

Application of Liposomes in the Textile Industry

F. Yu. Telegin, O. A. Belokurova, and N. P. Shchitova

Ivanovo State University of Chemical Technology, pr. F. Engel'sa 7, Ivanovo, 153000 Russia

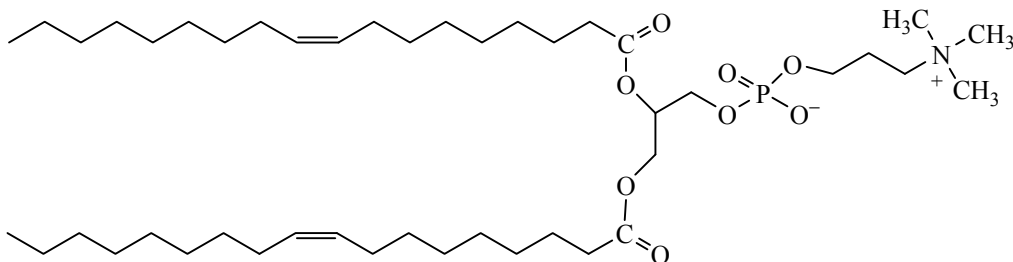
e-mail: telegin@isuct.ru

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Abstract—The results of the research of the role of liposomes in bleaching, dyeing, and finishing of wool and cotton, as well as sorption of dyes are discussed.

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Liposomes are finding application in pharmacology, medicine, cosmetology, and other fields. The practical importance of liposomes is associated with their specific structure, in particular, a closed membrane shell and ability to encapsulate various substances and fulfill the function of a target-oriented carrier for these substances. Successful use of liposomes in some fields has prompted research on the possibility of their use in textile finishing. Over the past decade the Ivanovo State University of Chemical Technology has been conducting active research and provided convincing evidence for a high efficiency of liposomal preparations in the finishing of textile materials.



Such a structure imparts to phospholipid molecules a remarkable property to spontaneously form in the aqueous medium membranes representing a double layer of lipid molecules, in which the polar heads face water and the nonpolar chains face the center of the bilayer. The tendency of the nonpolar chains to avoid, as much as possible, the contact with water results in that the bilayer, provided it is long enough, closes upon itself to form a hollow shell structure which was given the name “vesicle” (Fig. 1) [5].

Brief Information on the Structure and Properties of Liposomes

Liposomes were discovered by the British researcher A. Bangham in 1964, when he detected multilamellar phospholipid formations [1–3]. Later G. Weissmann proposed the name “liposomes” for these formations [4].

First liposomes were obtained from phospholipides. Structurally, phospholipids are amphiphilic compounds; their molecules consist of two parts which have quite different hydrogen environments. For example, phosphatidyl choline has the following structure:

It was found by X-ray spectroscopy and other spectral methods, as well as electron microscopy that phospholipid dispersions are structurally similar to biological membranes. The main difference between model phospholipid and biological membranes consists in their permeability. There is abundant evidence showing that the permeability of a bilayer for small molecules depends on other components (proteins, peptides, etc.) present in the bilayer.

Information on the fundamental properties of liposomes can be found in [6–12].

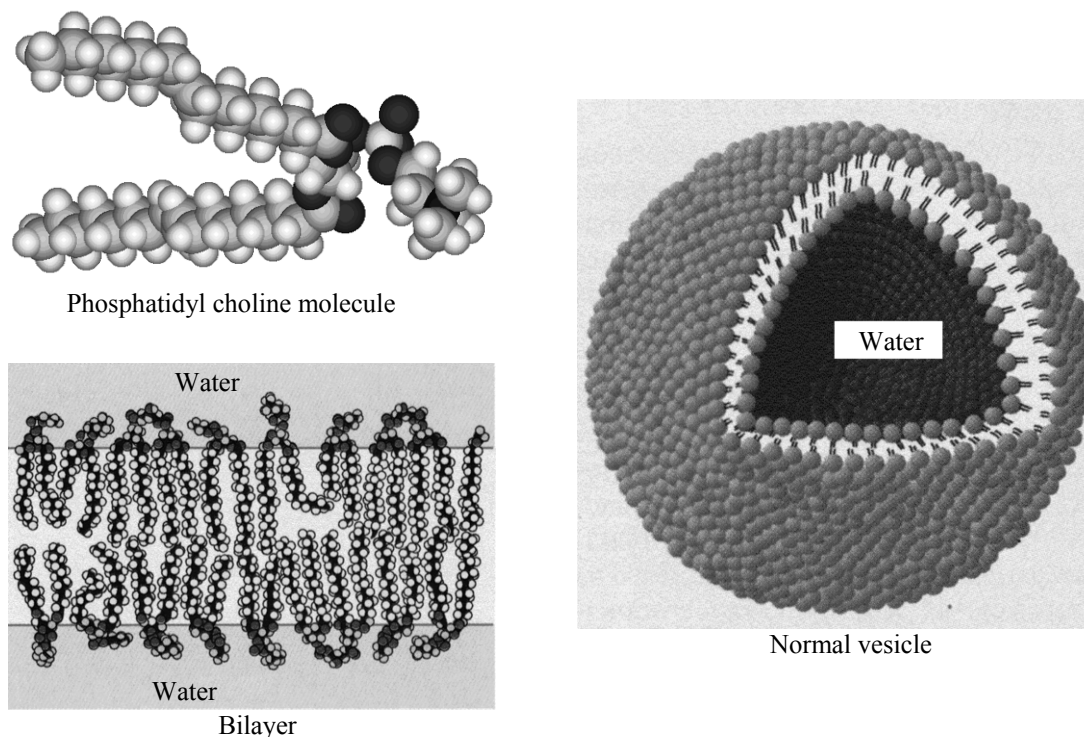


Fig. 1. Structure of a phosphatidyl choline vesicle.

According to traditional views, biological membranes, being complex mixtures of lipids, separate the space between cells or inside a cell. The lipid components of membranes are ideally suitable to fulfill this role. Most biological membranes are rich in proteins (50–60%). In particular, the protein fraction of the membrane of cuticular cells of wool fiber is 80 wt % [13]. In view of the high protein content, such membranes, while retaining a good separating ability, are highly penetrable for various molecules.

The polar lipid molecules form a bimolecular layer, whereas proteins can be bound to the bilayer surface (so-called external proteins) or integrated into the bilayer (so-called internal or integral proteins). In certain cases proteins can embed into the bilayer.

The properties of model membranes (liposomes) depend on the phase composition of the bilayer. While having a small thickness (~4 nm), the lipid bilayer features exceptional mechanical strength and flexibility. In a liquid crystalline bilayer, its components exhibit a high molecular mobility, so that the entire membrane behaves as a fairly fluid phase. Owing to this property, liposomes retain integrity under different damaging exposures, and the liposome membrane is capable to

self-healing its structural defects. At the same time, the flexibility of the bilayer and its fluidity endow liposomes with a high plasticity.

In terms of the practical application of liposomes, of exceptional importance is their ability to encapsulate and retain substances of different natures. Water-soluble substances are accommodated in the aqueous liposome interior. The fact that the bilayer contains a fairly extended hydrocarbon region allows it to incorporate hydrophobic molecules.

The bilayer can adsorb various substances, and the latter can also form chemical bonds with lipids or other membrane components. The range of substances which can be encapsulated in liposomes is quite wide: From inorganic ions and low-molecular compounds to large protein and nucleic acid molecules.

The diameter of unilamellar liposomes varies from 500 to 10000 nm. Small unilamellar liposomes are generally smaller than 50 nm, and large unilamellar liposomes are larger than 50 nm. Liposomes can reach 10000–1000000 nm in diameter (giant liposomes); they can comprise vesicles (multivesicular liposomes) and reach 2000–40000 nm in diameter.

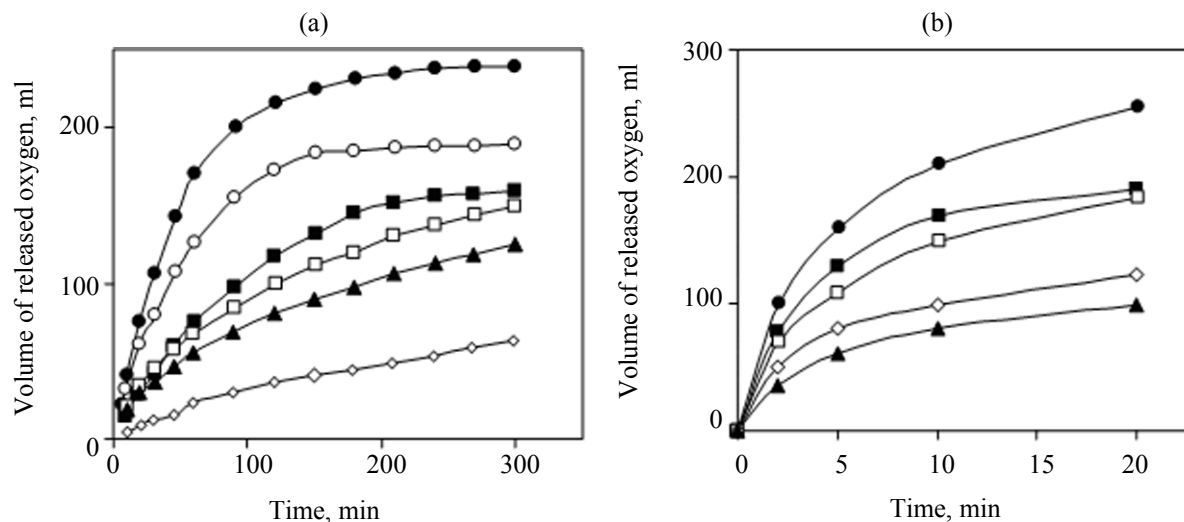


Fig. 2. Kinetic curves of hydrogen peroxide decomposition in the presence of (a) Fe^{2+} and (b) Mn^{2+} ions, and various stabilizers: (●) none, (■) sodium metasilicate, (▲) liposomes, (○) sodium ethylenediaminetetraacetate, (□) sodium pyrophosphate, and (◇) sodium silicate.

The structural features of liposomes, specifically their ability to encapsulate substances of different natures open up wide possibilities for their practical use.

The progress of liposome research and the introduction of liposomes into practice favor the development of new fields of science and technology (nanotechnology, nanochemistry, manufacture of nanomaterials) [14–27].

Liposomes in the Peroxide Bleaching of Textile Materials

Improvement of the processes of peroxide bleaching of textile materials is inexorably associated with the problem of searching for new, efficient, and environmentally safe hydrogen peroxide stabilizers. Even though there are a lot of compounds capable of inhibiting the catalytic decomposition of this oxidant, almost all of them are not free of certain disadvantages. Liposomal preparations can provide one of the alternative approaches to this problem.

The assessment of the ability of liposomal preparations to inhibit the decomposition of hydrogen peroxide, catalyzed by polyvalent metal cations (Fe, Cu, Mn) showed that the introduction of liposomes into bleaching bath compositions favors strong deceleration of hydrogen peroxide decomposition. Liposomal preparations exhibit the highest inhibitory efficiency in the presence of copper and manganese. As seen from Fig. 2, liposomes are more efficient than such widely used stabilizers as sodium metasilicate,

sodium pyrophosphate, sodium ethylenediaminetetraacetate, and even sodium silicate.

To find out the mechanism of the stabilizing action of liposomes on hydrogen peroxide, permeability of the lipid membrane with respect to the components of the bleaching solution, specifically hydrogen peroxide, sodium hydroxide and polyvalent metal cations (Fe, Cu, Mn), was studied. The experiment was conducted on an installation comprising an external reaction vessel having inside a Teflon cell with a hole ~1 mm in diameter in the wall. The external vessel and the internal cell were filled with distilled water, and the hole in the cell wall was used to add a drop of a heptane solution of phosphatidyl choline. Once the solvent (heptane) had evaporated, the drop transformed into a bilayer lipid film similar in structure to the lipid bilayer of biological membranes. After membrane formation, a substance to be studied was introduced into the water in the external vessel. The permeability of the membrane was assessed by the detection of the studied substance in the internal cell.

Experimental evidence was obtained to show that the lipid membrane is permeable exclusively for hydrogen peroxide. At the same time, according to the quantitative analysis for metals in the solution, liposomal preparations can bind dissolved metal ions. These facts can be explained in terms of the ability of phosphatidyl choline liposomes to adsorb and retain metal ions on the bilayer surface, due to ion bonding.

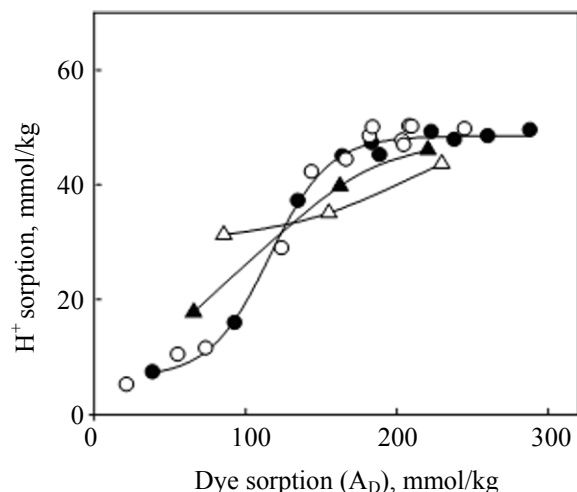


Fig. 3. Correlation between the sorption of hydrogen ions (A_H) and Acid Orange Anions (A_D) with wool fiber on dyeing in the presence of liposomes. Dyeing conditions: temperature 70°C, time 1.5 h. Liposome fraction, %: (●) none, (○) 0.035, (▲) 0.175, and (Δ) 0.7.

Analysis of experimental data gave insight into the mechanism of the stabilizing action of liposomes. On the other hand, liposomes, by encapsulating oxidant particles in the bleaching solution, act as a depot, from which the bleaching agent is released gradually. On the other hand, liposomes entrap polyvalent metal cations on the bilayer surface and do not let them to penetrate inside vesicles, this preventing the catalytic decomposition of hydrogen peroxide both inside the vesicle and in the bleaching solution.

Thus, the use of liposomes provides a radically new and promising solution of the problem of hydrogen peroxide stabilization.

The revealed regularities allowed efficient finishing technologies to be developed for various textile materials [14–22]. Introduction of liposomal preparations into the peroxide bath during bleaching of wool materials not only much enhances the efficiency of bleaching, but also impart a complex of valuable properties to these materials. Spontaneous encapsulation of hydrogen peroxide and use of these capsules as an efficient vehicle for the delivery of the oxidant to fiber material make it possible to improve bleaching at a halved oxidant content in the bath and to exclude a traditional hydrogen peroxide stabilizer from the bleaching composition. Moreover, adding liposomal preparations to the bleaching solution ensures better preservation of fiber materials. The strength loss is decreased by 15–35%, resistance to UV light is enhanced, and fabrics acquire a specific soft hand and elasticity. With worsted fabrics, essentially improved pilling resistance was observed (by 45–55%).

Liposomes in Textile Dyeing

The idea to introduce liposomes into the textile dyeing process arose in view of their ability to encapsulate dyes in solution and transport them to wool [23–29] and polyether fibers [30]. The suggestion on the use of liposomes as dye carriers in wool dyeing is based on the structural similarity of intercellular

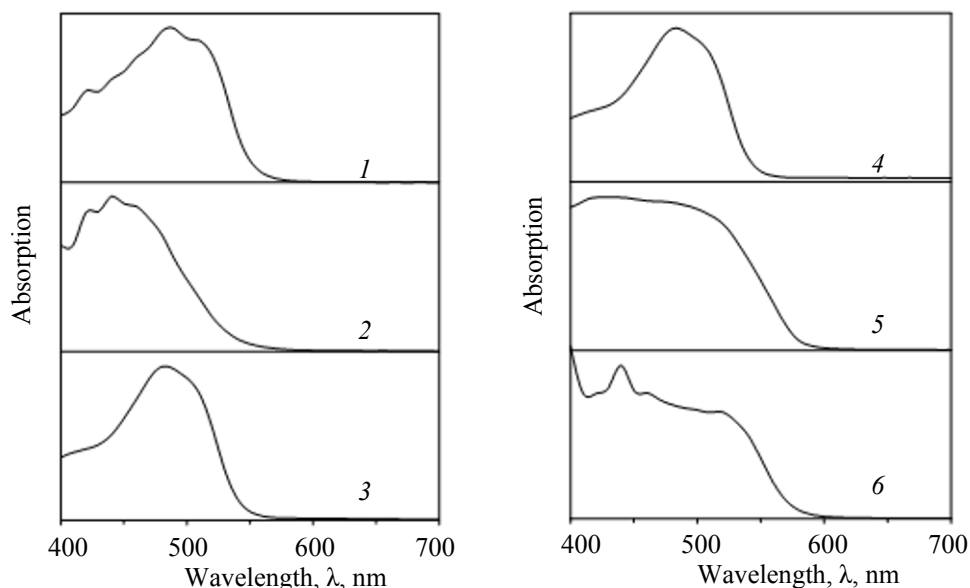


Fig. 4. Absorption spectra of acid orange in different media: (1) wool fiber; (2) wool fiber dyed in the presence of liposomes; (3) aqueous solution; (4) liposome solution; (5) cetyl alcohol; and (6) dye powder.

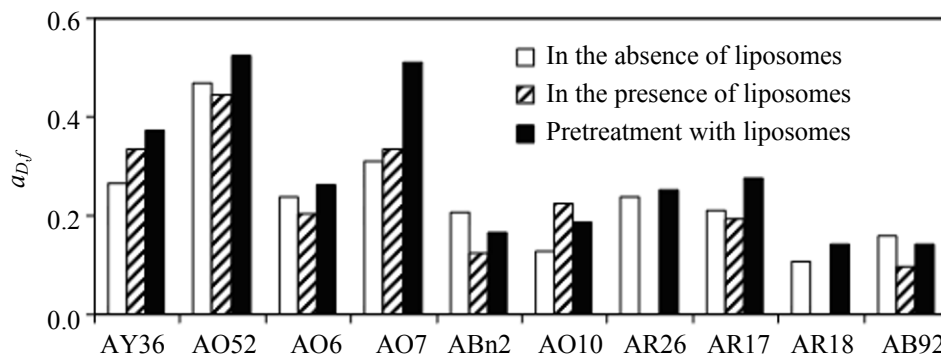


Fig. 5. Influence of the introduction mode of liposomes on the specific light absorption coefficient of absorbed dyes a_{Df} . Dye: (AY36) Methanyl Yellow, (AO52) Methyl Orange, (AO6) Tropeolin, (MR) Methyl Red, (AO7) Acid Orange, (ABn2) Acid Brown K, (AO10) Acid Orange lightfast, (AR26) Acid Purple, (AR17) Acid Bordeaux, (AR18) C.I. Acid Red 18, and (ABl92) Acid Blue 2K.

wool lipids to liposomes and on the role the intercellular fraction of wool lipids plays in chemical treatment. Dyes prefer to diffuse through more accessible regions, such as the cellular membrane complex (intercellular diffusion), that through cuticle cells (transcellular diffusion) [31, 32].

In this connection, of interest is to study the conducting mechanism of the cellular membrane complex of wool fiber on dye diffusion, modification by outer lipids of the inner lipid layer of wool fiber, and effect of the textile auxiliary capable of encapsulating hydrophilic and hydrophobic substances.

The kinetic study of wool dyeing in the presence of liposomes [33–37] showed that liposomes have a strong negative effect on the sorption of the Acid Orange Dye at high temperatures. At the same time, studying the effect of liposome concentration on the sorption of acid dyes by wool fiber (Fig. 3) revealed two regions of the hydrogen sorption capacity A_H of wool fiber, with opposite effects of liposomes on dye sorption. At $A_H < 120$ mmol/kg, increasing liposome concentration increases the sorption of acid dyes, whereas at $A_H > 140$ mmol/kg, the opposite tendency takes place.

Spectral studies of dyes in different media, including wool fiber dyed in the presence of liposomes showed the involvement in the dyeing process of a liposomal preparation results in the dye converts from the quinone–hydrazone form to the azo form [38, 39] (Fig. 4). This fact points to a change of the mechanism of wool dyeing with Acid Orange in the presence of liposomes and to the possibility to obtain colors more resistant to wet treatments and oxidation.

The color strengths obtained under different regimes of treatment of wool fiber with liposomes were compared for 11 azo dyes. The resulting data are presented in Fig. 5.

With the most part of dyes, the specific light absorption of wool fiber pretreated with liposomes before dyeing was much higher compared to that dyed by the traditional technology. This fact suggests a changed mechanism of dye sorption, which leads to a deeper penetration of dye to fiber and a monomolecular state of the dye in the dyed substrate. According to published data, the change of the mechanism is explained by a liposome-induced modification of the lipophilic intercellular substance of wool fiber. Evidence for this reasoning is provided by a correlation of the specific light absorption coefficient with the hydrophobicity parameter of the dye, which corresponds to the calculated octanol–water partition coefficient of the latter.

CONCLUSIONS

Liposomes can find application in the textile industry as multifunctional textile auxiliaries. Research on search for other practical applications in this industry is in progress.

Approaches to the modification of liposomes with the aim to enhance their hydrophilicity were found, which allowed to prepared nanosized liposomes (12–20 nm) [40, 41]. Methods for liposomal encapsulation of inks for jet printing are being developed [42, 43].

Quite an important advantage of liposomes is the environmental friendliness of textile finishing processes with their participation [44].

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