

PROTECTIVE AGENTS AS A POSSIBLE SUBSTRATE FOR BIOGENIC CYCLES

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Abstract - Protective agents are increasingly used for the preservation of stone monuments. Once applied to the rock, they constitute a veritable new substrate. Very little is known on the biological cycles which could develop on treated surfaces. This paper presents a synthesis on the main properties of protective agents, with particular regard to those of biological relevance; the results were obtained on the basis of multivariate analysis of solubility data. The aim of the paper is to provide biologists with an information basis for studies of biogenic cycles on treated surfaces.

Introduction

Lichens are amongst the most common organisms which may be harmful to stoneworks. According to Savoye & Lallemand (1980), and contrary to a common belief, lichens are not the first colonizers of bare rock: lichen ecesis occurs only after a micropedogenesis started by bacteria on a substrate prepared by chemical weathering. Organic matter, mostly zoogenous, is the primary substrate of the nitrogen cycle, started first by ammonificants, then by nitrifying bacteria; lichens appear only 5 years from the beginning of the cycle. The sulphur cycle starts slowly with the chemical neutralization of sulphuric acid by the rock bases; since sulphur is taken up by lichens as sulphate ion, also chemical weathering creates favourable conditions for lichen growth (Lazzarini & Tabasso, 1986; Carrol, 1970).

In recent times, chemical protective agents are increasingly used for the preservation of stone monuments. They include a wide variety of synthetic resins, with different chemical and physical properties. Once applied to the rock, they constitute a veritable new substrate. There is no detailed information on the biological cycles developing on treated rock surfaces, although the use of protective agents should not hinder the development of bacterial microsuccessions which could culminate in lichen ecesis. The study of biological cycles on these artificial substrates seems to be an interesting field, which could be of relevance for protection measures. Aim of this paper is to present to biologists a synthesis on the main properties of the principal families of protective agents, particularly of those with most direct biological relevance, such as solubility in water and polluting

Tab. 1 - Solubility of 33 organic compounds in 9 protective substances, expressed as normalized ponderal activity coefficients at infinite dilution.

	PERFLUORO POLYETHER FOMBLIN Y MET	PERFLUORO POLYETHER ISOTHYLAMMIDE/FOMBLIN A.	ACRYLIC RESIN PARALOID B 72	EPOXYLIC RESIN ARALDITE	SILOXANE OLIG.	POLYURETHANE	FLUOROCOMPOUND T6H6F	PERFLUOROPOLYETHER GALDEN D20	PERFLUOROPOLYETHER KRYTOX AX
1	WATER	13	11	7	10	10	9	13	13
2	n-PENTANE	7	6	5	8	4	6	4	7
3	n-HEXANE	7	7	5	8	4	6	4	7
4	n-HEPTANE	8	7	5	8	3	6	3	7
5	1 PENTENE	7	6	4	8	4	5	4	7
6	1 HEXENE	7	7	5	8	3	5	4	7
7	1 HEPTENE	8	7	5	8	3	6	3	7
8	METHANOL	12	10	6	8	7	6	10	11
9	ETHANOL	12	9	4	7	6	6	9	11
10	PROPANOL	11	8	4	7	5	5	8	11
11	METHYLACETATE	8	6	3	6	4	4	5	7
12	ETHYLACETATE	8	6	3	6	3	4	4	7
13	PROPYLACETATE	8	6	3	6	3	4	4	7
14	ACETONE	9	6	4	5	4	5	6	8
15	METHYL ETHYL KETONE	9	6	3	6	3	4	5	8
16	METHYL ISOBUTYL KETONE	7	5	2	6	1	3	2	7
17	ETHYLIC ETHER	7	6	3	7	3	5	4	7
18	TETRAHYDROFURANE	7	6	3	6	2	3	3	7
19	BENZENE	8	7	3	6	3	3	4	7
20	TOLUENE	8	7	3	6	3	3	4	7
21	ETHYLBENZENE	9	7	3	6	3	4	3	8
22	CHLOROFORM	6	5	1	5	1	1	3	6
23	TETRACHLOROMETHANE	6	5	1	5	1	1	2	6
24	METHYLENCHLORIDE	7	6	1	5	2	2	3	7
25	CHLOROPROPANE	7	6	3	6	3	4	4	7
26	CHLOROBUTANE	7	6	3	6	3	4	3	7
27	ACETO NITRILE	11	9	5	7	6	6	8	11
28	PROPIO NITRILE	11	8	4	7	6	5	7	10
29	BUTYRO NITRILE	10	8	4	6	5	5	6	10
30	NITROMETHANE	11	9	3	7	6	5	7	10
31	CYCLOHEXANE	7	7	3	7	3	5	4	7
32	METHYLCYCLOHEXANE	7	7	4	7	3	5	3	7
33	ETHYLCYCLOHEXANE	8	7	4	7	3	5	3	8

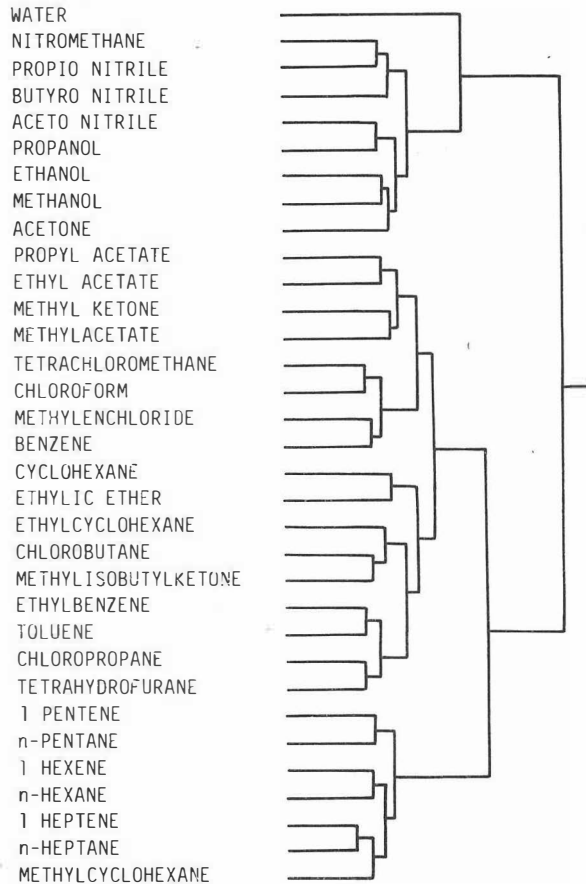


Fig. 1 - Dendrogram of the solvents, based on the data in Tab. 1.

gases, and their behaviour towards the main organic solvents.

Main properties of chemical protective agents

Stoneworks may be protected by two different approaches: a) modifying the environment, b) modifying the interface between the rock surface and the environment (Pasetti, 1984). The latter involves the use of protective substances. These may be subdivided into two main types: a) Plasters or washings for reducing the penetration of water; weathering acts on the new substrates, protecting the underlying rock (Guidotti, 1985); their use often creates aesthetical problems. b) Chemical protective agents, which are water repelling, transparent synthetic substances. The main characteristics of a protective agent are: A) Chemical and physical inertia towards the atmosphere (incl. pollutants), to avoid chromatical

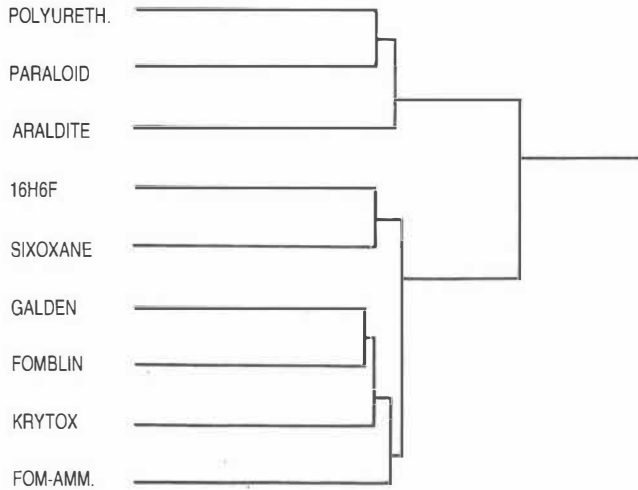


Fig. 2 - Dendrogram of the protective agents, based on the data in Tab. 1.

or physical modifications. B) Chemical and physical inertia toward the rock. C) Transparency and absence of colour. D) Hydrorepellence and insolubility in water and in the common organic solvents, to ensure the stability of the rock surface. E) Low volatility, to ensure duration in time. F) Permeability to gases (air and water vapour), to avoid the formation of a water film below the protective agent, seat of solubilization phenomena with the subsequent fall of crusts from the treated area; the rock pores should not be filled by the agent, which should just cover their internal surface to increase the surface tension on the pore walls, and hence to increase water-repellence. G) Reversibility of the treatment.

The main protective agents

The protective materials may be subdivided in: a) Metallic soaps b) Microcrystalline waxes, c) Organic polymers. The latter, which are the most widely used, include:

1) Epoxydic systems. Main properties (Marinelli, 1975): a) they cross-link at standard temperature without forming by-products, becoming insoluble; b) they require the use of medium-high polarity solvents, because of their high viscosity, or because they are solid at standard temperature. b) they resist well to water, alcohols, salt solutions, acids and to the most common organic solvents. c) they have a very good adherence to lithic materials. Main disadvantages: a) the treatment is non-reversible, b) with small amounts of solvent the pores are obstructed, with too little solvent the protection is insufficient, c) aromatic groups in the molecule make them chromatically instable to UV-rays d) they are hydrophobous also before cross-linking, which creates problems in cases of high humidity. Applica-

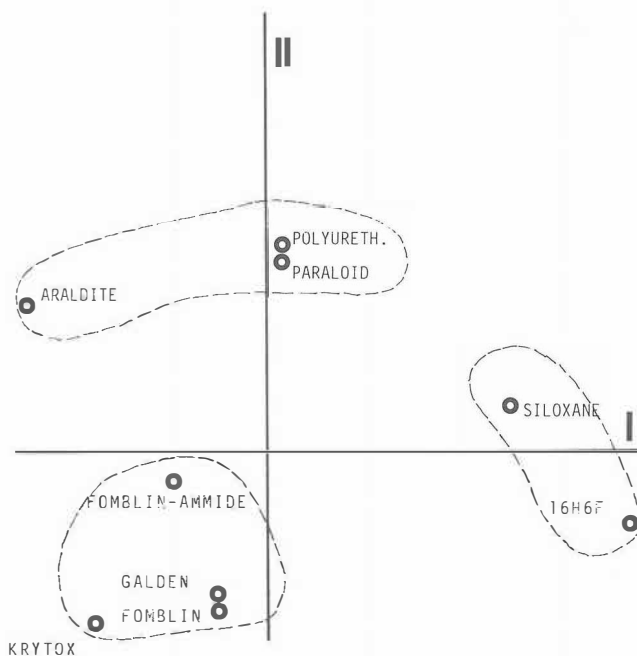


Fig. 3 - Ordination of protectives (centered on the similarity matrix of protectives), based on the data in Tab. 1.

tions: Loggetta del Sansovino in Venice (parts in Verona red marble).

2) Acrylic resins: thermoplastic polymers from several acrylic compounds; widely used, also together with siliconic products. Main advantages: a) Long-lasting effect, b) chemical inertia, resistance to UV-rays, c) good adherence to rock, due to a polar part in the molecule, d) reversible treatment. Main disadvantages: a) the film is often not continuous inside the pores, b) not very high resistance to water. Applications: Gate of the Arsenale and base of Colleoni's statue in Venice, sculptures of "anime oranti" in Rome, low-reliefs of the Orvieto Cathedral.

3) Poliuretanic systems: presently little used, but potentially interesting. They have optimal chemical inertia, stability under sunlight, rapid dessiccation, optimal water-repellence, high adhesion to the rock; the disadvantages are the same of the cross-linked polymers.

4) Organic Silica compounds: they are the most widely used in the last decade, with a very broad choice of substances; among the most used are alkyl-silanes, alkossi-silanes, polyxilossanes, oligomeric xylossanes. Their common properties are (Biscontin et al., 1986): optimal adhesion to the rock, good chemical inertia, high water-repellence, good permeability to water vapour, good resistance towards breaking off by thermic expansion. Main disadvantages: low resistance to UV-rays, non-complete reversibility, short duration, alteration in humid environ-

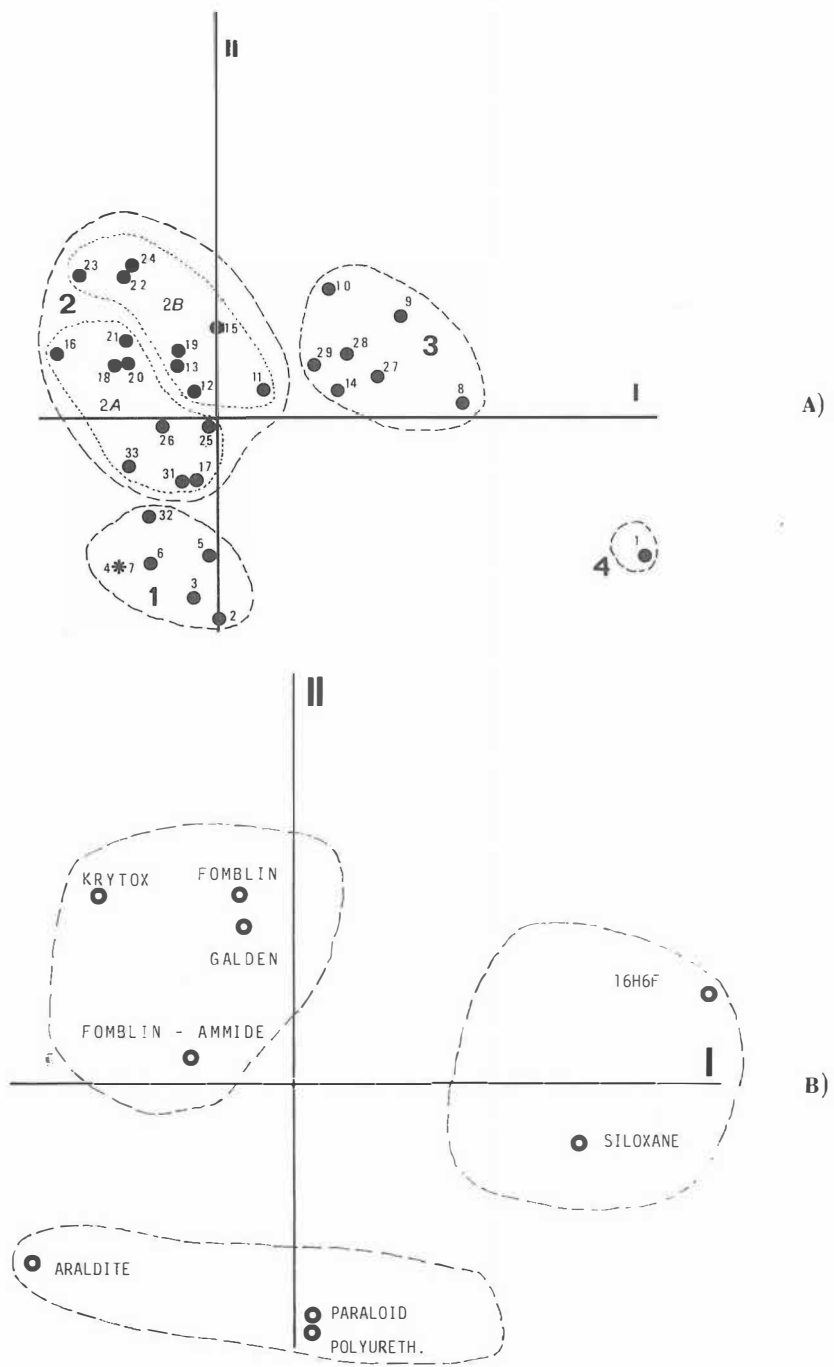


Fig. 4 - Reciprocal ordering of solvents (a) and protectives (b) (centered on the similarity matrix of solvents), based on the data of Tab. 1.

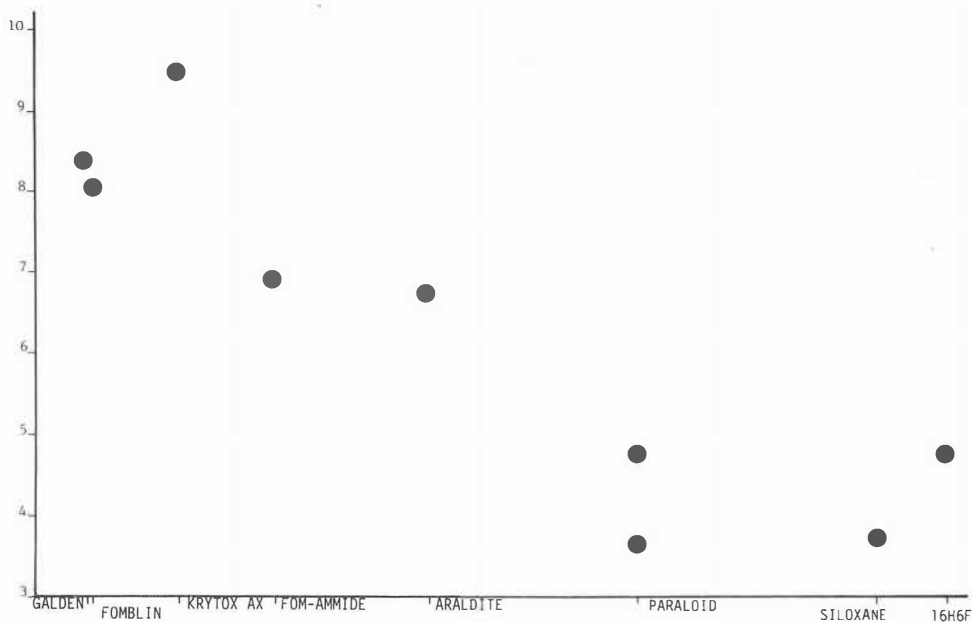


Fig. 5 - Relation between the scores of the protectives on the first canonical variate (x-axis, see Fig. 3) and their inertia (y-axis) expressed by averaging the values of Henry's constant of each solvent in each protective.

ments, loss of the protective agent by evaporation. The high variety of substances is the cause of wrong choices which proved to be detrimental to the stonework. Applications: Town Hall of Vienna, Justizpalast and Town Hall of Munich, Certosa of Milan.

5) Fluoro-compounds (Banks, 1974); they are chemically and thermally stable. There are different polymers, with different molecular weights, so to allow the choice to optimal viscosity. The fact that they are soluble in trichlorotrifluoroethane allows their use as impregnators of weakly porous materials (marbles). They are almost non-volatile at standard temperature, non toxic, insoluble in organic solvents, non inflammable, strongly water repellent. Laboratory and field experiments proved that Fomblin Y Met is permeable to water vapour, and that the treatment is easily reversible (Pasetti, 1984). The main disadvantages are: the use of potentially harmful chlorofluoro-compounds as solvents, the low surface tension, which helps the migration of the protective agents inside the rock, particularly when this is very porous. To overcome this problem some perfluoropolyesters have been synthesized, having some functional groups such esters, amide, acids: the presence of polar groups reduces the mobility of the molecule, creating bonds with the rock surface (Piacenti et al., 1985). Applications: Cathedral of Florence, S. Zeno Closter in Vienna, Antinori and Pitti Palaces in Florence.

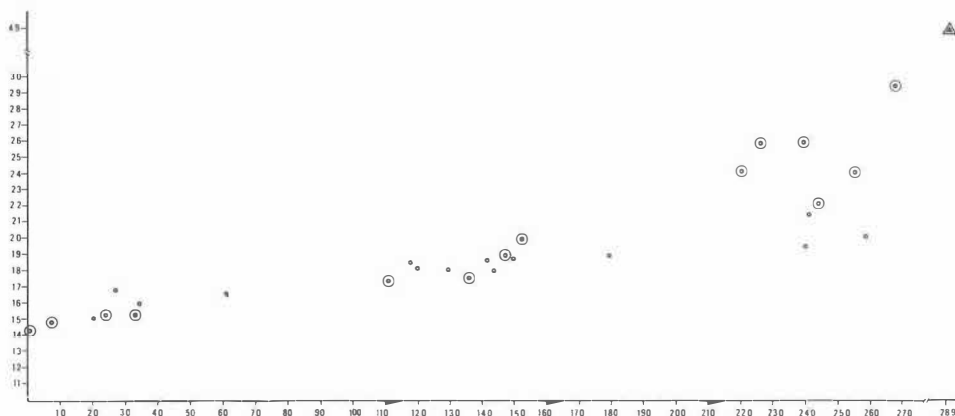


Fig. 6 - Relation between the scores of the solvents on the first canonical variate (x-axis, see fig. 4a) and their polarity, expressed by Hildebrandt's constant (y-axis).

Data and methods

The migration of a solute in a chromatographic column depends on the distribution ratio of the solute between the stationary phase (polymer or resin), and the mobile one (inert gas). The volume of mobile phase is necessary for moving the solute out of the column, is known as specific retention volume. From the magnitude of the chromatographic retention it is possible to derive some thermodynamic values which are bound to the solubility of the solute in a given solvent. In the case of gaseous solutes the relation is known as Henry's constant (Reid et al., 1977). In the case of liquids one uses the ponderal activity coefficient at infinite dilution (Laub et Pecsok, 1978). In this study we use the values of Henry's constant and of the ponderal activity coefficient for 10 gases, 33 solvents and water in the 11 stationary phases utilized during laboratory work.

This paper analyzes the interactions between both pollutants and protective agents, and organic solvents and protective agents. In both cases we selected the protective in such a way as to have representatives of two main groups: one including a series of partially fluorurated substances, the other a series of organic polymers, already used as protectives in several cases. The considered protective agents and the solutes are listed in Tab. 1 and Tab. 2.

The matrices of the solvents and the protectives (solubility expressed by gamma), and of the gases and the protectives (solubility expressed by Henry's constant), have been submitted to multivariate analysis, as follows:

1) Numerical Classification (Anderberg, 1973), to obtain groups of correlated variables. We have used the package of programs of Wildi & Orloci (1983), utilizing Correlation Coefficient as a resemblance measure, and Complete Linkage (see

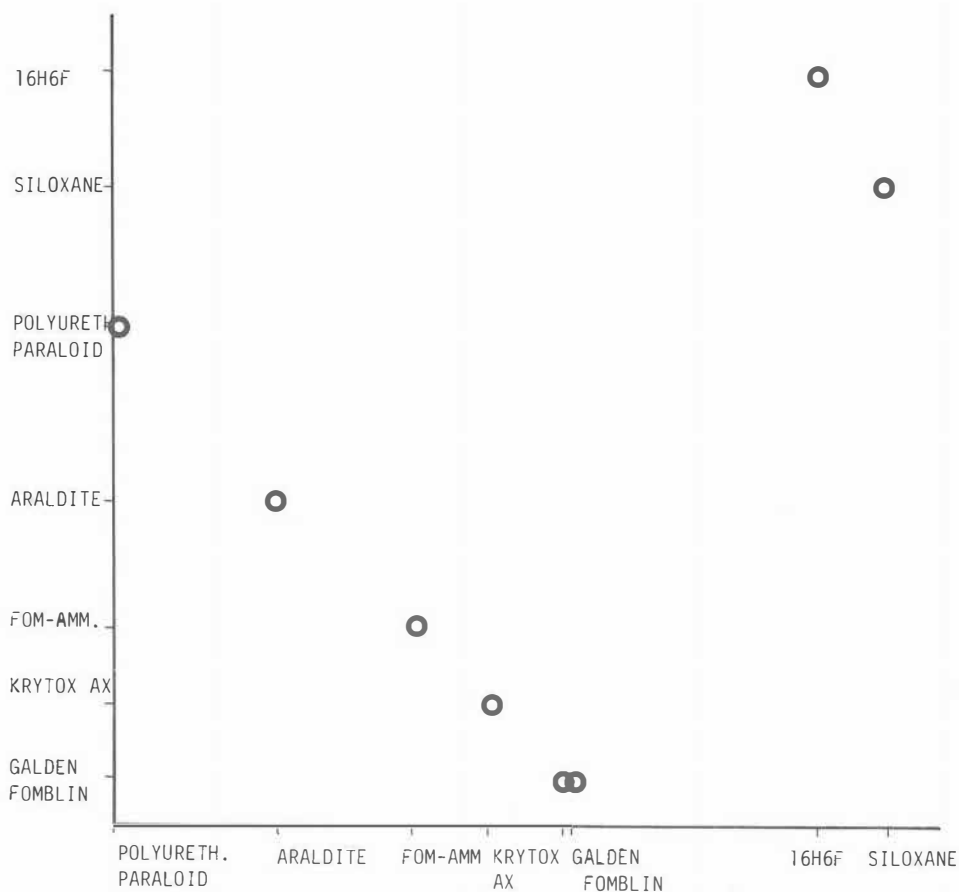


Fig. 7 - Comparison between the two ordinations of protectives: the two axes report the scores of the protectives on the first canonical variates as in Fig. 3 and 4b.

Orloci, 1978) as classification algorithm.

2) Reciprocal Ordering, to evaluate the possible existence of variation trends in the data structure. The ordination has been obtained by transforming the original data by deviation from expectation, and on a resemblance matrix based on Cross Product. Also in this case the package of Wildi & Orloci (1983) was used.

Results

Tab. 1 reports the normalized values of the ponderal activity coefficients relative to the solubility of 33 organic compounds in 9 protective substances. The data of Tab. 1 have been analyzed by classification and reciprocal ordination in

Tab. 2 - Solubility of 10 gases in 11 protectives, expressed as normalized values of Henry's constant.

	ARALDITE	KRYTOX AZ	KRYTOX AX	POLYURETHANE	SILOXANE OLIG.	PARALOID B72	FOMBLYN AMMIDE	FOMBLYN Y MET	GALDEN D 20	16H6F	12H8F
O ₂	5	8	5	2	7	9	9	1	1	0	1
N ₂ O	9	5	6	9	6	1	5	7	8	4	4
CO ₂	9	4	2	5	1	3	5	7	8	4	5
CO	9	7	9	6	1	9	8	4	5	3	4
FREON 13	9	4	5	9	6	2	4	6	4	4	4
SO ₂	9	5	6	3	4	9	4	7	6	4	4
PROPYLENE	9	5	6	7	4	8	5	7	6	2	2
ETHANE	8	7	9	8	7	9	4	8	9	4	6
H ₂ O	5	6	6	3	4	1	7	9	8	7	8
H ₂ S	0	8	8	0	0	3	4	4	7	4	5

order to: 1) Define group of solvents with similar behaviour towards the protective agents. 2) Define groups of agents with similar behaviour towards the solvents. 3) Detect possible correlations between groups of solvents and of protective agents. 4) Order the protectives in a sequence reflecting their solubility towards the entire complex of solvents.

The dendrogram of the solvents is shown in Fig. 1. By cutting the dendrogram at a value of Correlation Coefficient of - 0.88, four main clusters are formed, as follows:

Cluster 1) includes Paraffins, Cycloparaffins and Olefins

Cluster 2) includes mainly aromatic and chloro-compounds

Cluster 3) includes alcohols, acetone, and compounds with nitrile groups.

Cluster 4) includes only water.

The dendrogram of the protectives is shown in fig. 2. Three main clusters are formed, as follows:

Cluster A: includes 16H6F and syloxane

Cluster B: includes all the cross-linked resins: Polyuretanic, acrylic and epoxydic.

Cluster C: includes all the perfloro-compound: Crytox AX, Fomblin, Galden and Fomblinamide.

The correlation between groups of protective agents and solvents are shown in Fig. 3 and 4 (a, b) which report the position of the solvents (Fig. 4a) and of the protective agents (Fig. 4b) in the space defined by the two canonical variates of the reciprocal ordering. Fig. 3 has been obtained by centering the ordination on the similarity matrix of the protectives, Fig. 4 on the matrix of the solvents.

In Fig. 3 the protectives are disposed according to a horse-shoe at whose extremes are disposed Fomblin and 16H6F. This arrangement corresponds with a gradient of increasing inertia towards the solvents. This is evident in Fig. 5, where the x-axis reports the angular seriation of the protectives in Fig. 3, and the y-axis

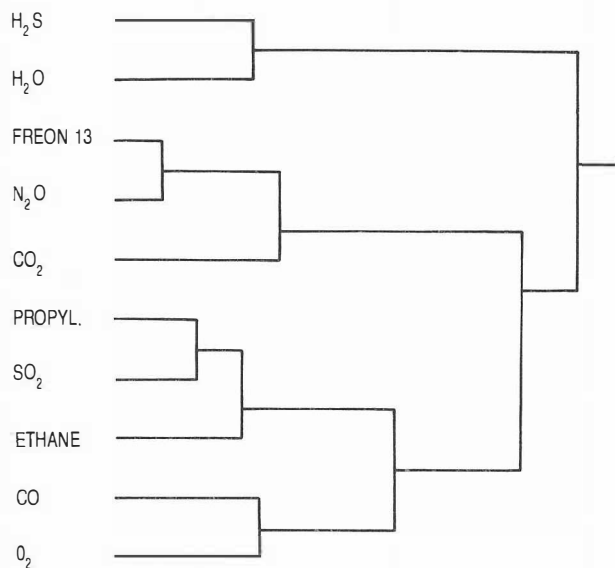


Fig. 8 - Dendrogram of the gases, obtained on the basis of the data of Tab. 2.

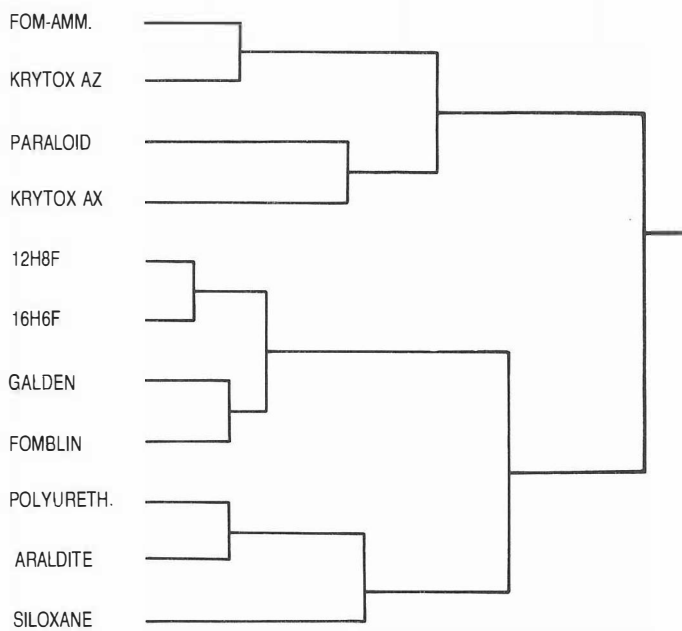
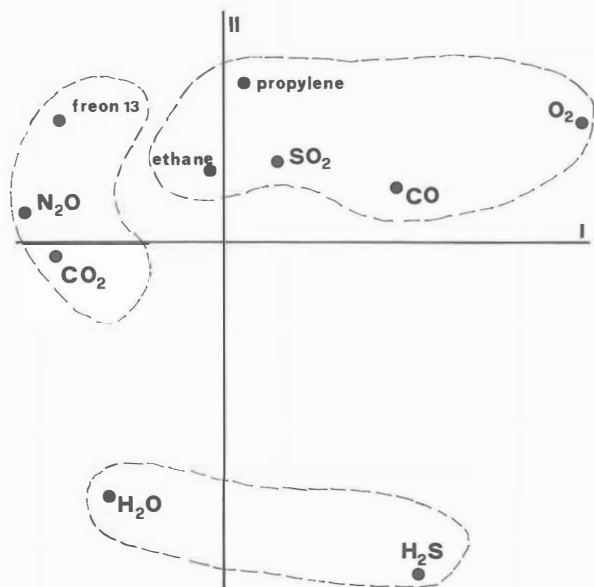
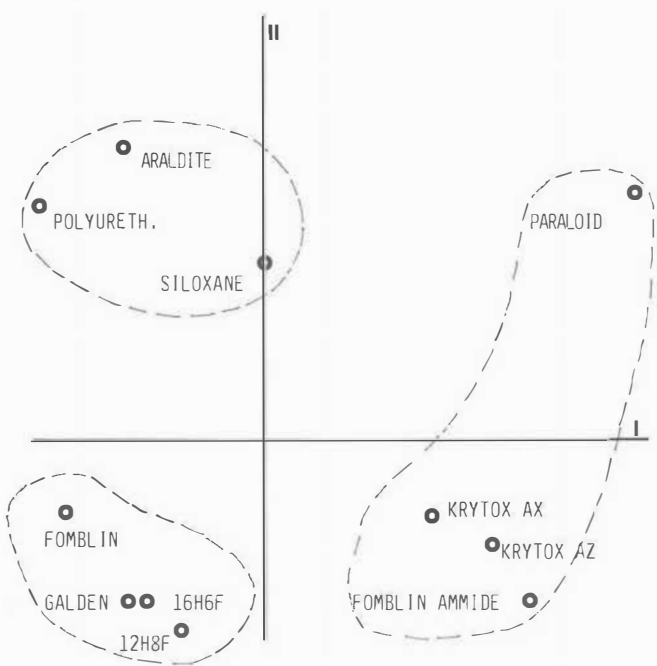


Fig. 9 - Dendrogram of the protective agents, obtained on the basis of the data of Tab. 2.



A)



B)

Fig. 10 - Reciprocal ordering of gases (a) and protective agents (10b), based on the data of Tab. 2.

expresses an index of inertia obtained by averaging the values of Henry's Constants of each solvent in each protective.

In Fig. 4a the solvents are disposed according to an horse-shoe corresponding to a polarity gradient, as shown by Fig. 6, where the x-axis reports the angular seriation of solvents in Fig. 4a, and the y-axis expresses Hildenbrand's constants. Fig. 4b shows the reciprocal ordination of protectives corresponding to that of the solvents in Fig. 4a. Their angular seriation, starting from Paraloid and Poliuretane to the Siloxane, corresponds to a gradient of increasing affinity for polar compounds. Fig. 7 shows the correlation between the two ordinations of protectives (Fig. 3 and 4 b): there is a negative correlation between the affinity for polar compounds and chemical inertia, with the exception of Siloxane and 16H6F, whose molecule has paraffinic part and a part with high chemical inertia (silica and fluoro), and which differ from the others by a far smaller molecular weight.

Tab. 2 reports the solubility of 10 gases in 11 protectives. Ordination and classification programs were also used to analyze these data: both dendrograms (gases and protectives) allow to distinguish three main groups, which are shown in Fig. 8 (protectives) and 9 (gases). The relations between gases and protectives have been studied by reciprocal ordering. The results are shown in Fig. 10a (gases) and 10b (protectives). The group B of protectives is very inert towards water and H_2S ; the group C is highly soluble in H_2S and in water, with synergic effects, but has a high inertia towards the other pollutants. In the ordination, the group B of protectives is dismembered: the Paraloid assumes an isolated position; this compound has a negative behaviour towards all gases, and the highest solubility towards water; the other members of cluster B have an inertia similar to the one of the other perfluoro-compounds, with the exception of a higher inertia towards H_2S .

Conclusions

These results may be a first information basis for further biological studies aiming at analyzing the micropedogenetic phenomena occurring on rock surfaces treated with protectives. In particular, a possible line of research, that can be carried out both in the laboratory and in the field, could be the comparative study of a few protective substances, one for each of the main groups discussed above. These groups have a different behaviour in respect with water and the main atmospheric pollutants, and probably should host different micropedogenetical processes. In any case, before starting a study on a single treated stonework one can refer to the group in which the protective is included, to get additional information which could allow a correlation between biological results and the main chemical properties of the new substrate.

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