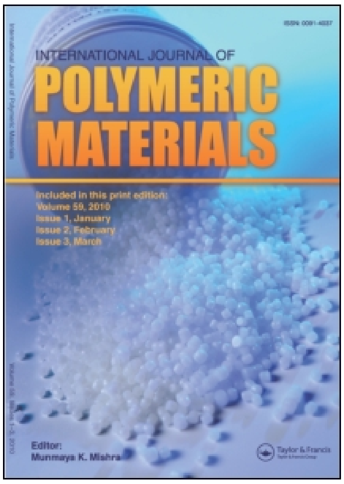

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Physico-Chemical Problems in Estimation of Service Steadiness (SS) of Polymer Materials

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Physico-Chemical Problems in Estimation of Service Steadiness (SS) of Polymer Materials

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The polymers ageing process investigation encounts too much problems of physical-chemistry polymer science.

The question is to understand the nature of stresses localization in radiation oxidized polyethylene with the characteristic time equal to several decades, the non-correlation between theoretical ideas as for sol's consistence changing and swelling coefficient in the ageing process of latex films, the photoageing of lightstable materials exposed by the light of different polychromic spectra.

KEYWORDS: Prognostication, properties of polymers, characteristics of processes, oxidation, photodegradation, radiation

To learn to understand the essence of processes leading to changes in practically important properties of polymer materials in service is one of the main applied problems in the theory of ageing of this materials.

To understand is not only to establish facts that a certain process goes on under given conditions but also to be able to describe quantitatively the process, taking into account mutual influence of different processes.

In academic studies, the detection of a process, the description of all particulars of its course are the end in itself. This is the essence of cognition of the world.

In order to solve an academic problem, the material is purified in a special manner, the necessary structure is important to it, and the material is placed in certain thoroughly controlled conditions. Only in this fashion can the existence of a present process in the material and a participation of a present species in it be proved with sufficient certainty and quantitative characteristics of the process or species be determined.

Studies of this sort prove the necessity of taking into consideration the revealed and quantitatively characterized process in all systems where such a process may take place. In the best case one cannot only speak of a possible occurrence of this process but also estimates quantitatively its scale and influence on other possible processes.

However, these are the necessary characteristics of processes encountered in practice. Academic studies are seldom directed to the appraisal of the sufficience of the available data for the description of a real process. This is usually the domain of applied research.

The use of a material under real conditions differs essentially from the ageing process studied in an academic laboratory.

First, this is by no means the material which was investigated in the laboratory. A real material contains a broad range of various admixtures of different origin. There are both additives purposely introduced into the material in order to impart to it practically important properties (colour, elasticity, necessary electric parameters, stability to various factors, etc.) and foreign impurities which entered into the material together with the initial substances or formed in the material in the course technologic processes of its working into article.

Second, the material in service is exposed to the effect of a broad range of factors. On the one hand, there are various agents, such as light, oxygen, mechanical stresses, gaseous and liquid aggressive media, acting jointly. On the other hand, the intensity of the effect changes continuously in time, winter is followed by summer, the period of intense operation by downtime, transportation or repair.

Third, the material acquires a certain shape in the article; it performs a certain function in the article. This gives rise to the generation of a set of specific internal aggressive factors, mechanical stresses, factors that lead to abrasion of the material, etc. All this affects the ageing of the material and it is unclear beforehand whether all possible processes have been taken into account in the course of preliminary "academic" studies underlying the ageing theory.

Thus, the practical use of the results of academic research always involves the problem of the fullness of theory of this material ageing in an article.

This problem has always two facets. First, this is the question of the perfection of theory of ageing of the polymer material and second, this is the question of the perfection of the theory of mechanisms and machines where this material is employed. It is evident that however perfect the ageing theory may be, one never will be able to predict the way of change of properties of the material in an article if it is not possible to characterize with sufficient accuracy its service conditions and to find indicators of its unfitness for further use. Only designer of the article can answer on this question. There is no sense in touching this problem in this report. Today we only discuss problems in the ageing theory and it is aware of the indubitable importance of its fullness.

Does the modern theory cover all processes significantly affecting the change of practically important properties or has it only analysed some of these processes?

What should be done with regard to other processes whose theories have not yet been developed?

It is a very difficult question, and an unequivocal answer cannot be given since all depends on concrete type of the material and of the article where it is used.

In the present report I shall dwell upon one, so to speak, academic side of this problem. I shall endeavour to show that when turning to the use of real material in practice, one often encounters new academic problem, seeks new approaches to theoretical issues, new ways of its solving. Mutual enrichment thus occurs:

- the theory is enriched with new methods and approaches,
- the practice—with soundly substantiated methods.

Of the whole variety of problems arising here I shall take only three examples:

- an almost classical object of the theory of ageing—polyethylene, its radiation-induced oxidation, oxidation of polyethylene (PE) articles;
- thermal ageing of the simplest vulcanizates, latex films;
- the problem of the effect of polychromatic luminous radiation.

Radiation-induced oxidative ageing of PE seems to be the simplest ageing process. This is initiated oxidation, the chain process without branching, with a constant initiation rate on all sites of the specimen. The process is complicated to some extent by little unhomogeneous distribution of free radicals which formed in the tracks of ionizing particles. But this factor is not very essential. An analysis indicates that on most commonly used . . .-irradiation the role of the track constituent of oxidation in PE is unsignificant. The role of track reactions on radicals can be assessed using the following data: about 1.10.12 primary electrons per second are formed in 1 g of PE at radiation power 50 rad/s; these electrons make tracks with average length of 2 mm.[1] The rate of initiation of radicals (Wi) is $3 \,.\, 10^{-7}\,\mathrm{M/s}^2$ which corresponds to the formation of 2.10.14 of radicals per second per gram or about 200 radicals per track. If the effective width of the track is taken to be 1 nm than the concentration of radicals on track is $5 \,.\, 10^{-5}\,\mathrm{M}$. Homogeneous approach to the problem using the data of effective biomolecular rate constant of the decay of the same radicals (Kt)[3] gives an almost identical concentration of free radicals:

$$[\mathrm{R}] = (Wi/Kt)^{1/2} = 3 \,.\, 10^{-5}\,\mathrm{M} \tag{1}$$

Hence, it can be thought that free radicals have enough time to spread evenly through the specimen.

PE oxidation is a chain process with quadratic type chain termination; this means that the efficiency of the process should depend in a complex manner on radiation power which determines the rate of initiation of free radicals.

Experiment brilliantly corroborated the theoretical ideas on specimens of commercial low density PE (LDPE). Hydroperoxides accumulated in it at a constant rate proportional to the square root of radiation power; the accumulation of carbonyl compounds featured also a constant rate which depended on power in a more intricate way:

$$W = d(\mathrm{C{=}O})/dt = aP + b(P)^{1/2} \tag{2}$$

where P is the power of irradiation and a and b are parameters.

This form of the dependence of the rate accumulation of carbonyl compounds on radiation power speaks of their formation both in initiation and termination events and in oxidation chain propagation events. Similar dependences were repeatedly described in the literature; this result is in an almost quantitative agreement with thermal oxidation data.

TABLE I

The dependence of the depth of the oxidized layer on radiation power

P (rad/s)	1000	500	250	52.8	51	22.2	20.7	16.0	13.7	7.2	2.0	1.0	0.1
d calc (mm)	0.038	0.053	0.073	0.146	0.148	0.21	0.22	0.24	0.26	0.33	0.51	0.64	1.26
d crck (mm)	0.04	0.06	0.08	0.14	0.18	0.25	0.27	0.31	0.37	0.42	—	—	

The rate of oxidation was very slowly depended on oxygen pressure in ordinary conditions.

Thus, the process of radiation induced oxidation would appear to be fully understood both at the qualitative and the quantitative levels.

However, this conclusion is a consequence of only a superficial consideration of the problem. Using the data on the formation of carbonyl compounds and hydroperoxides, it is not difficult to evaluate the rate of oxygen absorption. (Direct measurements are impeded by experimental obstacles).

The completion of oxidation and diffusion occurred and there is only limited oxidized layer.

Table I demonstrates how the depth of the oxidized layer should depend on radiation power. The thickness of the oxidized layer was calculated on the basis of traditional assumptions for a flat plate according to diffusion equation:

$$d = (2D[O_2]_0/(aP + b(P)^{1/2}))^{1/2} \tag{3}$$

where D—coefficient of diffusion, $[O_2]_0$—concentration of oxygen on surface.

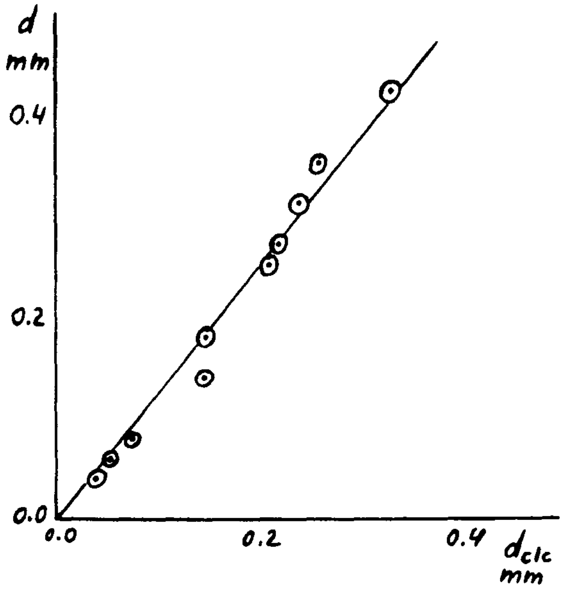

FIGURE 1 The dependence of the depth of cracks on the calculated oxidation depth for LDPE at room temperature. The systematic difference between these values is due to an error in estimation of oxidation parameters. ($a = 1.6 . 10^{-8}$ (M/(rad/s)); $b = 4.5 . 10^{-8}$ (M/(rad/s)$^{1/2}$); $2D[O_2]_0 = 2.5 . 10^{-8}$ M mm^2/s).

Figure 1 demonstrates how the depth of oxidized layer accords with the depth of cracks in thick PE films.

It can be seen that major expected dependences are followed. Even at relatively low values of radiation power the depth of oxidation does not exceed several millimeters; this means that articles several millimeters thick should have a zone in the centre where there is no oxygen and radiation cross linking, rather than oxidation, occurs. Thus, a sandwich type structure consisting of an oxidized surface layer and a radiation cross linked central portion should be formed. Mechanical stress should arise at the boundary between the portions; the magnitude and location of the stress should depend on the kinetics of the process taking place under the conditions of oxygen deficiency. But it is insufficiently well studied in the theory.

Mechanical stress should arise for two different reasons.

On the one hand, shrinkage of the oxidized layer occurs while the cross linked layer undergoes virtually no shrinkage. Regardless of a relatively low value of shrinkage (1–2 vol.%), it can give rise to high local stresses, particularly in sufficiently long specimens.

On the other hand, the thermodynamically equilibrium supermolecular structures of the oxidized and cross linked polymer are absolutely different which should also lead to the generation of mechanical stress at the boundary even if there is no difference in density and, accordingly, in macroscopic shrinkage of each of the layers.

There is at present no theory suitable for computations of such stresses. Experimental data point to the origination of substantial stresses; the material cracks, the depth and shape of cracks being exactly determined by chemical transformations going on in the material.

Figure 2 demonstrates that the cracks in the electric insulation of a wire differ

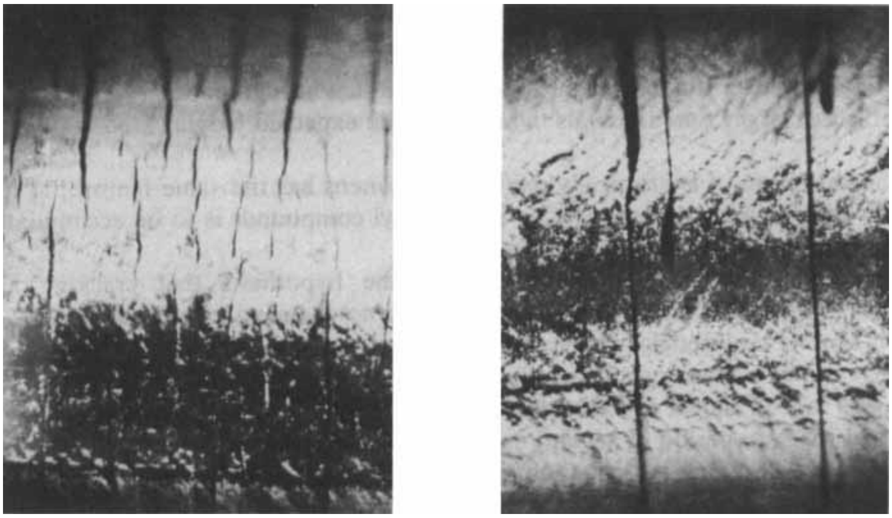

FIGURE 2 Photographs of PE insulation on a round wire cracked under the action of light (1) and radiation (2).

even outwardly upon exposure to dissimilar agents, light and radiation. Radiation exposure to the formation of thin, regularly repeated, girbling cracks penetrating the specimen to a similar depth which exactly coincides with the depth of the oxidized layer. Exposure to light induces irregular structure consisting of cracks of different depth resembling the birch bark.

A qualitative explanation of this fact can be easily provided. Under the action of radiation, initiation occurs uniformly throughout the whole material; at large oxygen pressure the rate of oxidation is virtually independent of the pressure which is a well established fact. Thus, the upper layer oxidizes throughout its depth at a constant rate. The zone of transformation from oxidation to cross linking is very narrow and only the oxidized layer cracks, as if compensating for the shrinkage that has occurred.

The situation in photoageing is much more complicated; the intensity of light decreases with depth and accordingly the rate of oxidation slows down. The effective depth of penetration of light into the polymer changes because of light absorption by ageing products. Thus, the zone of mechanical stresses is distributed almost throughout the whole thickness of the specimen, the cross linking zone is completely absent if light intensity is not too much; hence exposure to light leads to a more complicated picture including cracks of different depths some of which penetrating even into unoxidized zones of the specimen.[4]

Taking the academic approach, a simpler radiation oxidation system was chosen for a deeper theoretical understanding of the problem. It was evident that the depth and cracking time should be determined by oxidation laws. The depth of the cracks, d, is also depended on diffusion coefficient, D, and the cracking time is determined by the time of attaining a certain critical conversion extent. Both should in a specific way depend on radiation power.

However, the truth proved to be more complicated than such an obvious hypothesis. The crack depth indeed changed with radiation power in according with the oxidation theory (Figure 1).

But the cracking time did not correlate with a certain critical concentration of reaction products. It can be seen from Figure 3 that at high power levels cracking occurs after larger time intervals than it could be expected judging from oxidation rates.

The shrinkage of isotropically oxidized specimens has the same feature; at low power levels a higher concentration of carbonyl compounds is to be accumulated to attain one and the same shrinkage value.

This phenomenon was explained using the hypothesis that cracking and shrinkage exhibit a sort of time lag with respect to chemical transformations since much time is required for the structure rearrangement leading to shrinkage and localization of stresses producing cracking.

It was indeed shown in experiments that at certain irradiation doses specimens cracked within a period of several days after the end of irradiation.

The simplest relaxation equation was used for a quantitative description of the phenomenon:

$$dE/dt = (E - E_0(W, t))/t_0 \qquad (4)$$

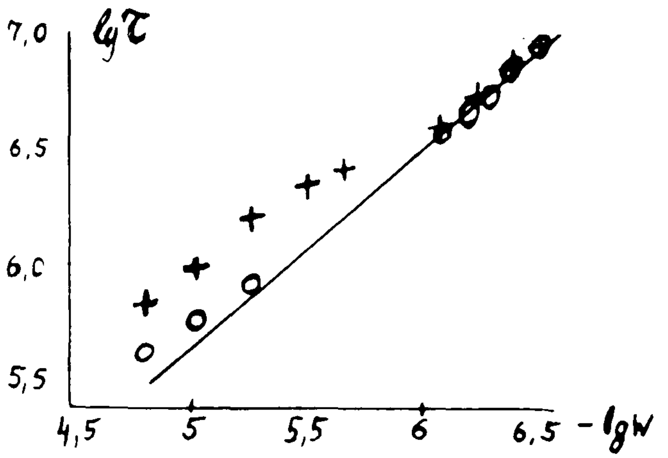

FIGURE 3 The dependence of cracking time on the rate of radiation-induced oxidation at different radiation power levels: 1—cracking in the course of irradiation; 2—cracking after relaxation in the absence of radiation.

where E is a parameter describing shrinkage and crack formation, $E_0(W, t)$ is the equilibrium value of this parameter due to chemical changes that occurred in the system, t_0 is a parameter of the effective time lag of changes of the macroscopic properties of the material as against a chemical change that took place in it.

Equation (4) can in this case be easily solved since the rate of E_0 change is invariable in time and depends only on radiation power. The evaluation of this time lag gave in fact identical value both for shrinkage and cracking: 3.6.10.6 s, i.e. about eight hundred hours or three weeks. This indicates that there exists a certain type of mobility in LDPE with time constant equal to about one month determining the kinetics of changes of its mechanical properties. A broad spectrum of relaxation times including those of motions of this type was known earlier; however, it was only in this study that we were able to ascertain that this particular motion are responsible for crack formation in PE.

The consideration of the kinetics of changes of mechanical properties of the structure formed in the course of radiation-induced oxidation showed that it cannot be described by additive combination, "bonding together," of the isotropically oxidized and cross-linked layers. The mechanical properties of a radiation oxidized system are always worse (Figure 4). The nature of such loss of properties still needs explanation.

Thus, this virtually applied study of the object which appears to be most thoroughly investigated in theoretical research proved the insufficient completeness of the ageing theory, disclosed a new phenomenon—slow relaxation of material's structure leading to stress concentration and crack formation—and raised the problem of the causes of this phenomenon, of the mutual influence of the oxidized and cross-linked layers giving rise to the deterioration of the mechanical properties of the sandwich type structure forming in the course of ageing.

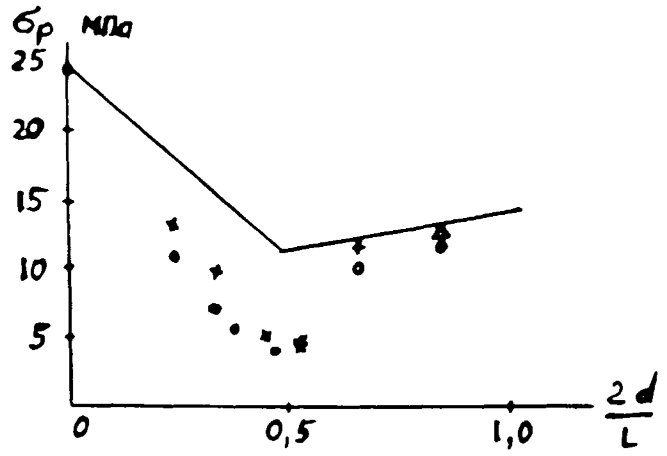

FIGURE 4 The dependence of tension of rupture on the relative thickness of the oxidized layer. Different symbols refer to specimens of different thickness (0.5–1.5 mm) irradiated at different powers (0.1–1.0 Gy/s).

In order to solve these problems it is needed to set up fundamentally new studies of PE ageing under the conditions of shortage of oxygen; within the framework of ageing theory these conditions have always been considered insignificant since it seemed that ageing takes place either in vacuum or at oxygen surplus and that the intermediate region is not so essential. It was found, however, under these particular conditions determines the kinetics of changes of properties of real, sufficiently thick articles.

Figure 5 gives an example of another practically important situation where ageing under oxygen shortage conditions proves to be the major process determining changes of properties of an article.

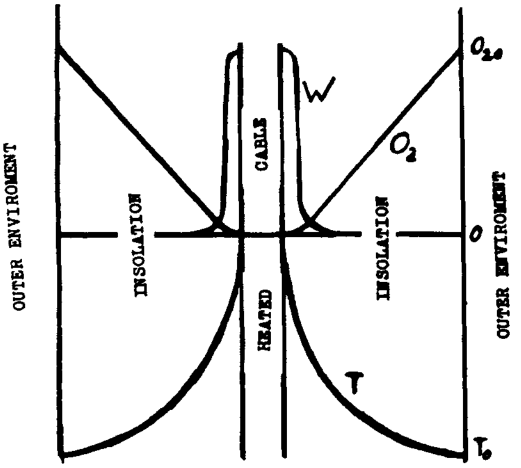

FIGURE 5 Changes of the oxygen concentration and the oxidation rate in a polymeric electrical insulation with heated central wire.

Displayed in Figure 5 is a scheme of oxidation of a heated cable with polymeric insulation. The outer surface has room temperature; no oxidation takes place in the outer layers but the layers adjacent to the heated wire undergo oxidation. Therefore, the concentration of oxygen in the outer layers decreases linearly reaching in fact a zero level in the oxidation zone, at the surface of the conductor. Because of this, oxidation actually occurs under the conditions where the partial pressure of oxygen is at a level of several tenths or even hundredths of the equilibrium pressure corresponding to the normal external pressure.

There is another example of an applied study which led to the theoretically unpredictable results.

The object taken for study was a latex film prepared from a nature latex cured with sulphur and containing rather large of a thermal stabilizer, a sterically hindered phenol.[5]

Thermal ageing of this latex film at temperature not exceeding 90°C was studied. Under these conditions there is almost no chain oxidation of the material; only the antioxidant is consumed.

Nevertheless, properties of the material undergo changes; first of all, the most important of the films, such as tear resistance, decreases rapidly. At 90°C it drops to $\frac{1}{3}$ of the initial level within a period of three days (Figure 6).

Changes of mechanical properties are accompanied by alteration of the structure of the material, the concentration of the sol fraction and the equilibrium value of swelling in toluene growing. It is known from the theory that these

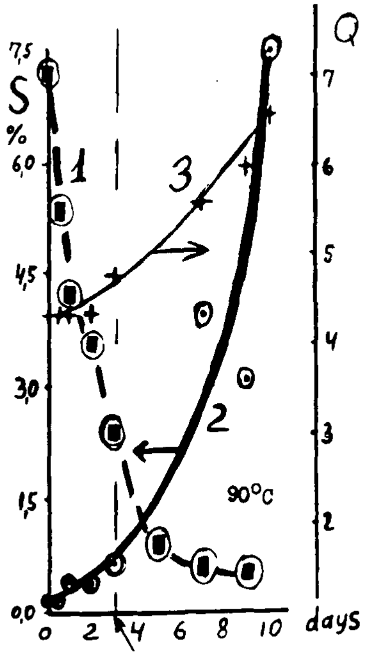

FIGURE 6 Changes of properties of a latex film on thermal ageing at 90°C: 1—tear resistance; 2—sol concentration; 3—equilibrium swelling value.

values are mutually correlated; in the case of an ideal network this correlation is based on the Flory–Rehner equation.

However, the experiment has not corroborated these views.

At the beginning of the process the latex film contains an extremely low amount of sol (0.2%).

In the course of ageing the quantity of sol grows rapidly whereas the equilibrium swelling value undergoes virtually no changes. The swelling value starts changing only in a case where the amount of sol reaches 0.7%. Further on (at $S > 1\%$), these characteristics changes in accordance with the theoretical ideas but this is already of no practical value since well before that tear resistance dropped much lower than the allowable value and the material has actually lost all its practically important properties.

Thus, the modern theory does not reveal the main cause of the changes of the properties of the latex film; under the conditions where the changes occur, the theoretical ideas are not valid.

Giving the third example, I would like to show how the resolving of practically problems of estimation of SS stimulates the development of fundamenally new methods of studying the mechanism of the process.

In estimation of material light stability one always faces, at first, an unresolvable problem. It is necessary to find out the spectrum range of the effect of light on the material, to learn how it changes under the action of light with different wavelengths.

The problem seems to be unresolvable because it is needed to determine the spectrum range of the effect on very stable materials which under the action of full, e.g. solar light, undergo degradation within a period of months, years and decades.

The traditional way of classical photochemistry and photography involving monochromatization of acting radiation is unacceptable since monochromatization is always a considerable reduction of the intensity of light entailing corresponding retardation of the ageing process. However, the latter is impossible because measurements under total, polychromatic radiation take months and sometimes years.

There is only one way out: to reject the traditional approach and to seek something radically different. The required approach has been found. In fact, the spectrum of action in itself, the dependence of the efficiency, the quantum yield on the wavelength are not needed. Needed is a method of calculation of the kinetics of the process under the action of light of any spectral composition (in a certain wavelength range with certain restrictions on the shape of the spectrum). As to this problem, it has a fundamentally different, non-monochromatic solution: it is needed to arrange such a set of polychromatic radiation sources which would provide for the solution of the thus reformulated problem.

The required system of light sources was successfully created using a standard xenon lamp and especially selected light filters also from a standard catalogue of coloured glasses.

To this end a computer programme was developed. The programme made it possible to select from the available set of light sources (light filters) an optimum set reproducing with the highest accuracy the spectrum of action radiation without any substantial reduction of the rate of the procession the whole. The same programme allows the researcher to calculate or refine the parameters of a dark model and to predict the kinetics of changes of the properties of a material under the action of light of any spectral composition.[6]

The specific feature of the approach being developed is the fact that it is an interpolation type, i.e. the accuracy of the result is independent of the spectral composition of radiation under service conditions.

The set of light filters used makes it possible to predict the kinetics of photochemical transformation not in the least worse than on employing the traditional set of interference light filters or a monochromator replacing pseudo-monochromatic light sources. This set has two indisputable advantages: its utilization does not call for the use of any devices for monochromatization (with ensuing requirements for the monochromator optics and for the geometry of the beam of light in employing interference light filters), the rate of the process under study does not fall drastically since each of the filters in the set transmits a large portion of the whole light flux.

The calulation error can be judged from the accuracy of reproduction of the action spectrum using the set of filters. No differences can be noticed in Figure 7 depicting the use of only three light filters.

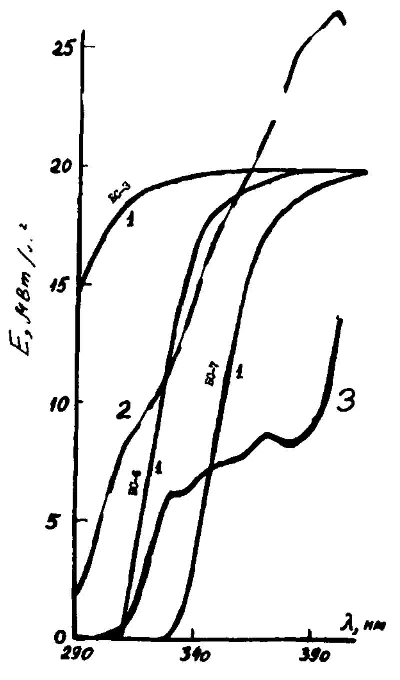

FIGURE 7 The result of simulation of the standard solar spectrum (A) and of the spectra of the sun at different heights above the horizon (B) with the help of three light filters (6C-3, 6C-6, 6C-7) and a high pressure xenon lamp: 1—the absorption spectra of the light filters employed; 2—the simulated spectrum; 3—the spectrum of xenon lamp.

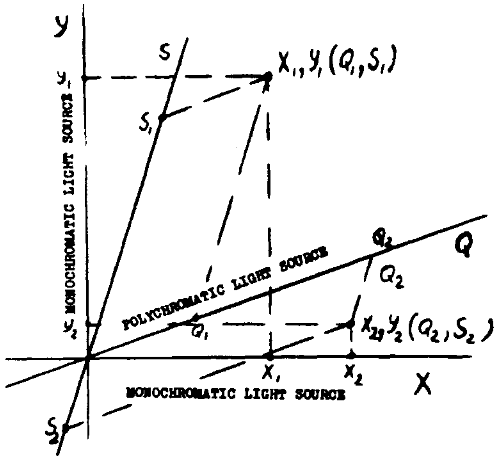

FIGURE 8 The principle of operation of the algorithm of method.

The principle of operation of the algorithm used is clarified in Figure 8. Shown in Figure 8 is a two-dimensional space which schematically characterizes all possible polychromatic light sources which can be synthesized from two monochromatic sources whose intensity is represented by two coordinates of this space. Practically realizable combinations occur in the first quadrant whereall coordinates are positive.

Any non-monochromatic radiation is visualized as a direction in this space along the straight line emanating from the coordinate origin. Practically realizable are only directions within the area having all positive coordinates.

Any two polychromatic sources form an oblique-angle system of coordinates in a given space. In making calculations one may use positive and negative intensities of the sources; hence, employing the oblique-angle system of coordinates one is able to characterize any point in the really existing set of polychromatic light sources.

By extending this procedure to spaces of higher dimensionalities, it is possible to simulate any spectra of action.

This procedure opens up new possibilities not only of an applied nature, not only for resolution of the problem for which it has been developed.

In photochemistry this is the method of revealing the spectra of action of products engaged in complex photochemical processes; in technology this is possibly the sensor making it possible to achieve optimum colour rendition using a given photographic material and a given radiation source; some other applications seem feasible.

Conclusion

The examples considered here are only an illustration of the main point of this report: the formulation of the task of applied researchs as the establishment or the sufficiency of modern theoretical views on the process under consideration not only allows applied problems to be competently indeed formulated and resolved but also enriches present-day scientific, academic studies with new methods and approaches, reveals bottlenecks in modern theoretical ideas, helps in formulating really topical problems of today.

This report only touched upon the problem generated by an attempt to understand the physico-chemical essence of the process. A rigorous analysis of the problem of the estimation of SS generates some problems of a different kind also related to physical chemistry of the ageing.

These problems are caused by the specific feature of a mathematical description of the kinetics of changes of properties of real material in a real article. Mathematics puts forward special requirements to models using for this purpose. But these problems is the quite other report.

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