

## Polymer coating interactions with chemically aggressive agents

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**The physico-chemical and chemical phenomena occurring between coatings and chemical agents in contact, are studied. Several experimental techniques for coatings characterization in such environments are described, with suggestions and criteria for choice, defining conditions and design of testing methods for coatings evaluation in chemically aggressive environment**

*Key words:* polymer materials, coatings, protective coatings, chemical properties, spectrometry, colorimetric analysis, micro hardness, testing method.

### Introduction

CONTEMPORARY development trends in the area of polymer coatings for military application, allow comprehending the quality improvement of this class of materials in three basic directions, imposed by specific functional conditions. Apart from the conventional quality components required for coatings for military application, physical-mechanical and camouflage properties, characterization of coatings behaviour in chemically aggressive environment is involved in recent standardization documents.

Chemical and physical-chemical characteristics of coatings are in permanent focus of studies in the field of paints and coatings investigation and production. However, having in mind that coat is only a part of a complex article and serves as the first barrier in its interaction with the surroundings. Of special interest is the investigation of particular coating pairs mutual influence – aggressive agent, chosen with respect to real conditions of application. Initial level should be the definition of the testing procedures and evaluation criterions, and its implementation in material quality standardization, as a prerequisite to adequate coating function.

Chemical characteristics of organic coating materials have been subject of several previous MTI investigation programmes, principally referring to resistivity to aggressive agents occurring in conventional exploiting conditions (acids, alkali, mineral fuels and oils etc.), but also in some cases, to special aggressive agents like ingredients of decontamination fluids. Despite the difficulties occurring in direct application of those investigation results in material quality control procedures, due to lack of evaluation criteria, complexity of testing techniques etc., they were excellent basis in research activities for selection, formulation and development of new coating materials.

The objectives of activities described in this paper are:

- The choice and systematisation of testing methods in current practice, testing methods applied in foreign armies practice and other methods that could be modified to be suit certain demands, with performance analysis of

each method with respect to material quality control requirements regarding chemical and diffusion characteristics.

- Defining of the conditions and procedure parameters for experimental samples testing by selected methods
- Recommendation of a suitable set of chemical characteristics testing methods to use in coating quality control standardization documents, according to:
  - feasibility in existing laboratory potentials
  - standardisation capability according to SNO 0001/00,
  - reproducibility, comparability and selectivity.

### Chemical characteristics testing

One of the basic functions of the coating is to form a barrier between the surface of the object and its surroundings.

When the coating is in contact with chemical agents from the surroundings, interaction can occur on the contact surface, causing mechanical and chemical damages (abrasion, destruction etc.), or agent can penetrate the body of the coating, inducing physical-chemical and chemical reactions (swelling, degradation etc.). Since the usual average thickness of the conventional coatings is 30  $\mu\text{m}$ , so that the values of the diffusion coefficients in solid state are in the range of  $1\mu\text{m}^2/\text{s}$ . The overall analysis shows that agents with the best diffusion characteristics need few dozen seconds to reach the substrate through the coating [3].

It should not be taken for granted that all interactions of the coating with alien agents are necessarily harmful. Almost all coatings used in building construction are characterized to have good diffusion properties for vaporising. Some marine paints, the so called self-abraded, are capable of preventing the growth of marine organisms on the body of the vessels and its negative effects (increase of fuel consumption).

Whether interactions are undesirable or not, they are expected and therefore it is necessary to define the testing methodology which can be implied in investigation and re-

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search phases of new products development, as well as in material quality control process by standardized procedures. The subject of the analysis given in this report being - defining the procedure and requirements for material quality control, will be founded on the analysis of macro phenomenon occurring in real systems substrate, coating, surrounding, with informative comments of phenomenon on micro structural level, when necessary.

Depending on paint formulation, film application and forming conditions, type and morphology of substrate, coatings based on polymers are more or less porous. Extent of porosity is determined by number, shape and dimension of the pores in the area unity (approximation of one dimension – thickness – is legitimate because of coating specific geometry).

Assume that porosity, as the result of defects caused by wrong formulation of paint, poor surface preparation etc. is out of scope. In other words, if porosity as internal characteristic of the material is the subject, it should be emphasized that sub micrometric dimensions are in question, so fundamental studies on this level demand state-of-the-art equipment and inadequate expenses compared to the expected effects. However, numerous studies deal with problems in this field.

Widely accepted systematisation of the possible mechanisms that take place during contact of coating with alien molecules, as suggested by J.C. Long and H.F. Payne in the study of water molecule penetration through the structure of coating based on alkyd resin:

- mass transfer by free movement of water molecules through discrete pores of relatively wide size, compared to molecular size,
- water molecule adsorption on the intramolecular surfaces of polar macromolecules, followed by the development of imbibition pressure which distends the coating and permits volume diffusion of moisture through it,
- solution of water in highly polar groups in polymer chains with subsequent diffusion in accordance with Fick's law, followed by formation of secondary bonds and other characteristics of real solutions.

The first mechanism (Fig.1) of the three suggested above, appears in cases of misbalance in pigment – binder ratio, where presence of solid particles in extent, disables the macromolecules of a vehicle to arrange in a relaxed position with minimum of retained stress and optimal packaging density, generating the conditions for cavitation porosity. Such a case occurs in primer coatings, where porosity, i.e. permeability, plays a certain role in the regular function, regarding the electrochemical character of this class of coatings.

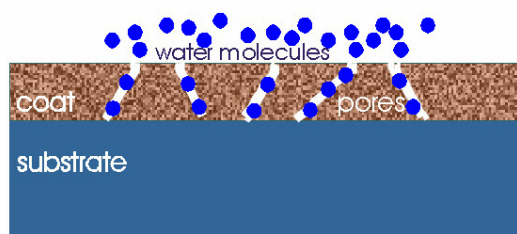


Figure 1.

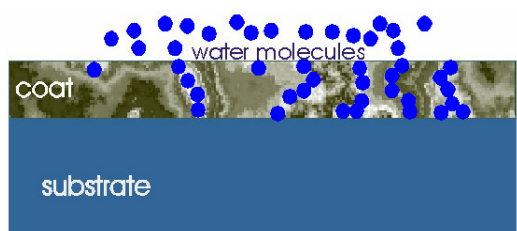


Figure 2.

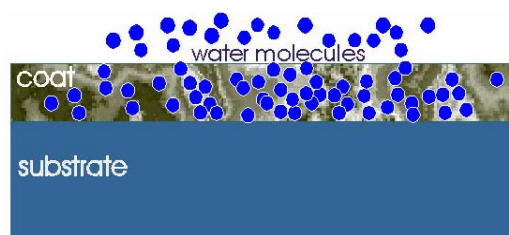


Figure 3.

The second case (Fig.2), which is the most common, does not allow the existence of single, discrete pores in the coating, which are formed by agent molecules moving through polymer structure and their retention in suitable places, in dynamical balance.

The third mechanism (Fig.3) is possible in rare cases when, for particular reasons, high polar resin is used as a vehicle (for instance in antistatic or electro conductive coatings), as well as when non polar agent (for instance aliphatic hydrocarbon) is in contact with the coating based on highly low polarity (also a rare situation due to problems concerning application, and flow of paint).

Regardless of the mechanism, pores formation provokes a dramatic increase in contact surface, thus all coating chemical agent interaction effects are quantitatively multiplied.

If the mean diameter of a pore is  $10\text{\AA}$ , and the distance between two neighbouring pores is  $5000\text{\AA}$ , meaning that total pores area represents four parts per billion of surface, the enlargement of active contact surface, compared to ideally non-porous coating, is about 30%, measured by precise gas absorption techniques. Further increase in pores participation causes the enlargement of active surface size with geometrical progression (if pores takes four by 10.000 parts of surface area, active surface is multiplied 30 times), and process is self-accelerated by making distances between macromolecules larger and creating a space for new coming agent molecules inside the coating structure [4].

As alien molecules approach the molecules of coating ingredients, all chemical reactions thermodynamically possible in certain conditions start to propagate.

If the consideration is limited to a vehicle resin only, which is predominantly responsible for chemical contacts with the surroundings, the number of possible critical reaction sites is reduced to bonds in main macromolecular chain, on whose stability mechanical properties of solid coating structure depends, as well as the bonds in side chains in branched polymers which additionally strengthen the structure and finally numerous secondary bonds which consolidate the polymer matrices structure of coating.

The most frequently occurring bonds, listed by stability (i.e. strength), are saturated carbon – carbon bonds, ether (epoxy) bonds, urethane bonds, amide bonds, amine bonds, ester bonds, in main as well as in side macromolecular chains, and also all secondary bonds established between polarized atoms of different functional groups.

Chemical and physical changes in the coating will occur in certain intensity, depending on the number and site of chemical reactions in progress. Reaction products will participate in the total diffusion process according to the same physical principles as molecules of agent, since, after the time required, dynamical balance, of chemical reactions and mass transfer, establishes.

Consequently, the kinetics of the whole agent – coating interaction process, will depend on:

- Physical chemical parameters of a particular coating – agent case (diffusion, adhesion etc.)

- Structural and morphological characteristics of the coating (porosity, micro voids existence, thickness etc.),
- Chemical characteristics of the vehicle resin (cross linking level, strength and number of primary and secondary bonds etc.),
- Chemical characteristics of the agent,
- Extensive thermodynamic parameters of the system, first of all temperature,

thus a complete theoretical modelling of the process, with known and measurable elements associated in valid relations, is practically impossible.

The previous survey provides conclusions that are sufficient for establishing the necessary initial conditions for the development of methodology that permits the qualitative and quantitative evaluation of diffusion and chemical influence of certain agents on the specified characteristics of a particular coating:

- The measure for degree of diffusion process is mass of the diffuser per unit of the coating volume, or relative enlargement of coating volume by swelling, in equilibrium stage,
- The measure for degree of chemical influences are measurable changes of relevant physical characteristics of coating,
- Criteria for evaluation are valid exclusively for particular coating – agent couple,
- Criteria for evaluation are valid exclusively for defined terms of temperature and duration of contact.

Briefly, the correct test methodology must define the following:

- the temperature and duration of the contact,
- the chemical composition of the agent,
- the testing procedure that ensures an accurate determination of absorption, direct, by measurement of quantities, or indirect, by observing the selected relevant mechanical characteristics of the coating, and
- the criteria for final quality evaluation of paint.

From the range of methods for diffusion process quantification, those that meet the following criteria will be presented:

- the feasibility with present available personal and laboratory resources,
- the results accuracy
- the simplicity of technique.

#### Testing of coating chemical resistance by contact method

The oldest and most commonly used method for coating chemical resistance testing is based on the description of the coating status after it has spent a certain period of time in contact with the defined medium in controlled conditions.

The coating status description, namely the comparison with the status before the contact initiation, can be quantitative through the measurement of some exact characteristic with limited level of allowed changes or qualitative, through arbitrary, descriptive evaluation regarding the recommended criterion.

Manner of active medium choice can be:

- selective, regarding the real exploiting conditions (for instance, paint for parts of automotive hydraulic brakes system must resist the attack of hydraulic fluid based on vegetative oils with a number of additives, so this particular fluid is defined as contact medium), or
- representative, as the most suitable representative of a group of materials with similar chemical characteristics (for example, butter as a medium for resistance testing of paints

for kitchen furniture represents a variety of nutritive materials of similar chemical composition and consistency).

The first approach gives more accurate and reliable results, as long as exploiting conditions are constant and controlled.

Contact may be realized by immersing a sample of coating (in appropriate form, usually applied on steel panel) into the medium, or by applying the medium (by means of drops or appropriate carrier impregnated with medium) to the defined surface of the coating sample.

Testing conditions are attempted to resemble as much as possible the real exploiting conditions, or defined in such a way to accelerate the expected effects (by rising the temperature, concentrations etc.), resulting in reducing the time for achieving the experimental results, which then may be converted to real conditions by applying additional calculation with empirically determined coefficients.

In order to elaborate and determine the procedure parameters, samples of polyurethane paint of alien and proper origin were investigated, varying the mode of contact with media of different chemical nature (immersing of coating sample and applying the medium to surface of coating), and measuring all the measurable characteristics of coating, prior and after the exposure. The results are displayed in tables T-2 to T-5.

In order to elaborate and determine the procedure parameters, samples of polyurethane paint of alien and proper origin were investigated, varying the mode of contact with media of different chemical nature (immersing of coating sample and applying the medium to surface of coating), and measuring all the measurable characteristics of coating, prior and after the exposure. The results are displayed in tables T-2 to T-5.

The tested samples are designated according to Table 1:

**Table 1.** Designation of samples

designation	origin	type	hue
D2-1	D (proper)	2 (two pack)	1 light green
D2-2			2 brown
D2-3			3 black
I1-Z	I (alien)	1 (single)	Z dark green
I1-B			B brown
I1-C			C black
I2-Z		2 (two pack)	
I2-B			
I2-C			

**Table 2.** Chemical resistance of urethane two-pack paint (SNO 1564, SNO 7511, ton 1), contact method, sample D2-1

Medium	Testing conditions		Characteristic			
	Temperature °C	Time of exposure h	Coating appearance (swelling, blistering, cracking)	Gloss % (angle 45°)	Hue %	Hardness s
Water	23±2	0	-	14,5	17,0	122
		24	✓	18,0	17,0	121
1N HCl	23±2	0		13,5	17,0	-
		24	✓ (1)	-	-	-
0,1N HNO <sub>3</sub>	23±2	120	○	13,5	17,5	-
		0		14,0	17,0	-
5% Na <sub>2</sub> CO <sub>3</sub>	23±2	120	✓ (1)	13,5	17,5	-
		0		14,5	17,5	-
		120	✓ (1)	14,0	18,0	-

25% HCl	23±2	0		15,0	16,5	-
		24	✓ (1)	14,0	21,0	-
25% HNO <sub>3</sub>	23±2	0		13,5	16,5	-
		1	●	-	-	--
25% H <sub>2</sub> SO <sub>4</sub>	23±2	0		14,0	17,0	-
		24	○	-	-	-
25% C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> xH <sub>2</sub> O	23±2	0		13,5	16,5	-
		24	✓	13,5	17,0	-
25% CH <sub>3</sub> COOH	23±2	0		13,5	17,0	-
		24	✓	12,5	18,0	-
25% NaOH	23±2	0		14,0	17,0	-
		24	✓ (1)	13,5	23,0	-
Mineral oil:						
insulating lubricant, JUS B.H3.561	23±2	0		13,5	17,0	100
		24	✓	13,5	16,5	106
engine lubricant typ D, JUS B.H3.169	100±2	0		14,5	17,5	102
		96	✓	15,0	17,0	115
Liquid fuels:						
diesel fuel, JUS B.H2.410	50±2	0		15,0	13,5	110
		120	✓	14,5	13,5	105
jet fuel GM-1	50±2	0		14,5	13,0	100
		120	✓	13,5	13,0	102
gasoline 67 octan	50±2	0		13,0	14,5	102
		120	✓	11,0	13,0	104
mixture izooctan / gasoline (20:80, vol.)	23±2	0		13,0	14,0	102
		16	✓	13,0	13,5	106

- ✓ unchanged regarding the starting quality
- (1) visible change of hue (bluish)
- coating is partially disbanded of substrate
- coating is completely disbanded of substrate (peeling)

**Table 3.** Chemical resistance of urethane two-pack paint (SNO 1564, SNO 7511, ton 3), contact method, sample D2-2

Medium	Testing conditions		Characteristic			
	Temperature °C	Time of exposure h	Coating appearance (swelling, blistering, cracking)	Gloss % (angle 45°)	Hue %	Hardness s
Water	23±2	0	-	8,5	8,0	112
		24	✓	8,5	9,0	120
1N HCl	23±2	0		8,0	9,0	-
		24	✓ (1)	-	-	-
0,1N HNO <sub>3</sub>	23±2	0	○	8,0	8,0	-
		120	✓ (1)	8,5	9,0	-
5% Na <sub>2</sub> CO <sub>3</sub>	23±2	0		8,0	9,0	-
		120	✓ (1)	8,0	9,0	-
25% HCl	23±2	0		8,5	8,5	-
		24	✓ (1)	8,5	12,5	-
25% HNO <sub>3</sub>	23±2	0		8,5	16,5	-
		1	●	-	-	--
25% H <sub>2</sub> SO <sub>4</sub>	23±2	0		14,0	9,5	-
		24	○	-	-	-
25% C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> xH <sub>2</sub> O	23±2	0		8,0	10,0	-
		24	✓	8,0	10,0	-
25% CH <sub>3</sub> COOH	23±2	0		8,0	9,5	-
		24	✓	8,0	9,5	-
25% NaOH	23±2	0		8,0	8,5	-
		24	✓ (1)	7,0	12,5	-

Mineral oil:						
insulating lubricant, JUS B.H3.561	23±2	0		8,5	9,5	115
		24	✓	8,5	9,0	120
engine lubricant typ D, JUS B.H3.169	100±2	0		8,0	9,0	116
		96	✓	8,0	9,0	120
Liquid fuels:						
diesel fuel, JUS B.H2.410	50±2	0		8,0	9,0	111
		120	✓	7,5	9,0	115
jet fuel GM-1	50±2	0		8,5	9,5	114
		120	✓	7,5	8,5	114
gasoline 67 octan	50±2	0		9,0	9,0	115
		120	✓	9,0	8,5	120
mixture izooctan / gasoline (20:80, vol.)	23±2	0		8,5	8,0	116
		16	✓	8,0	8,5	120

- ✓ unchanged regarding the starting quality
- (2) visible change of hue (bluish)
- coating is partially disbanded of substrate
- coating is completely disbanded of substrate (peeling)

**Table 4.** Chemical resistance of urethane two-pack paint (SNO 1564, SNO 7511, ton 11), contact method, sample D2-3

Medium	Testing conditions		Characteristic			
	Temperature °C	Time of exposure h	Coating appearance (swelling, blistering, cracking)	Gloss % (angle 45°)	Hue %	Hardness s
Water	23±2	0	-	14,5	17,0	122
		24	✓	18,0	17,0	121
Chemical agents:						
1N HCl	23±2	0		13,5	17,0	-
		24	✓ (1)	-	-	-
0,1N HNO <sub>3</sub>	23±2	0		14,0	17,0	-
		120	✓ (1)	13,5	17,5	-
5% Na <sub>2</sub> CO <sub>3</sub>	23±2	0		14,5	17,5	-
		120	✓ (1)	14,0	18,0	-
Acids:						
25% HCl	23±2	0		15,0	16,5	-
		24	✓ (1)	14,0	21,0	-
25% HNO <sub>3</sub>	23±2	0		13,5	16,5	-
		1	●	-	-	--
25% H <sub>2</sub> SO <sub>4</sub>	23±2	0		14,0	17,0	-
		24	○	-	-	-
25% C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> xH <sub>2</sub> O	23±2	0		13,5	16,5	-
		24	✓	13,5	17,0	-
25% CH <sub>3</sub> COOH	23±2	0		13,5	17,0	-
		24	✓	12,5	18,0	-
Alkalies:						
25% NaOH	23±2	0		14,0	17,0	-
		24	✓ (1)	13,5	23,0	-
Mineral oil:						
insulating lubricant, JUS B.H3.561	23±2	0		13,5	17,0	100
		24	✓	13,5	16,5	106
engine lubricant typ D, JUS B.H3.169	100±2	0		14,5	17,5	102
		96	✓	15,0	17,0	115
Liquid fuels:						
diesel fuel, JUS B.H2.410	50±2	0		15,0	13,5	110
		120	✓	14,5	13,5	105
jet fuel GM-1	50±2	0		14,5	13,0	100
		120	✓	13,5	13,0	102
gasoline 67 octan	50±2	0		13,0	14,5	102
		120	✓	11,0	13,0	104
mixture izooctan / gasoline (20:80, vol.)	23±2	0		13,0	14,0	102
		16	✓	13,0	13,5	106

- ✓ unchanged regarding the starting quality
- (3) visible change of hue (bluish)
- coating is partially disbanded of substrate
- coating is completely disbanded of substrate (peeling)

**Table 5.** Chemical resistance of urethane paint, contact method,

Aggressive medium	Temperature, oC	Duration, h	Method	Characteristic																							
				Coating appearance (swelling, blistering, cracking)*						Adhesion**					Hue**					Gloss**							
				I1-Z	I1-B	I1-C	I2-Z	I2-B	I2-C	I1-Z	I1-B	I1-C	I2-Z	I2-B	I2-C	I1-Z	I1-B	I1-C	I2-Z	I2-B	I2-C	I1-Z	I1-B	I1-C	I2-Z	I2-B	I2-C
Demineralized water	23±2	24	M1	0	0	0	0	0	0	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
3,5 % NaCl	23±2	168	M1	0	0	0	0	0	0	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Engine oil D JUS B.H3.169	100	96	M1	0	0	0	0	0	0	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Diesel fuel JUS B.H2.410	50±2	168	M1	0	0	0	0	0	0	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Jet fuel GM1 JUS B.H2.230	50±2	168	M1	0	0	0	0	0	0	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Gasoline 86	50±2	168	M1	0	0	0	0	0	0	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Benzene / isooktane 20:80 (%v/v)	23±2	168	M1	0	0	0	0	0	0	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
1N HCl	23±2	24	M2	1	1	1	2	2	2	±	±	±	±	±	±	+	+	+	±	+	+	±	+	+	±	+	+
1N HCl	23±2	3	M1	2	2	2	5	5	5	+	+	+	-	-	-	±	±	±	-	-	-	±	±	±	-	-	-
0.1 HNO <sub>3</sub>	23±2	168	M1	0	0	0	1	1	1	+	+	+	±	±	±	+	+	+	±	+	+	+	+	±	+	+	+
5% Na <sub>2</sub> NO <sub>3</sub>	23±2	168	M1	0	0	0	0	0	0	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

\*changes compared with reference (unexposed) sample (visual evaluation based on JUS ISO 4626/1,2 i 4): (0) no changes; (1) very slight change; (2) slight change; (3) moderate change; (4) extensive change; (5) intensive change.

\*\*changes compared with reference (unexposed) sample (evaluation based on comparison of measured numeric values): (+)no changes; (±) change <10%; (-) change >10%

The survey of results displayed in previous tables shows that the contact method provides data sufficiently conclusive for evaluation of determined coating – agent pairs behaviour, by defined criterions, whether descriptive or quantitative, for changes of coating characteristics during exposure. The choice of chemical agent involved as contact medium for quality control testing, depends on exploiting conditions, projected reliability and durability level and other technical requirements for article overlaid with the coat.

#### IHV value determination method

Previous theoretical analysis shows that physical and mechanical characteristics of the coating are directly related to quantity of diffuser agent and to diffusion parameters of the system. The same conclusion applies for eventual accompanying chemical reactions.

The conventional methods for physical mechanical characteristics measurements are neither sufficiently sensitive nor precise enough to describe those changes accurately. Hardness, just as other mechanical characteristics of coatings, is commonly determined by indirect, comparative methods, based on comparison of secondary effects affected by hardness changes, as a response to precise controlled mechanical impacts applied on the coating. The most frequently used methods for coating hardness evaluation are based on measuring the rate of mitigation of amplitude of pendulum leaning on the surface of the coating and of the reference material (glass for instance). The results are expressed in percents (with 100 for reference), or as a time or number of revolutions for required amplitude attenuation.

For more profound analysis, the methodology that deals with hardness as a basic structural characteristic of a material has to be applied; in other words, defining hardness as resistance of the material to penetration of an object from the outside is required. Since the dimension of coating in direction of penetration is few tens of micrometer, and the size of indentation should not be greater than 50% of thickness of coating, it is obvious that all elements of measuring and experimental technique must be on the highest level of accuracy and sensitivity. This is achieved by utilizing of Knoop's micro hardness tester, with indenter geometry that allows the depth of indentation under 10 µm, the loads smaller than 10 g, and fully balanced indentation dynamics, to eliminate all inertial disturbances during the impact. The figure below shows the shape of the indenter.

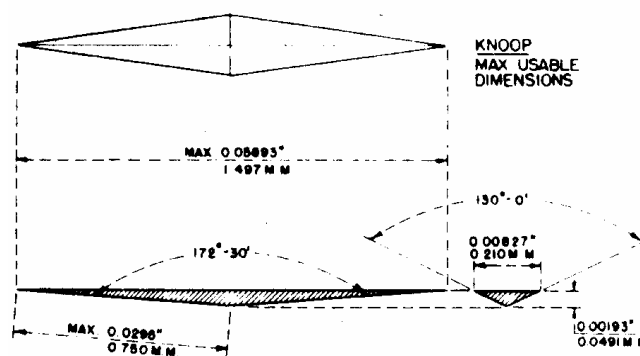


Figure 4. Shape and operating scheme of KNOOP indenter

Regarding the earlier theoretical analyses, the changes of the coating hardness, affected by chemical agent action, happen in intermolecular space, therefore the measurement of changes should also be localized as much as possible. For that purpose, the mathematical model that engages the internal characteristics of material (Young's module  $E$  in this case) with measurable features involved in testing technique (force  $F$  and depth of indentation) has been developed.

$$IHV = cE^{1/2} = dF / dy$$

where  $c$  is the coefficient of proportionality,  $y$  length of indentation and  $IHV$  value describes the hardness behaviour when infinitesimal load is applied.

The experiment is carried out in the range where dependence between related parameters is assumed to be linear allowing, by means of graphical or analytical procedure, i.e. by plotting  $F$  against  $F/y$  values, to induce the  $IHV$  value for zero value of force (load).

Based on previous work of several authors, the  $IHV$  value determinations were used in order to define the methodology for examining the influence of decontaminating agents on urethane and alkyd paints coatings, as most widely used for protection of military equipment.

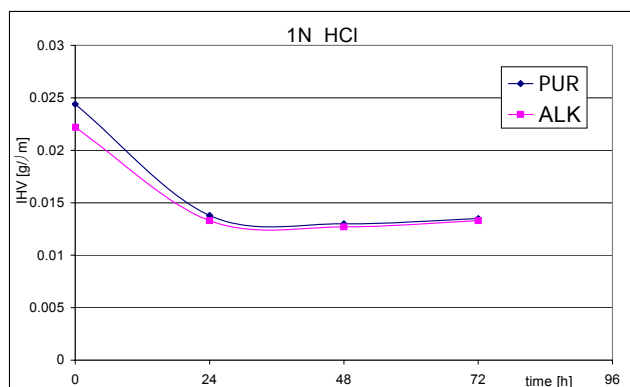


Figure 5.

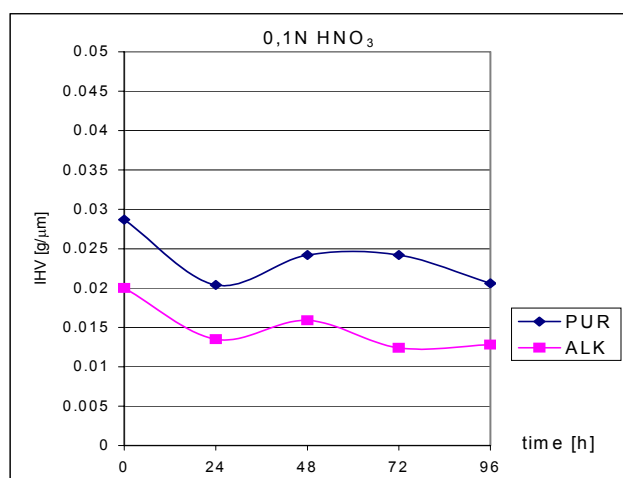


Figure 6.

Figures 5 and 6 show the results of examination of resistivity of urethane and alkyd paints to attack of aggressive mediums frequently used for decontamination

The  $IHV$  value is decreasing if alien agent causes the capillary swelling or chemical bonds deterioration in polymer matrices increasing in cases when new bonds are formed and additional cross linking occurs under the influence of the alien agent. However, they remain constant in cases when coating is chemically inert and has reduced permeability. Monitoring the rate and magnitude of  $IHV$  value changes gives the picture of influence of diffusing agent on coating quality. Due to the fact that measurements are carried out in the boundary area of apparatus sensitivity, the smallest changes in repeated experiment conditions affect results above the acceptable level. The problem of evaluating criterions additionally complicates the application of this method for quality control. Nevertheless, the obtained results shown in this work were valuable for comparative study of investigated coatings behaviour in chemically aggressive conditions<sup>(2)</sup>.

#### Chromophore absorption method

Theoretical analysis shows that dependence between coating porosity, diffusion and absorption of agent, determine the rate of chemical interaction, which is the objective of this study.

If the medium, diffusing through the coating, is dyed with neutral chromophore, measuring the chromatic characteristics of the coating surface gives the numeric quantification of the diffusion process dynamics.

In the effort to develop the original method for exact, quantitative evaluation of diffusion process, within the projected tasks of this work, the preliminary investigation has been carried out in order to analyse the possibility of using the colorimetric measurements for this purpose. Assuming that transparency is negligible, the methodology used permits direct transition of spectral reflectance, that is measurable, to spectral absorbance, which is the quantitative measure of the absorbed substance, as  $A = 100 - R$ , with additional calculation to transform spectral values to exact, comparable set of coordinates, as part of theoretically defined space.

The experimental model, established to meet requirements of such methodology, consisted of absorbing component, represented by layer of nitrocellulose filled with titan dioxide, and chromophoric absorbed component, represented by vaporised nitrobenzene. Chromophoric, diffusion and absorption characteristics of system were sufficient for preliminary evaluation of method applicability.

Spectrophotometric measurements were carried out by means of spectrophotometer BECKMAN UV 5240 in 400 - 720 nm range, with tungsten lamp as a radiation source.

Spectrophotometer was equipped with integration sphere BECKMAN 133215, designed for diffuse reflection measurements.

Processing of spectrophotometric data was done by weighted-ordinate method with CIE 1964 standard observers tristimulus values and relative spectral power  $S(\lambda)$  of CIE standard illuminant  $D_{65}$  and wavelength interval of 10 nm.

Measured and adopted factors are involved in the following equations for tristimulus values of testing samples:

$$X = k \int_{390}^{730} R(\lambda) S(\lambda) \bar{x}(\lambda) d\lambda \quad Y = k \int_{390}^{730} R(\lambda) S(\lambda) \bar{y}(\lambda) d\lambda$$

$$Z = k \int_{390}^{730} R(\lambda) S(\lambda) \bar{z}(\lambda) d\lambda \quad k = 100 \left( \int_{390}^{730} S(\lambda) \bar{y}(\lambda) d\lambda \right)^{-1}$$

$$L^* = 116 \left( \frac{Y}{Y_n} \right)^{\frac{1}{3}} - 16; \quad a^* = 500 \left[ f \left( \frac{X}{X_n} \right) - f \left( \frac{Y}{Y_n} \right) \right];$$

$$b^* = 200 \left[ f \left( \frac{Y}{Y_n} \right) - f \left( \frac{Z}{Z_n} \right) \right]$$

where  $X_n, Y_n, Z_n, S$  are taken from the references.

In the mathematical space, defined in such a way, the difference between two samples, viz. the colour difference, is defined as:

$$\Delta E = \left[ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{\frac{1}{2}}$$

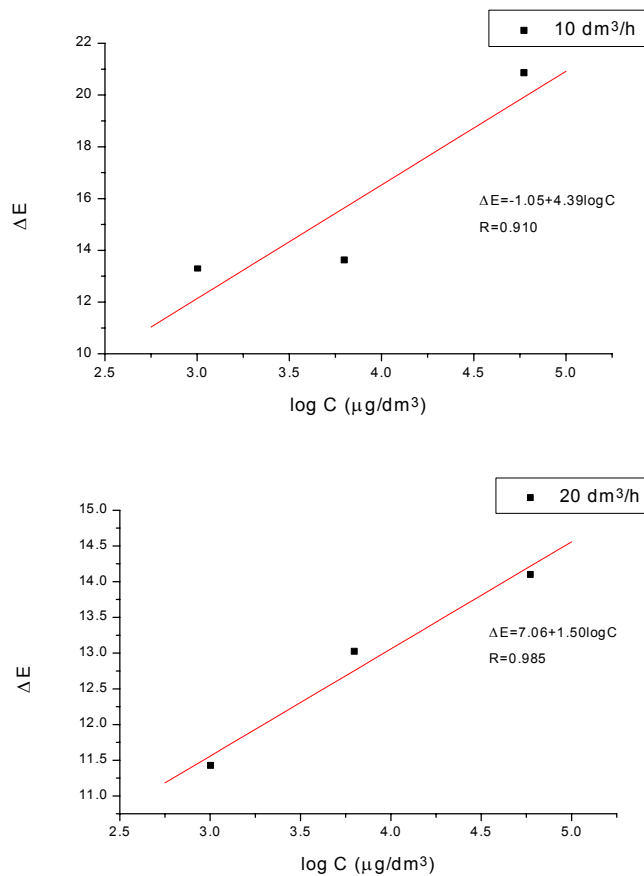
The calculated trichromatic characteristics ( $X, Y, Z, L^*, a^*, b^*$ ) and colour difference  $\Delta E$  of reference and test samples are given in Table 5. Fig.7 contains examples showing the influence of chromophore concentration in stream on colour difference between test and reference samples. Using mathematical coleration methods, the curve

$$\Delta E = k \log c + a$$

can be constructed and factors  $k$  and  $a$  calculated from series of experimental data. Solving the upper equation as

$$c = 10^{\frac{\Delta E - a}{k}}$$

gives the possibility for analytical determination of concentration by spectrophotometric measurements.



**Figure 7.** Dependence between colour difference and NB sample concentration in stream, with constant flux 10 dm<sup>3</sup>/h

**Table 6.** Spectrocolorimetric values of samples exposed to stream of inert fluid with different concentration of chromophore, and colour difference (with unexposed sample as reference).

NB (temperature/flow)	$\Delta E$	$X$	$Y$	$Z$	$a^*$	$b^*$	$L^*$
NB-20/10	13,28	79,10	82,68	74,74	-2,79	10,49	92,88
NB-40/10	13,60	77,54	81,22	73,15	-3,10	10,63	92,23
NB-60/10	20,84	73,92	76,95	61,09	-2,10	17,56	90,30
NB-20/20	11,42	80,20	83,88	77,83	-2,84	8,62	93,40
NB-40/20	13,02	79,78	83,41	75,99	-2,91	10,40	93,19
NB-60/20	14,10	74,34	77,08	69,90	-1,51	10,05	90,36

The described model was designed with constant characteristics of absorbent and variations in characteristics of absorbed medium (concentration). It is obvious that the model can be rearranged in other possible experimental combinations (constant concentration and different characteristics of absorbent), provided that the calculated correlation factors ( $k$  and  $a$  in equations) are valid exclusively for concrete model and range of values determined by the range of experimental data as a basis for calculation.

#### Method of determining the parameters of diffusion

The diffusion process, by definition, involves the rate of mass transfer in the defined direction, and is described by Fick's law equation:

$$dm/dt = DSdc/dx$$

or, in finite form,  $dm/dt$  represents the rate of mass transfer,  $dc/dx$  concentration gradient in the direction of transfer, and  $D$  is the coefficient of proportionality, characteristic of a particular pair diffuser agent – diffusion medium. Provided that the other conditions are constant, the system is characterized by the possibility of determining the diffusion coefficient through time dependent local mass difference measurements.

Consequently, keeping the other parameters in control, any constituent of the given equation can be determined, even when the diffusion coefficient is unknown, as a comparative category for particular pair of materials involved in process of diffusion. For e.g., measuring the mass transferred through the test coating, its porosity can be compared with the reference coating of the same origin, that were e.g. formatted in different conditions.

For coatings permeability measurements, most direct, but at the same time most demanding method is determining the amount of agent passing through the test sample of coating separated of substrate. The main problem is to obtain the free film of coating with continual properties through large enough areas that enables precise, quantitative mass measurements and represents the diffusion characteristics of coating attached to substrate. Other, more or less complicated procedures such as peeling of the coating from low adhesive surface (polytetrafluoroethylene, polyethyleneterephthalate, etc.) or formation of the coating on surface of hard material soluble in solvent inert for coating (on gelatine, soluble in water, on tin or lead soluble in mercury etc.) are also in use. Regardless of the degree of perfection, it is impossible to differentiate between the original porosity of coating, as a subject of interest, from induced porosity generated through disbanding process. However, when satisfactory film of coating is produced, it is placed in the

cell constructed in such a way to define the working area and to enable quantitative measurement of agent passing through the coating from one side of the cell to another.

Electrochemical methods, with electrochemical cell designed with coated metallic substrate as one electrode and chemical agent as part of electrolyte should also be mentioned. Potentiostatic and potentiodynamic measurements indirectly describe the porosity and other diffusion parameters of coating. Such methods demand high precise equipment and developed methodology of result evaluation, so they are predominantly used in the research projects. Most simplified variation based on this principle is the method with indicated chemical or physical actions (for e.g. sound), where diffusion of agent through the coating is accelerated by electrical voltage. Similar methods are in use for field investigations of coating defects, macro porosity, cracking etc.

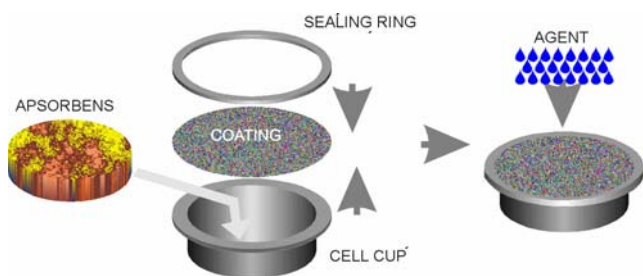


Figure 8. Cell permeability testing

Absorption methods have recently been introduced into laboratory practice. Solving the differential equation of Fick's law, they connect the mass of absorbed agent with diffusion coefficient. In order to analyse the possibility of applying such methods for coatings evaluation, the investigation of diffusion characteristics of coating systems for corrosion protection of military equipment in contact with chemically aggressive agents for contamination and decontamination, was performed.

Diffusion coefficient is commonly determined by applying the sorption methods, based on determination of mass increment of coating sample immersed in a medium containing constant concentration of chemical agent, in determined time intervals to equilibrium point. Diffusion coefficient, for the given initial conditions, is calculated according to equation:

$$D = (\pi / 4t) (\delta Q_t / Q_0)^2$$

where:  $D$  - Diffusion coefficient,  $m^2/s$ ;  $t$  - time,  $s$ ;  $\delta$  - coating thickness,  $10^{-6}$  m;  $Q_t / Q_0$  - amount of medium remaining in the mass of coating sample at the moment  $t$  and in equilibrium.

Table 7. Diffusion coefficients ( $D$ ) and maximum sorption concentrations (MSC) of tested aggressive agents and coatings

Agent	Coating type			
	AKB		PUR	
	$D$ , $m^2/s$	MSC, $mol/dm^3$	$D$ , $m^2/s$	MSC, $mol/dm^3$
2,2-dihlordialkilsulfid (K-1)	$1,76 \times 10^{-13}$	3,08	$2,10 \times 10^{-14}$	1,56
O-alkilmetilfluorofosfonat (K-2)	$9,83 \times 10^{-14}$	2,4	$2,21 \times 10^{-15}$	$2,21 \times 10^{-2}$
O-alkil-S(N,N-dialkilaminoalkil)-alkiltiofosfonat (K-3)	$2,60 \times 10^{-15}$	$9,24 \times 10^{-3}$	$1,52 \times 10^{-15}$	$5,05 \times 10^{-2}$
2-metoksietanol (D-2)	$3,26 \times 10^{-13}$	5,22	$1,03 \times 10^{-13}$	3,16
2% NaOCl (D-3)	$4,21 \times 10^{-14}$	2,15	$3,01 \times 10^{-14}$	1,85

The described methodology was used to investigate the influence of several chemically aggressive agents belonging to group of contaminants (K-1, K-2 i K-3) and decontaminants

(D-2 i D-3) on the coatings of urea formaldehyde (AKB) and urethane (PUR) type. Samples of coatings on the metallic substrate were immersed into aggressive mediums. In certain time intervals the quantity and composition of agent sorbed in the coating was determined by gravimetric and adequate instrumental methods. On the basis of experimental results, diffusion coefficients ( $D$ ) and maximum sorption concentrations (MSC) were calculated. Results are shown in Table 7.

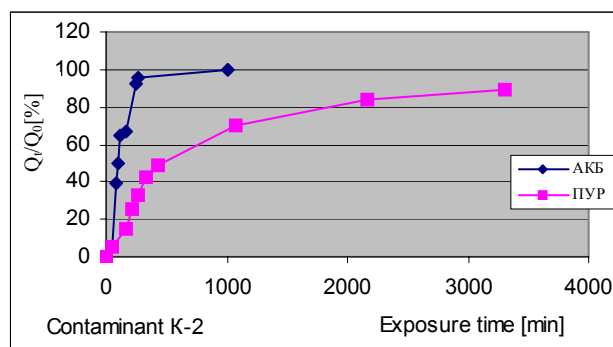
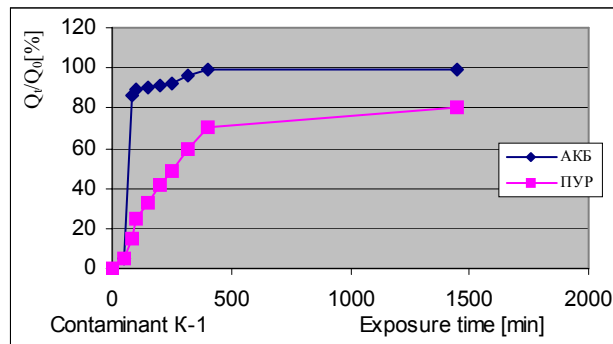


Figure 9. Swelling kinetics for PUR and AKB coatings in contaminants

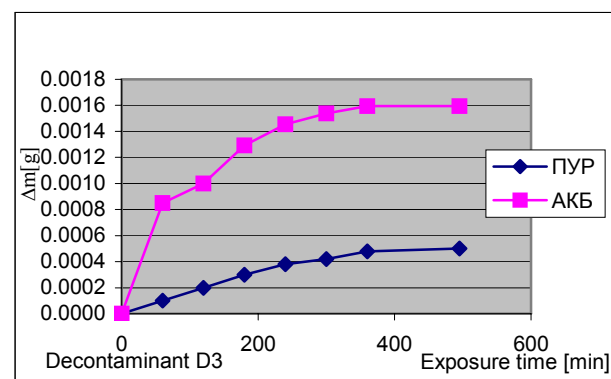
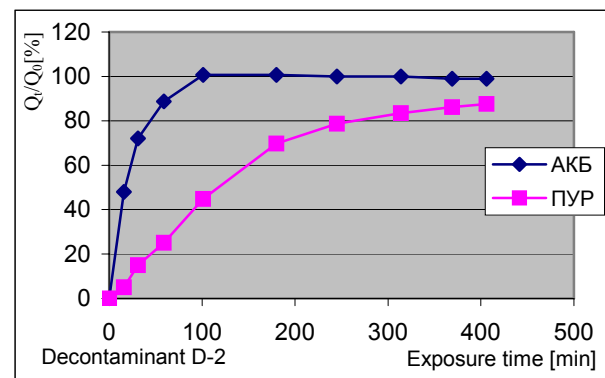


Figure 10. Swelling kinetics for PUR and AKB coatings in decontaminants



The presented results of swelling kinetics investigation of coatings in tested mediums shows that coating based on urethane resin as vehicle exhibits lower diffusion permeability, higher chemical resistivity and protective potential, in comparison to ureaformaldehyd resin based coating, in all tested aggressive mediums. The contaminant K-1 is most aggressive for tested coatings, and the most suitable decontaminant to use.

Method of diffusion parameter determination can be applied for coating contamination evaluation, efficiency of decontamination process of coated articles, as well as to analyze the possibility of application of certain corrosion protection systems in specific exploiting conditions.

For the standardization purposes, that require precise definition of all testing conditions, equipment, procedures and evaluating criterions, large number of additional experiments and verifying tests are necessary, in order to ensure the reproducibility, repeatability and other characteristics required for standardized methods.

#### *Chemical resistivity testing in MIL –DTL-64159*

For comparative analysis of methodology implemented in foreign standards for quality control of coatings for general protection of military equipment, in the following survey parts of MIL–DTL-64159 related with testing of chemical characteristics are listed.

#### *3.6.9 Water resistance.*

When tested as specified in 4.4.20, a film of the coating shall show no blistering or wrinkling and no more than a slight whitening or softening immediately upon removal from the water. Film softening shall not exceed a 2 pencil hardness difference from an unexposed film with identical cure history prior to water exposure. After 2 hours air drying, the portion of the panel that was immersed shall be almost indistinguishable with regard to adhesion, hardness, colour, and gloss from an unexposed film with identical cure history prior to water exposure.

#### *3.6.10 Hydrocarbon resistance.*

When tested as specified in 4.4.21, a film of the coating shall show no blistering or wrinkling when examined immediately after removal from the hydrocarbon test fluid. When examined 2 hours after removal, there shall be no excessive softening, whitening, or dulling. Film softening shall not exceed a 2 pencil hardness difference from an unexposed film with identical cure history prior to water exposure. After 24 hours drying, the portion of the panel which was immersed shall be almost indistinguishable with regard to hardness, adhesion, and general appearance from a panel prepared at the same time but not immersed and shall have no more than a 0.5 gloss unit increase over the original 60 and 85 degree gloss values.

#### *3.6.11 Acid resistance.*

When tested as specified in 4.4.22, a film of Green 383, 34094, shall have no blistering and show no change from the original colour.

#### *3.6.13 DS2 resistance.*

When tested as specified in 4.4.24, a film of the coating shall show no blistering, wrinkling, or film softening when examined immediately after washing with water. Film softening shall not exceed a 2 pencil hardness difference from an unexposed film with identical cure history prior to DS2 exposure. After drying, there shall be a maximum colour change of 2.5 N.B.S. units when comparing a portion of the untested panel to that of the tested area.

#### *3.6.14 Chemical agent resistance.*

When tested as specified in 4.4.25, a film of the coating shall desorb a maximum of 40 micrograms of agent GD and 180 micrograms of agent HD.

#### *4.4.20 Water resistance.*

Prepare a steel panel pre-treated and primed as specified in 4.4.18 and mix the coating as specified in 4.4.15. Spray the coating on a dry film thickness of 0.0018 to 0.0022 inch and air dry for 168 hours. Coat all exposed unpainted metal surfaces with wax or suitable protective coating and immerse in water at  $25 \pm 10$  C ( $77 \pm 20$  F) for 168 hours as specified in ASTM D 1308, section 6.4. At the end of the test period, remove and examine for compliance with 3.6.8.

#### *4.4.21 Hydrocarbon resistance.*

Prepare a film of the coating as specified in 4.4.20. Air dry the specimen for 168 hours and then immerse for 168 hours in a hydrocarbon fluid conforming to JP8 at  $25 \pm 10$  C ( $77 \pm 20$  F). At the end of the test period, remove and examine for compliance with 3.6.10. 18

#### *4.4.22 Acid resistance.*

Using the film prepared and dried as specified in 4.4.20, place a 3 to 5 mL spot of a 10 percent by volume acetic acid solution on the surface of the coating. Cover with an appropriate size watch glass and allow to stand for 1 hour. Rinse thoroughly with water, allow to dry, and examine for blistering and colour change for compliance with 3.6.11.

#### *4.4.24 DS2 resistance.*

Spray one 4 by 12 inch steel panel as specified in 4.4.20. Air dry the panel a minimum of 168 hrs. Scribe a 1 inch diameter wax ring using a china marker on the painted surface of the panel. Place approximately 1 mL of DS2 agent on the panel surface. Do not cover: allow to stand 30 minutes then thoroughly wash with water. Examine for compliance with 3.6.12.

#### *4.4.25 Chemical agent resistance.*

**4.4.25.1** Panel preparation. Spray eight 3 by 3 inch steel panels, zinc phosphate pre-treated according to TT-C-490, type 1 with epoxy primer conforming to MIL-P-53022 or MIL-P-53030 to a dry film thickness between 0.0009 and 0.0011 inch. Air dry 2 hours and spray the coating to be tested to a dry film thickness between 0.0018 and 0.0022 inch. Air dry the panels for 7 days.

**4.4.25.2** Test conditions. Because the desorption rate of agents from paint is temperature dependent, all agent tests will be conducted at  $25^\circ$  C. Extremely toxic materials are used in this testing. Agent HD, a vesicant agent, is also a known carcinogen. Agent GD is a toxic nerve agent, exposure to which is difficult to treat. Consequently, all work will be performed in an approved fume hood, and appropriate measures to protect individuals at risk of exposure must be taken.

**4.4.25.3** Test apparatus. The test apparatus used for both HD and GD testing consists of a temperature controlled Plexiglas box (approximately 0.5 m x 0.5 m x 1 m) containing five separate test cells. Four of these cells are used to test sample CARC panels; the fifth is used to test a control panel, all five tests to be run simultaneously. The test cells are machined from aluminium and consist of two parts that are clamped together to hold the test panels in place. A gas-tight seal is maintained by means of O-rings. Agent desorbed from the test panels is entrained by dry nitrogen that passes through a Miller-Nelson HCS401 temperature-humidity-flow controller, with final temperature controlled by a YSI Model 72 proportional temperature controller. The nitrogen passes

through an external chamber fitted with a bleed valve before entering the test cells. Determine the agent recovered in micrograms for compliance with 3.6.13.

**4.4.24.4 Test Procedure.** Place a 5 cm<sup>2</sup> circular template on the area of the test panel to be contaminated with agent. Use a grease pencil to mark a circle around the template; the grease mark serves to keep the agent from spreading out of the designated area. Place 50 microliters of agent (HD or GD) on the test area using a microliter syringe. Place a glass cover slip (microscope slide) over the test area to minimize evaporation of the agent. After 30 minutes remove the cover slip, rinse the agent from the panel with isopropanol and allow to air dry for approximately 45 seconds. Place the panel in the test cell, which has been maintained at 25° C, with the coated area positioned so that the nitrogen stream will pass across the contaminated area. Nitrogen is used instead of air to eliminate the possibility of reaction of the desorbed agent over the time of the test, which is 22 hours. Pass the nitrogen through an impinger containing the appropriate solvent, n-decane for HD and iso-octane (2,2,4-trimethylpentane) for GD. The flow of nitrogen across each sample shall be 200 mL/min, maintained by mass flow controllers. Terminate the test after exactly 22 hours.

**4.4.25.5 Analysis.** Transfer the contents of each impinger to a 25-mL volumetric flask. Rinse the impinger twice with the same solvent and add the rinse to the flask. Bring the volume up to the mark with solvent and mix well. Transfer a 1-mL portion to a GC vial for analysis. Perform the analysis on a Finnigan-MAT GQC ion-trap mass spectrometer equipped with a 25 m MS-5 capillary column, using helium as the carrier gas. Standardize the mass spectrometer by serial dilutions of an agent solution in the appropriate solvent, analyzed in the same conditions. The instrument conditions are as follows: introduce the samples from an AST 2000 auto sampler, volume of 1 microliter, onto the GC column in splitless mode; injector temperature of 280° C. Temperature program the column from an initial temperature of 50° C to 120° C at a rate of 10°/min; followed by an increase of 25°/min to a final temperature of 200° C. Acquire mass spectra in electron impact mode over the mass range of 50-150 for HD and 50-200 for GD. Under these conditions, HD has a retention time of 8.15 minutes. Integrate the peak areas of the relevant portion of the reconstructed ion chromatograms for the ion at m/z 109. Under the cited conditions GD elutes as a pair of completely resolved diastereomeric enantiomers with retention times of 9.56 and 10.04 minutes. Integrate the peak areas of the relevant portion of the reconstructed ion chromatograms for the ion at m/z 99. Construct the standard response curve for HD and GD using the integrated area on the y axis and concentration (mg/mL) on the x axis. Use the linear regres-

sion analysis function of an Excel spreadsheet, which will calculate the slope, intercept, and correlation coefficient of the standard response curve. The slope and intercept of the standard response curve are used to calculate concentration of the agent (HD or GD) in the impinger solutions. Calculate the total amount of agent (in micrograms) that outgassed from the CARC panel by multiplying the concentration of agent in the impinger solution (micrograms per milliliter read from the standard curve) by the volume of the impinger solution (25 mL).

## Conclusion

- Based on analysis of various methods, the applicability of contact and absorption method was examined and experimentally approved, while the indirect methods such as those using comparison of spectrophotometric and IHV characteristics, were described and discussed according to their limitations and disadvantages.
- For evaluation of coatings behaviour in contact with chemical agents, contact and absorption methods similar to ones described in MIL -DTL-64159 requirements, are recommended. Proposed methods are feasible in domestic laboratories and industrial practice, and, with minor adaptation in the choice of testing characteristics, criteria and necessary laboratory equipment, can be applied for coatings quality control and verification.

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## Interakcije polimernih prevlaka sa hemijski agresivnim agensima

Analizirani su hemijski i fizičko-hemijski fenomeni koji se javljaju pri interakcijama osnovnih komponenata strukture premaza u kontaktu sa agresivnim agensima prisutnim u uobičajenim eksploatacionim uslovima. Opisane su različite metode za karakterizaciju ponašanja premaza u takvim uslovima, predloženi kriterijumi za izbor i definisanje uslova ispitivanja i prikazani rezultati probnih laboratorijskih ispitivanja predloženim metodama.

*Ključne reči:* polimerni materijali, premazi, zaštitni premazi, hemijske osobine, ispitivanje karakteristika, spektrometrija, kolorimetrijska analiza, mikrotvrdoća, metoda ispitivanja.

## Interactions entre les enduits polymères et les agents chimiques agressifs

On a analysé les phénomènes chimiques et physico-chimiques qui se manifestent pendant les interactions des composants basiques de la structure des enduits en contact avec les agents agressifs dans les conditions habituelles d'exploitation. On a décrit les différentes méthodes pour la caractérisation du comportement des enduits dans telles conditions; on a proposé les critères pour le choix et la définition des conditions d'essais. On a présenté aussi les résultats des essais effectués au laboratoire à l'aide des méthodes proposées.

*Mots clés:* matières polymères, enduits, enduits de protection, propriétés chimiques, essais de caractéristiques, spectrométrie, analyse calorimétrique, microdureté, méthode d'essai, application militaire.

## Взаимодействие полимерных покрытий со химически агрессивными агентами

Здесь анализированы химические и физико-химические феномены, являющиеся при взаимодействиях основных составляющих структуры краски в контакте с агрессивными агентами присутствующими в привычных эксплуатационных условиях. Также описаны различные методы для характеристики поведения краски в таких условиях, предложены критерии для выбора и определения условий для исследования и показаны результаты испытательных лабораторных исследований предложенными методами.

*Ключевые слова:* полимерные материалы, краска, защитные краски, химические характеристики, испытывание характеристик, спектрометрия, колориметрический анализ, микротвердость, метод испытывания, военная подготовка.