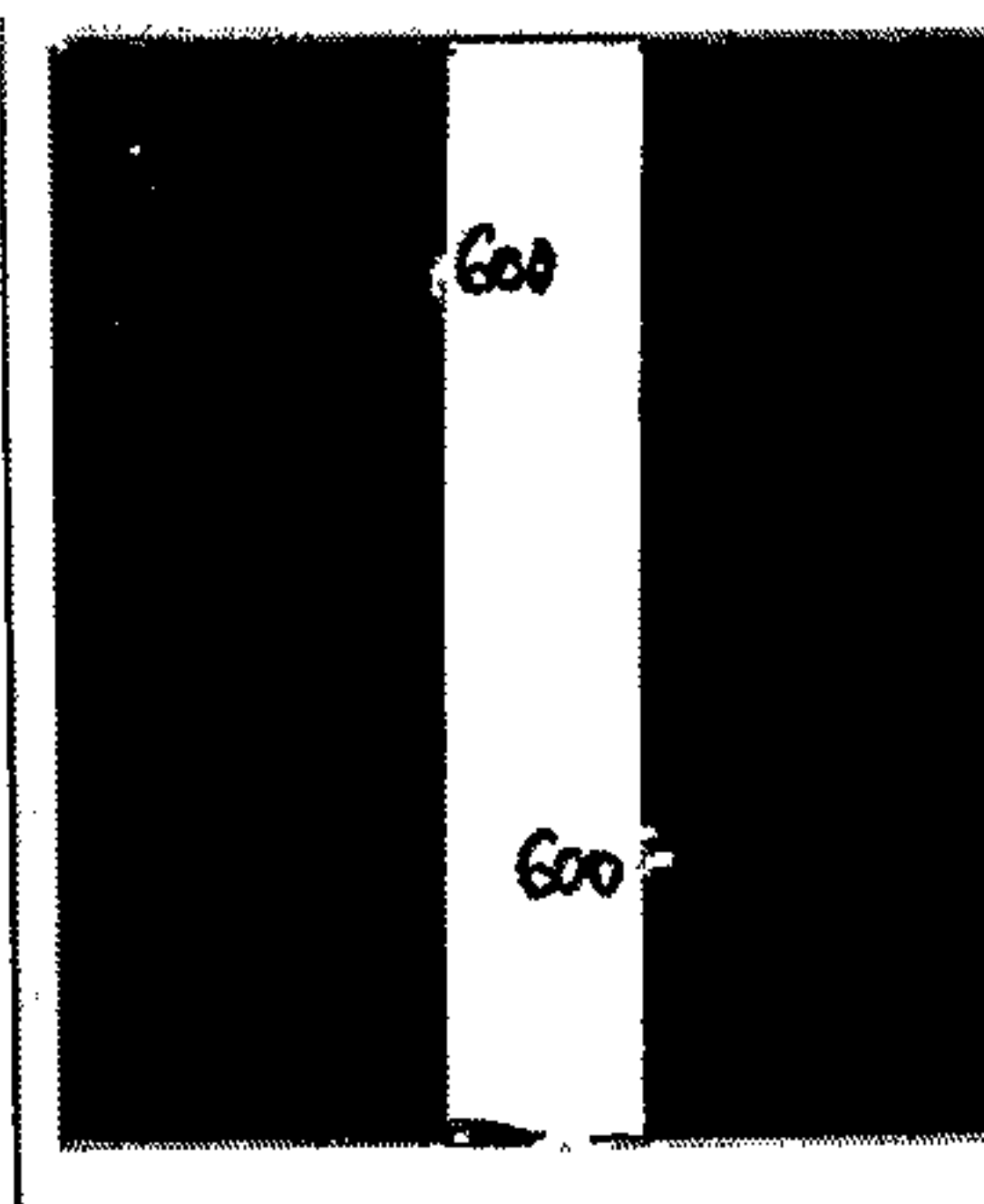
No UV Exposure:



Untreated



Sanded



0.1% LiBH₄ (Proglyde)
SOWO (MPK/MEK), 30min

The example illustrates that the reactivation protocol provides improved inter-coat adhesion for samples exposed to accelerated aging and UV exposure with similar result provided to those samples not exposed to UV.

This example is relevant to polyurethane coating that has undergone UV exposure for extended periods before requiring reactivation and over-coating, for example, in-service airplanes.

- 101 -

Example 31. Example shows a comparative paint stripping experiment between composite panels incorporating a primer, intermediate and polyurethane topcoat layers. In the example the stripping behaviour of aged Desothane HS 70846X white (C2) reactivated with the reduction method under the conditions listed prior to over-coating with Desothane HS S601X relative to untreated and sanded references.

t = initial



Top row (from left to right): 17, 18, 19, 20

Bottom row (left to right): 21, 22, 23, 24

17 -- Untreated

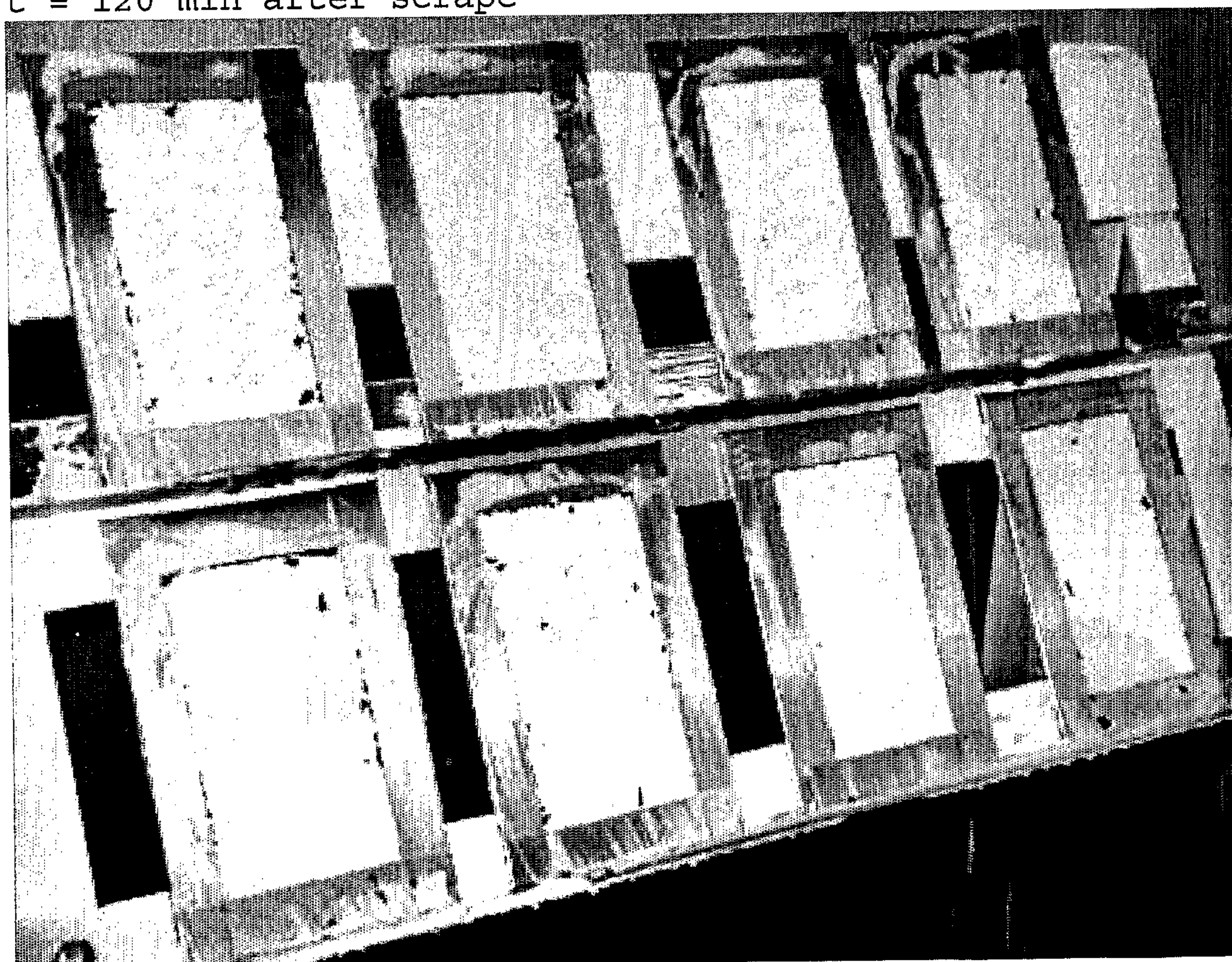
18 -- Sanded

19, 20 -- 0.05% Lithium Borohydride t-Butyl Acetate:
Proglyde 2:98 (SOHO)

21, 22 -- 0.01% Lithium Borohydride t-Butyl Acetate:
Proglyde 2:98 (SOLO)

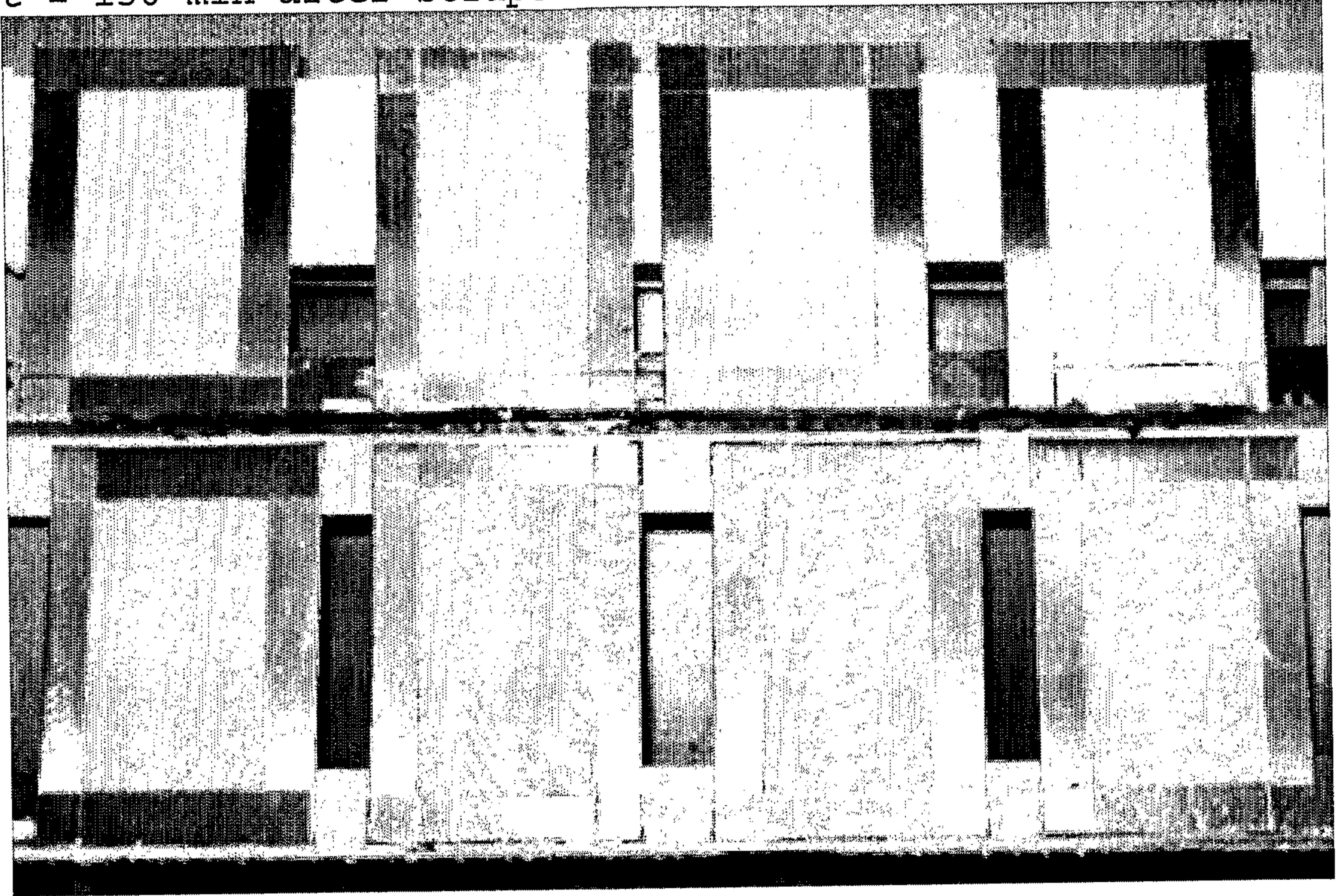
23, 24 -- 0.05% Lithium Borohydride t-Butyl Acetate:
Proglyde 2:98 (SOLO)

- 102 -

 $t = 120 \text{ min}$  $t = 120 \text{ min after scrape}$ 

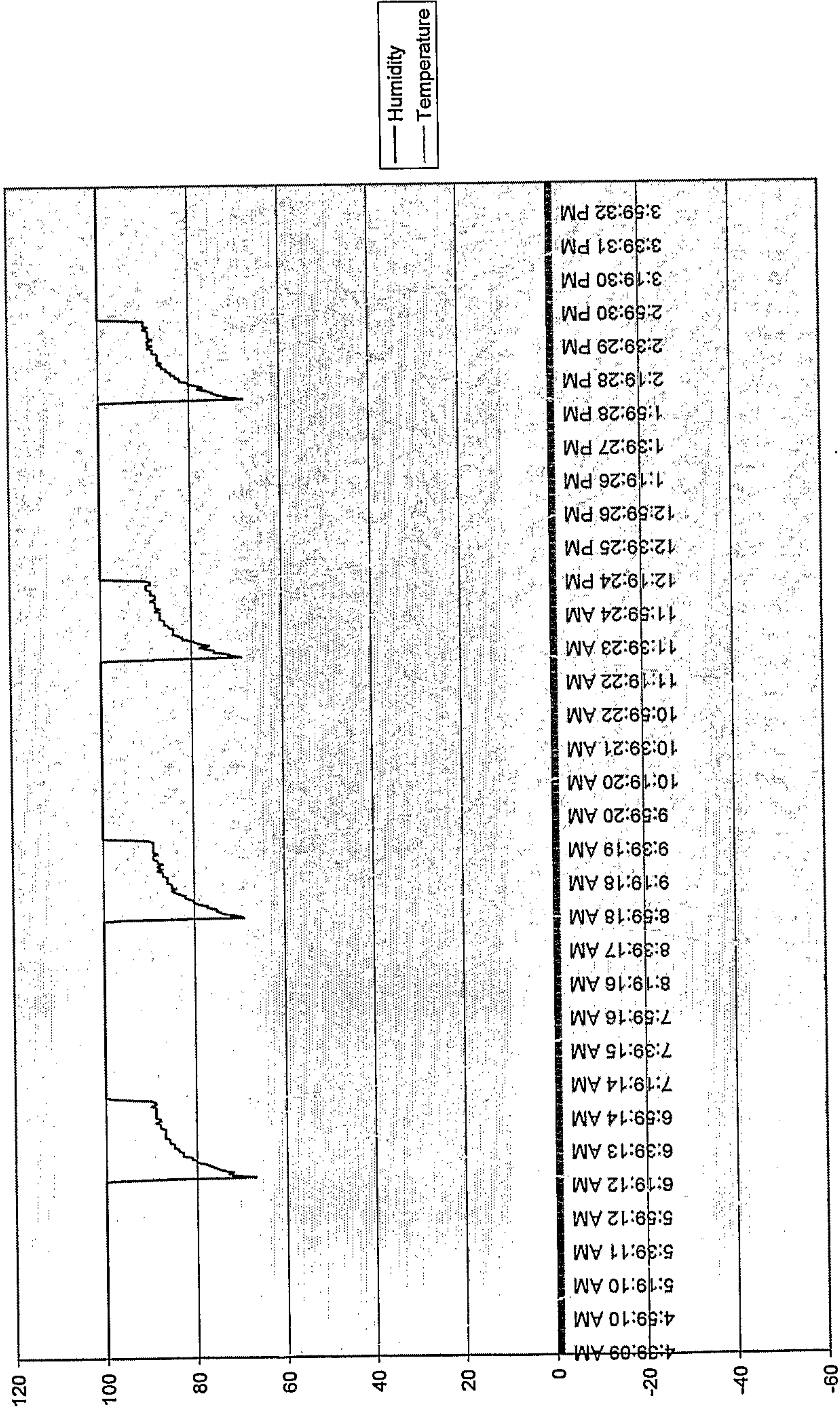
- 103 -

t = 150 min after scrape



The example illustrates that the chemically reactivated samples strip in a similar time frame to the sanded and untreated references.

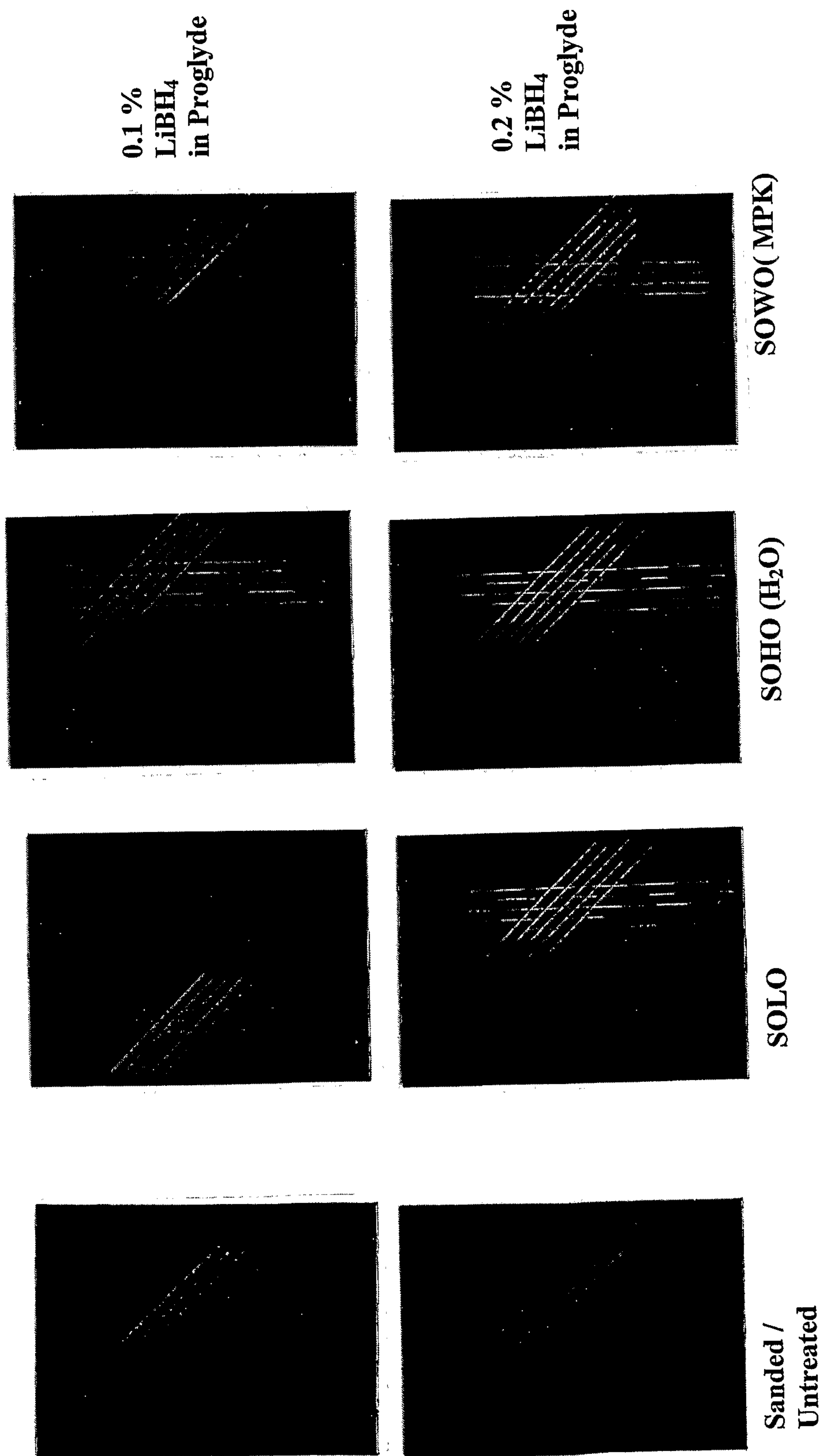
Example 32. The following example shows the impact on paint adhesion and appearance of Desothane HS S601X applied over untreated and reactivated aged Desothane HS 70846X coatings (themselves applied over primed aluminum) under cycling temperature and humidity for 500 cycles according to the protocol below.



Thermal cycle: from -40 °C to 71°C: 1Hr, 71°C to -40°C: 1.5Hr

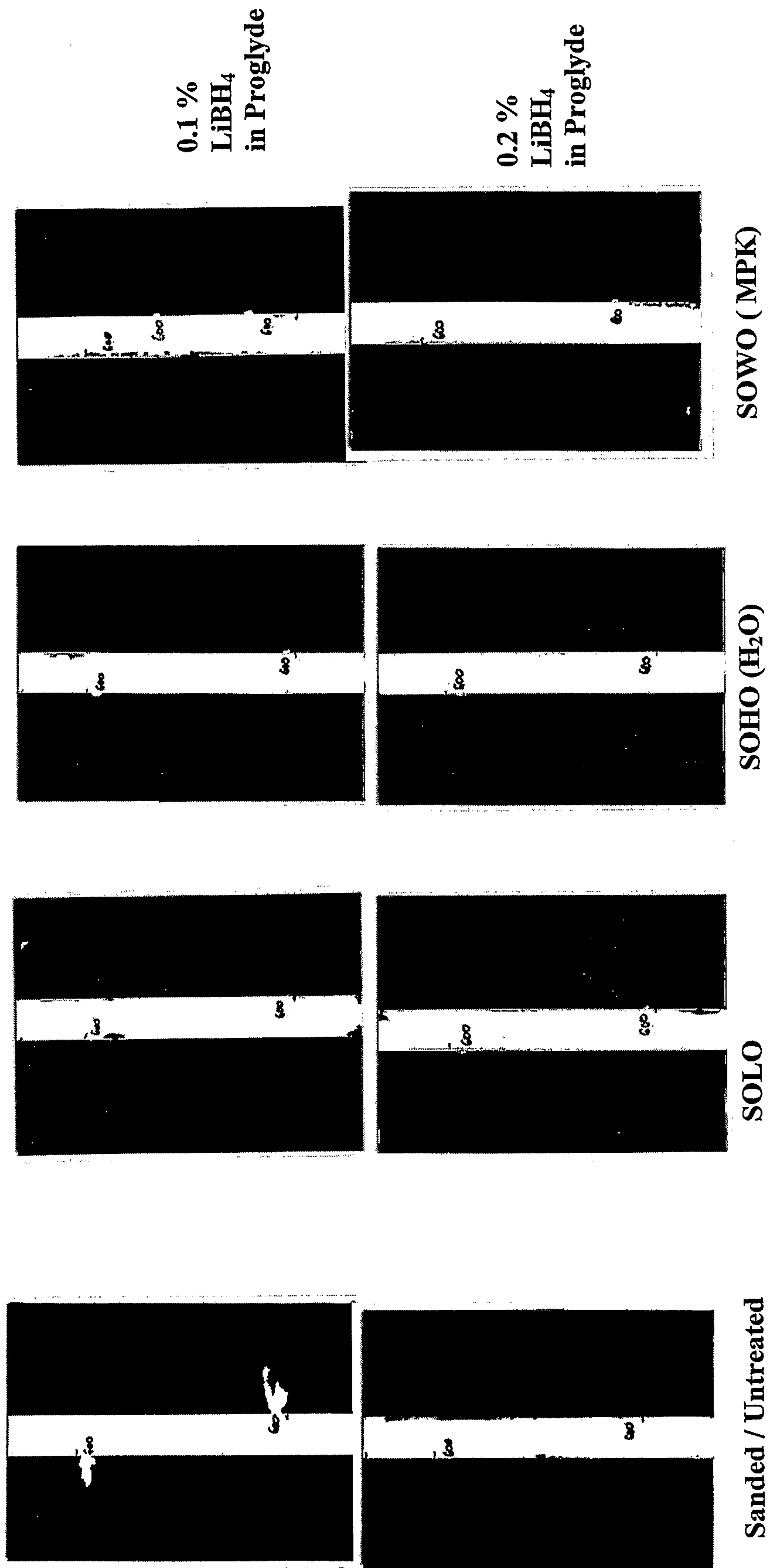
- 105 -

(i) Scribe adhesion was rated "10" for all samples

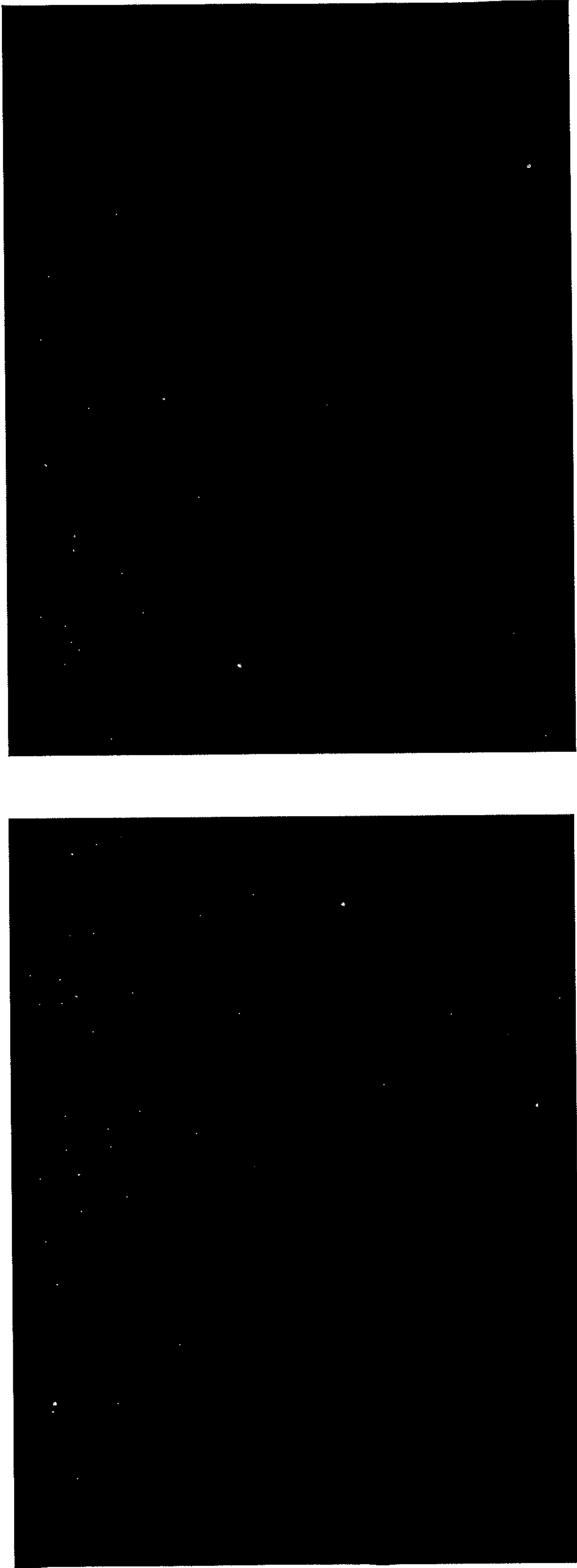


- 106 -

(ii) SIJA adhesion testing provided improved inter-coat adhesion similar to sanded following the cycling protocol.



(iii) No change of paint finish was noted in terms of “micro-cracking” or “pin head defect formation” following the cycling



Untreated

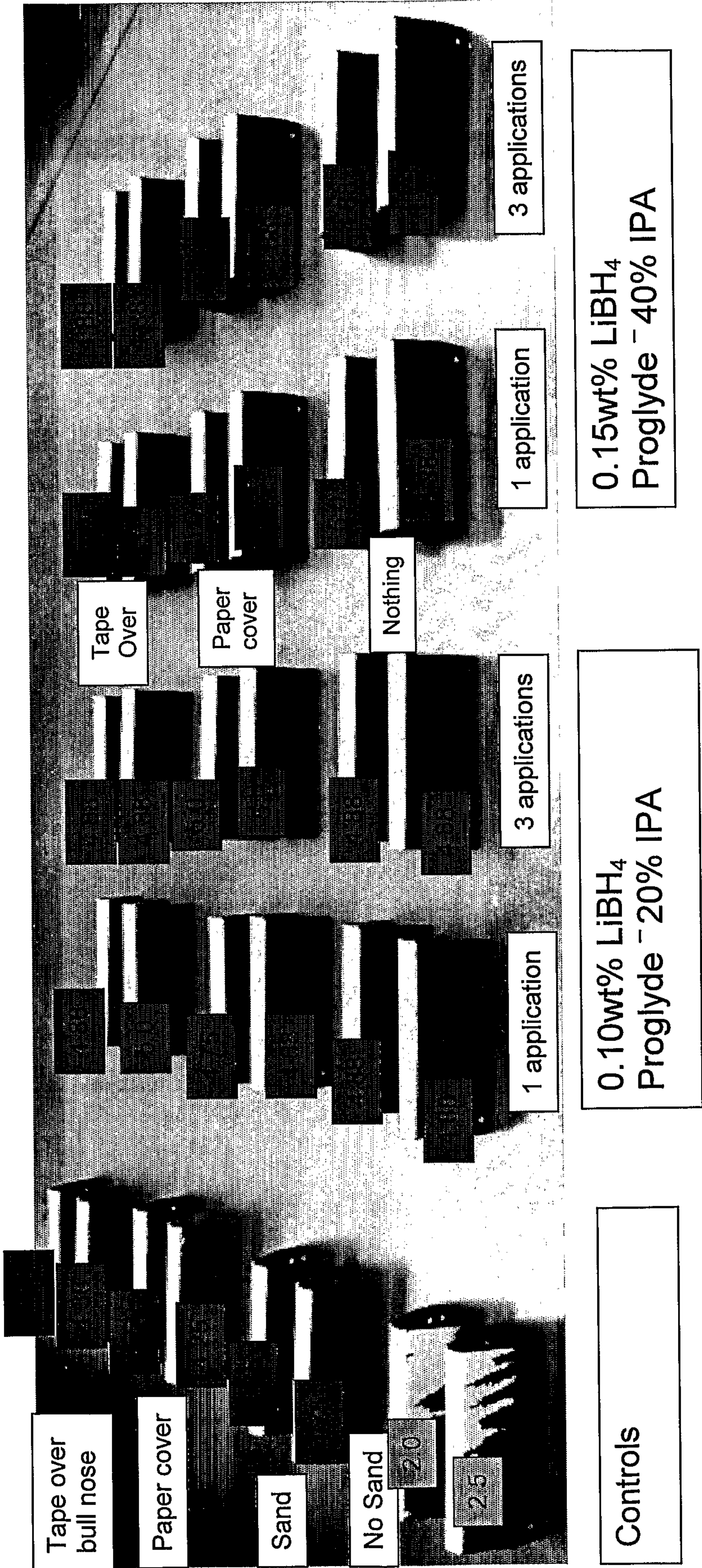
0.2% LiBH₄ Proglyde SOLO

The examples illustrate that no apparent reduction in adhesion or over-coat appearance occurs following cycling of temperature and humidity.

Example 33 Example demonstrates the paint adhesion and overcoat paint quality of rain erosion foils following simulation of typical paint masking hangar operations and heat cure. The examples show rain erosion foils, (incorporating primer, intermediate coating, and) topcoated with Desothane HS CA8000/B70846X base with C thinner cured /aged for 5 days at 3% RH and 120°F which were reactivated for 1.5 hours using SOHO (prior to wash off) or the SOLO process indicated.

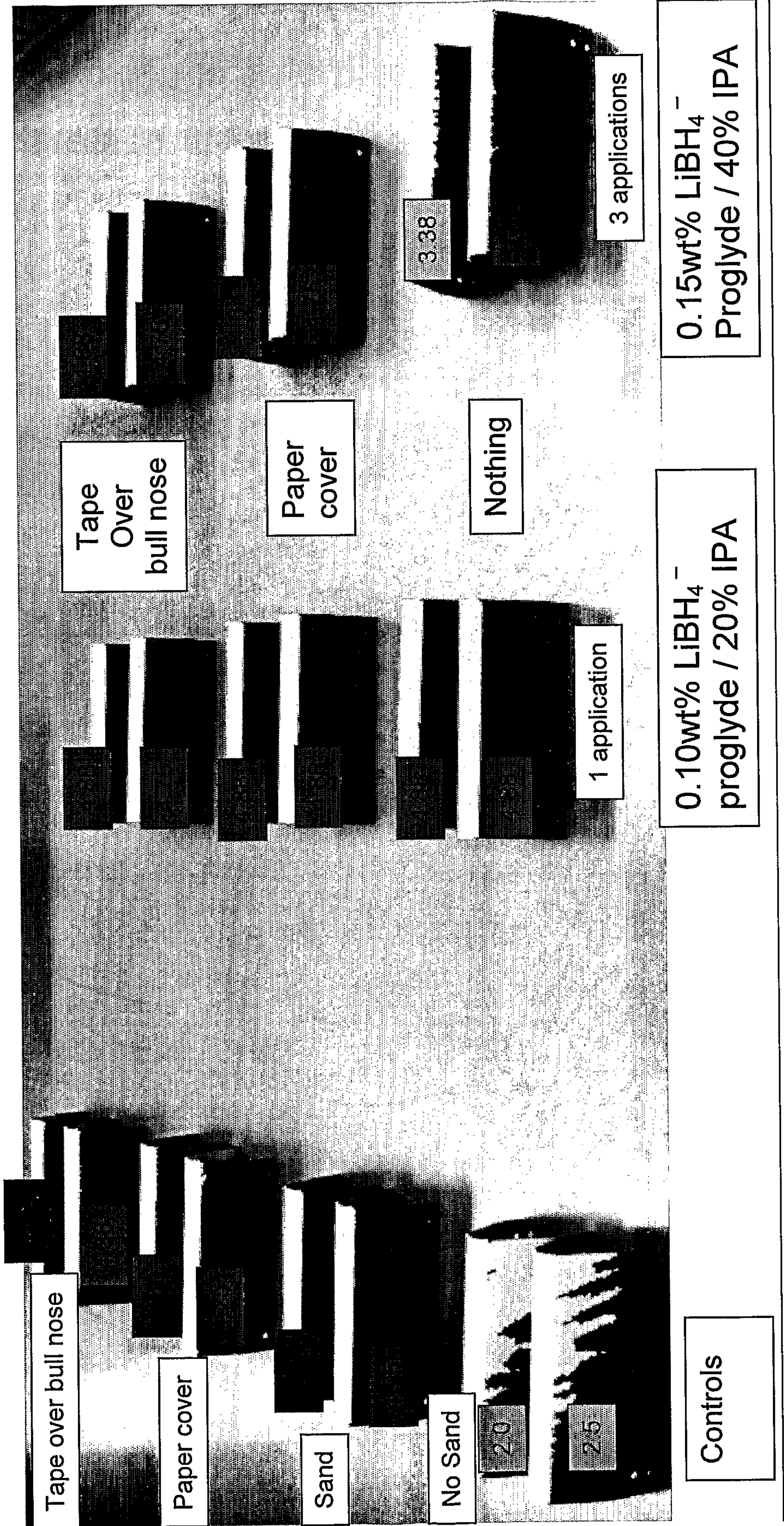
Following reactivation the samples either underwent a 6 hour 120F thermal cycle directly (then left under ambient conditions overnight) or alternatively prior to the thermal treatment were wrapped with Kraft paper or had 4 bands of masking tape perpendicularly wrapped around the samples. After removal of the paper and tape (wiping the tape lines with IPA) the samples were painted with Desothane HS CA8000/B50103 base with C thinner and following cure tested for adhesion and paint appearance relative to unreactivated and sanded controls.

(i) SOHO Reactivation



**1 application / 3 application refers to the number of times the reactivation solution was applied to the white paint.

(ii) SOLO Reactivation



**1 application / 3 application refers to the number of times the reactivation solution was applied to the white paint

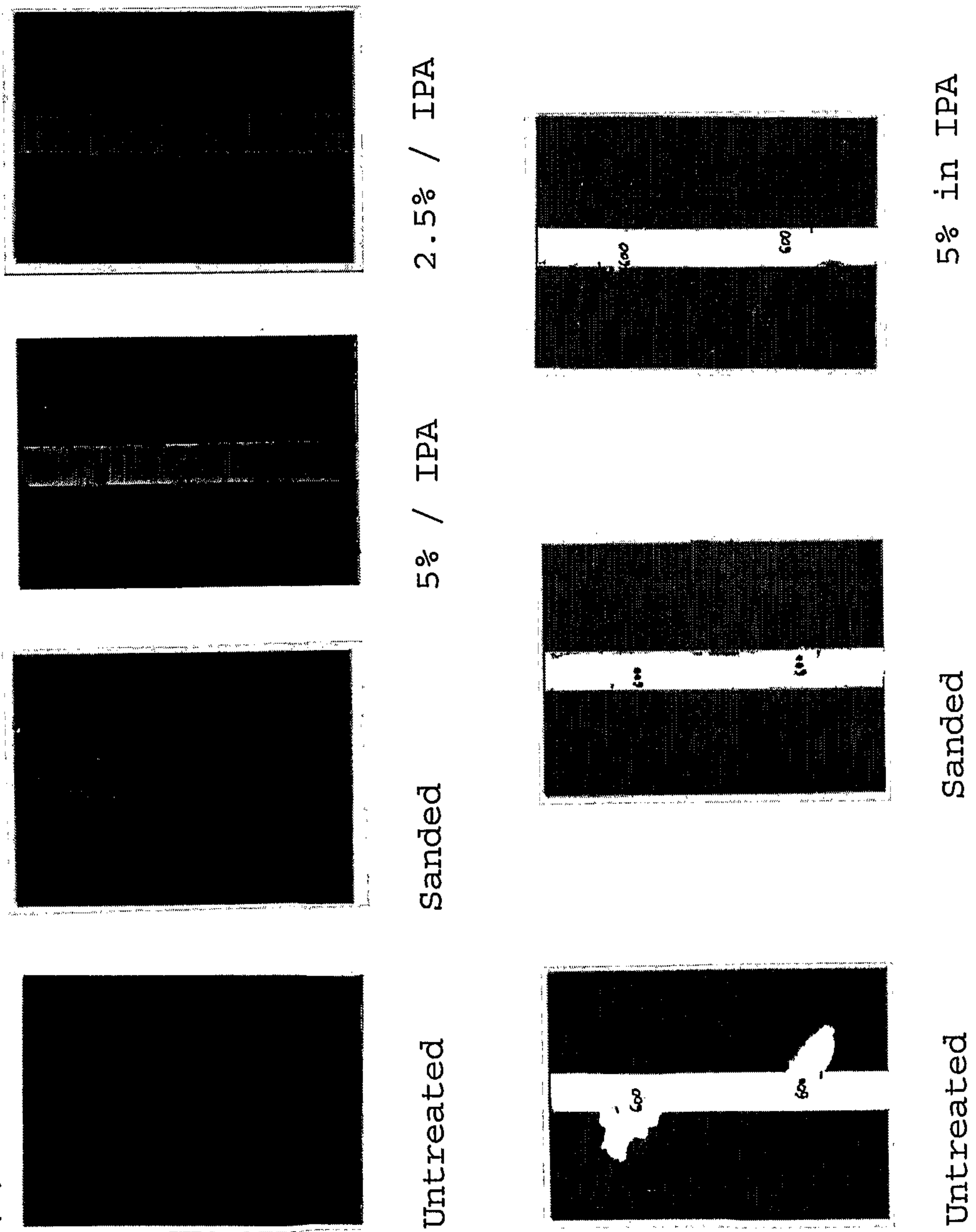
Results indicate:

- All the foils except for a random SOLO foil passed with good marks
- Excellent paint appearance was noted: No ghosting seen from the tape being on the foil that was cured for 6 hours and then being solvent wiped with IPA and no deleterious effects from application of Kraft paper were noted
- No significant difference from a 1 application situation and a 3 application situation

- 112 -

Example 34. The following example illustrates the inter-coat adhesion of aged Desothane 70846X and S400X red untreated and reactivated with tetraisopropyl titanate or sanded reference prior to over-coating with S601X blue and 5070X light blue.

(i) SIJA adhesion

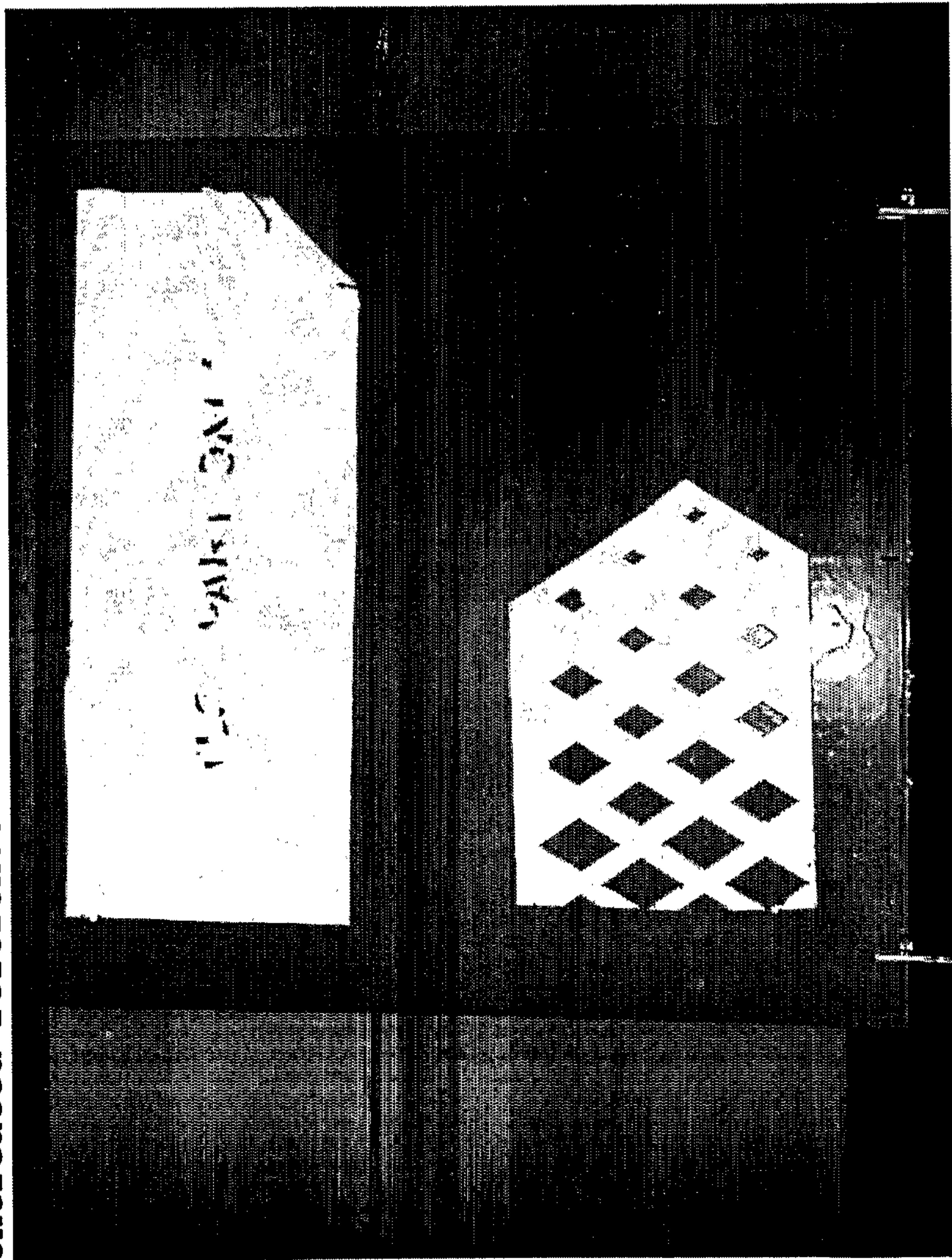


- 113 -

The example illustrates that treatment of the aged surface with tetraisopropyl titanate provides improved adhesion with different coloured aged polyurethane substrates and over-coatings.

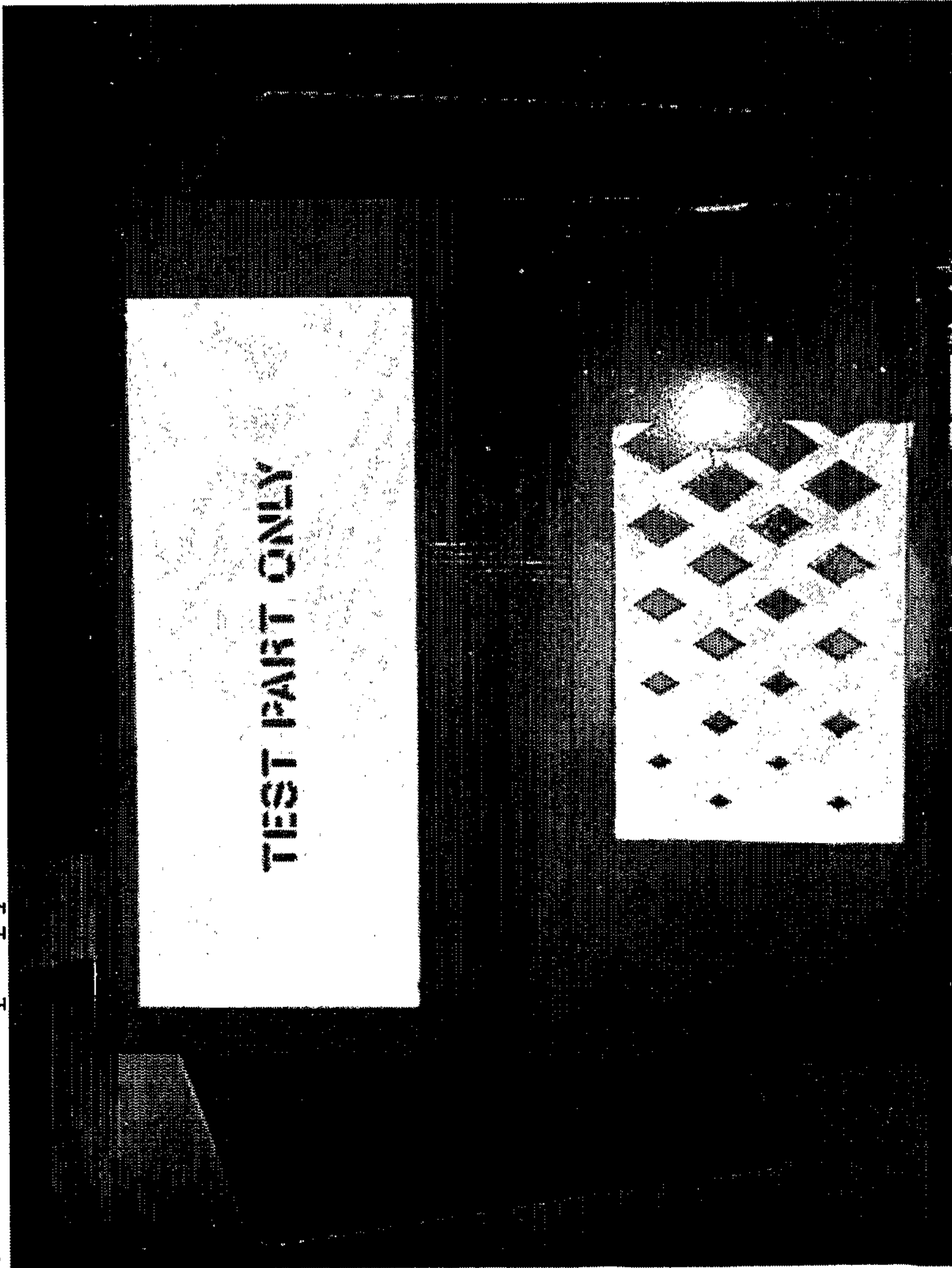
(ii) The following example demonstrate the reactivation solution based on tetraisopropyl titanate may be used in conjunction with materials such as stencils and design masks and tapes for the production of decorative painted finishes.

Untreated reference



- 114 -

5% tetraisopropyl titanate in IPA



The example illustrates that the use of the treatment solution based on tetraisopropyl titanate applied as a treatment solution for aged Desothane HS 70846X prior to over-coating with Desothane HS 5070X improved adhesion compared with the untreated reference and also provided minimal letter swelling or figure distortion, when it is applied SOLO directly over the design stencil prior to over-coating with polyurethane.

- 115 -

The scope of the claims should not be limited by the preferred embodiments set forth in the examples, but should be given the broadest interpretation consistent with the description as a whole. The present
5 embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method of activating an organic coating present on a substrate to increase
5 adhesion of the coating to a further coating and/or to other entities selected from adhesives, sealants, pin hole fillers and pressure sensitive decals or logos, the method comprising:

10 applying an activation treatment to the organic coating present on the substrate wherein the activation treatment consists of (1) a solvent, (2) a surface chemistry and/or surface topography modifying agent which facilitates surface reduction, surface exchange or transesterification, or light induced surface modification, and (3) optionally an additive, wherein:

15 the activation treatment increases adhesion of a further coating and/or other entities selected from adhesives, sealants, pin hole fillers and pressure sensitive decals or logos to the coating on the substrate, and wherein

20 the agent which facilitates surface reduction is a reductant;

the agent which facilitates surface exchange or transesterification is a metal alkoxide or a chelate thereof; and

25 the agent which facilitates light induced surface modification is a free radical initiator or a combination of a free radical initiator with a tertiary amine and/or a mono or multi-functional unsaturated species.

2. The method according to claim 1, wherein the surface chemistry and/or surface topography modifying agent is a reductant.

30

3. The method according to claim 1 or claim 2, in which the reductant is selected from sodium borohydride, lithium borohydride, potassium borohydride, zinc borohydride, calcium borohydride and alkoxy, acetoxy and/or amino derivatives thereof; sodium cyanborohydride; borane and borane complexes; lithium aluminium
35 hydride; diisobutyl aluminium hydride; calcium hydride; sodium hydride; sodium bis(2 methoxyethoxy) aluminiumhydride); and selectrides.

4. The method according to claim 1, wherein the surface chemistry and/or surface topography modifying agent is a metal alkoxide or a chelate thereof.
5. The method according to claim 4, in which the metal alkoxide or chelate thereof contains a metal selected from Groups 4A, 5A, 3A, 4B, 5B and 6B, Li, Be, Mg, La, Fe, Zn, Nd and Gd.
6. The method according to claim 5, in which the metal alkoxide or chelate thereof contains a Group 4B metal.
- 10 7. The method according to claim 6, in which the Group 4B metal alkoxide is a titanium alkoxide or a zirconium alkoxide.
- 15 8. The method according to claim 7, in which the titanium alkoxide or zirconium alkoxide is a tetra-C₁₋₈alkyltitanate or a tetra-C₁₋₈alkylzirconate.
9. The method according to claim 8, in which the tetra-C₁₋₈alkyl titanate or tetra-C₁₋₈alkyl zirconate is tetra-propylzirconate or tetra-n-propyltitanate.
- 20 10. The method according to claim 9, in which the tetra-propyltitanate or tetra-propylzirconate is tetra-n-propyltitanate or tetra-n-propylzirconate.
- 25 11. The method according to claim 1, wherein the surface chemistry and/or surface topography modifying agent is a free radical initiator or a combination of a free radical initiator with a tertiary amine and/or a mono or multi-functional unsaturated species.

- 118 -

12. The method according to claim 11, in which the free radical initiator is a visible light activated initiator selected from camphorquinone and derivatives thereof; benzophenone and derivatives thereof; diethylaminobenzophenone; and phenylphosphineoxide derivatives.

5

13. The method according to claim 12, in which the tertiary amine agent is selected from N,N-dimethyl toluidine, N,N-dimethylamino ethylmethacrylate, methyl imidazole, NNN'N'tetramethyl-1,4-butane diamine and NNN'N'tetramethylphenylenediamine, and in which the multi-functional unsaturated
10 species is selected from acrylates, methacrylates and acrylamides.

14. The method according to any one of claims 1 to 13, in which the modifying agent is present in an amount of at least 0.001% based on the total weight of the combination of solvent and agent.

15

15. The method according to claim 14, in which the modifying agent is present in an amount in the range of 0.01% to 20% based on the total weight of the combination of solvent and agent.

20 16. The method according to any one of claims 1 to 15, in which the modifying agent is prepared in-situ from its constituent components.

17. The method according to any one of claims 1 to 16, in which the solvent is an organic solvent selected from at least one of ester based solvents, ketones,
25 alcohols, ethers, amides, aromatics and halogenated solvents.

18. The method according to claim 17, in which the solvent is selected from ethyl acetate, ethoxyethyl acetate, isopropyl acetate, tertiary butyl acetate; methyl propyl ketone, methyl amyl ketone, methyl isoamyl ketone, methyl ethyl ketone; ethanol, methanol, ethoxyethanol, n-propanol, isopropanol, butanol, tertiary butanol, secondary butanol, ethylene and propylene glycols and C₁₋₆ alkyl ethers thereof, tetrahydrofuran and N-methyl pyrrolidinone.

19. The method according to claim 17, in which the solvent is a combination of dipropylene glycol dimethyl ether : tertiary butyl acetate; dipropylene glycol dimethyl ether: isopropanol, n-propanol, methanol, ethanol, n-butanol, isobutanol, secondary butanol, tertiary butanol, ethoxy ethanol and/or ethylhexanol; ethylene glycol monomethyl ether: ethanol, methanol, ethoxyethanol, isopropanol and/or n-propanol; dipropylene glycol-monomethylether, dipropylene glycol-monobutylether, and/or dipropylene glycol; combinations tetrahydrofuran: triglyme; tetrahydrofuran: dipropylene glycol dimethylether; methylethyl ketone: ethoxyethyl acetate; methyl amyl ketone: ethoxyethyl acetate; N-methyl pyrrolidinone: ethyl acetate; ethyl acetate: benzyl alcohol; dipropylene glycol dimethyl ether: polyethylene; and methyl propyl ketone: methyl ethyl ketone.

20. The method according to claim 17, in which the solvent is an alcohol or ether or combination thereof.

21. The method according to claim 20, in which the alcohol is selected from an alcohol having a molecular weight of less than about 150 and the ether is selected from an ether having a molecular weight of less than about 300.

22. The method according to claim 20 or claim 21, in which the alcohol is selected from isopropanol or n-propanol and the ether is dipropylene glycol dimethyl ether.

- 120 -

23. The method according to claim 20, in which the solvent is a combination of isopropanol or n-propanol and dipropylene glycol dimethyl ether.
24. The method according to claim 23, in which the dipropylene glycol dimethyl ether is present in an amount of less than 50% based on the total weight of the combination of isopropanol or n-propanol and dipropylene glycol dimethyl ether.
25. The method according to any one of claims 1 to 24, in which the solvent is present in an amount in the range of 80% to 99.99% based on the total weight of the combination of solvent and agent.
26. The method according to any one of claims 1 to 25, in which an additive is also applied to the organic coating.
27. The method according to claim 26, in which the additive is selected from at least one of rheology modifiers, film formers, wetting agents, surfactants, dispersants, anti foaming agents, anti corrosion reagents, stabilizers, levelling agents, pigments, dyes and Lewis acids.
28. The method according to claim 27, in which the additive is selected from at least one of rheology modifiers, surfactants, dispersants, anti foaming agents, anti corrosion reagents, stabilizers, levelling agents, pigments and dyes.
29. The method according to claim 28, in which the additive is selected from at least one of surfactants, anti foaming agents, anti corrosion reagents, stabilizers, pigments and dyes.

- 121 -

30. The method according to claim 29, in which the additive is selected from at least one of stabilizers, pigments and dyes.

31. The method according to any one of claims 26 to 30, in which the additive is present in an amount of less than about 10% based on the total weight of the combination of solvent, agent and additive.

32. The method according to any one of claims 26 to 31, in which the solvent, agent and additive when present are applied either simultaneously, sequentially or separately.

33. The method according to any one of claims 26 to 32, in which the solvent, agent and additive when present are applied simultaneously in the form of an activation treatment.

34. The method according to any one of claims 26 to 33, in which the solvent, agent and additive when present are applied via a spray, brush, dip, knife, blade, hose, roller, wipe, curtain, flood, flow, mist, pipette or combinations thereof.

35. The method according to any one of claims 1 to 34, in which the organic coating is a polyurethane, epoxy, polyester, polycarbonate and/or acrylic coating.

36. The method according to any one of claims 1 to 35, in which excess solvent and/or agent are removed by solvent or water rinsing; dry, water or solvent wiping; air or gas knife; vacuum application; squeegee; and/or natural or forced convection evaporation.

- 122 -

37. The method according to claim 3, wherein the selectride is potassium tri-sec-butylborohydride.

38. A coated substrate having an activated coating, wherein the adhesion of
5 the coating to a further coating and/or other entities selected from adhesives, sealants, pin hole fillers and pressure sensitive decals or logos has been enhanced by application of the coating method according to any one of claims 1 to 37.

39. The substrate according to claim 38, in which the substrate is a metal,
10 composite, plastic, elastomer or a material containing, glass, wood or fabric.